

Comprehensive Studies of Magnetic Properties of Metal-Organic Frameworks and Molecular Compounds

A Dissertation Presented for the

Doctor of Philosophy

Degree

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Pagnareach Tin

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DEDICATION

To my parents, who sacrificed everything that they had to allow me to have a better education and a better future. To my wife and sister, who have shown full support and unwavering love at every moment.

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ABSTRACT

Single-ion magnets (SIMs) are at the forefront of molecular electronic spin magnets with potential applications in magnetic memory storage devices. However, the magnetic properties of the SIMs are yet to be completely understood, especially the magnetic properties of large anisotropy systems. A part of this dissertation is to utilize optical and neutron spectroscopies such as far-IR magneto-spectroscopy (FIRMS) and inelastic neutron scattering (INS) to quantify the anisotropy and study the phonon properties of the SIMs as two-dimensional (2-D) metal-organic frameworks (MOFs) or coordination polymers (CPs), and molecular compounds. In addition, *ab initio* calculations are used to understand the origin of the anisotropy and the electronic structure of the systems. Furthermore, the systems studied in this dissertation can also be quantum bit (qubit) candidates. Qubits are the building blocks of quantum computers. The properties of qubits can be determined using pulsed electron paramagnetic resonance (pulsed EPR). The results yielded the spin-lattice relaxation time and the spin-spin relaxation time, where both relaxation times are crucial in determining the effectiveness of the qubit candidates. The second part of this dissertation focuses on studying the symmetry-protected topological states of a Haldane one-dimensional (1-D) spin-1 chain as a 2-D MOF. The topological properties of the Haldane spin-1 chain can be highlighted by the Haldane energy gap between the non-magnetic singlet ground state and the triplet excited state, the fractionalized edge states, and the system's robustness to external perturbations through symmetry-protection. Optical and neutron spectroscopies in addition to the magnetic susceptibility measurements were used to quantify the energy gaps as well as the anisotropy that governs the system. Furthermore, the spin

chain is found to exhibit a critical field and critical temperature where the system shows a phase transition. These studies in this dissertation, in part, aim to give a comprehensive understanding of the magnetic anisotropy and phonon properties of the SIM and qubit systems as well as to have a comprehensive understanding of the topological properties of the Haldane 1-D spin-1 chain system.

TABLE OF CONTENTS

1. Chapter 1. Introduction.....	1
1.1. Magnetic Systems.....	2
1.1.1. Single Molecule Magnets (SMMs) or Single-Ion Magnet (SIMs).....	2
1.1.2. Quantum Bits (Qubits).....	7
1.1.3. Haldane One-Dimensional (1-D) Spin-1 Chains.....	9
1.2. Metal-Organic Frameworks (MOFs).....	9
1.3. Experimental Methods.....	14
1.3.1. Far-IR Magneto-Spectroscopy (FIRMS).....	15
1.3.2. High-Field/-Frequency Electron Paramagnetic/Spin Resonance (HFEP or HFESR).....	17
1.3.3. Inelastic Neutron Scattering (INS).....	18
1.3.4. Pulsed Electron Paramagnetic Resonance (Pulsed EPR).....	19
1.4. Current Dissertation.....	20
1.4.1. Chapter 2.....	20
1.4.2. Chapter 3.....	21
1.4.3. Chapter 4.....	22
1.4.4. Chapter 5.....	22
 2. Chapter 2. Advanced Spectroscopic and Computational Studies of a Cobalt(II)	
Coordination Polymer with Single-Ion-Magnet Properties.....	24
2.1. Abstract.....	26

2.2. Introduction.....	27
2.3. Results and Discussions.....	31
2.3.1. <i>Single-Crystal Structure of Co-TODA at 15(2) K</i>	31
2.3.2. <i>Studies of the Magnetic Transitions by FIRMS and HFEPR to Determine Spin-Hamiltonian Parameters</i>	32
2.3.2.1. FIRMS.....	32
2.3.2.2. HFEPR.....	35
2.3.3. <i>INS Studies of the Inter-KD Transition and Phonon Properties</i>	40
2.3.4. <i>Computational Studies of the Magnetic Anisotropy in Co-TODA</i>	43
2.3.5. <i>Calculated Spin Densities and a Correlation with the D Parameter</i>	46
2.3.6. <i>Studies of Spin-Lattice (T_1) and Spin-Spin (T_2) Relaxation Times in the Ground KD by Pulsed X-band EPR</i>	48
2.4. Experimental Section.....	54
2.4.1. FIRMS.....	54
2.4.2. HFEPR.....	55
2.4.3. INS.....	55
2.4.4. <i>Electronic Structure Calculations</i>	56
2.4.5. <i>DFT Calculations of INS Spectrum and Spin Densities</i>	57
2.4.6. <i>Pulsed X-Band EPR</i>	58
2.5. Conclusions.....	59

3. Chapter 3. Hexacoordinate Co(II)-MOF-Based Single-Molecule Magnet with	
Very Large Magnetic Anisotropy and Qubit Properties.....	61
3.1. Abstract.....	63
3.2. Introduction.....	63
3.3. Results and Discussions.....	66
3.3.1. <i>Single-Crystal X-Ray Diffraction</i>	67
3.3.2. <i>Determination of Spin-Hamiltonian (SH) Parameters and Spin-Phonon</i>	
<i>Couplings Through FIRMS and HFEPR</i>	69
3.3.2.1. FIRMS.....	69
3.3.2.2. HFEPR.....	74
3.3.3. <i>Determination of the Inter-Kramers Magnetic Transition and Phonon</i>	
<i>Properties with INS and DFT Calculations</i>	77
3.3.4. <i>Studies of the Magnetic Anisotropy and the Magneto-Structure by Ab</i>	
<i>Initio Computations</i>	80
3.3.5. <i>Determination of the Qubit Properties Using Pulsed X-band EPR</i>	84
3.4. Experimental Methods.....	91
3.4.1. <i>Single-Crystal X-Ray Diffraction</i>	91
3.4.2. <i>FIRMS</i>	91
3.4.3. <i>HFEPR</i>	92
3.4.4. <i>INS</i>	92
3.4.5. <i>Electronic Structure Calculations</i>	92
3.4.6. <i>DFT Calculations of INS Spectrum and Spin Densities</i>	93

3.4.7. Pulsed X-band EPR.....	94
3.5. Conclusions.....	95
4. Chapter 4. Haldane Spin-1 Chain in a Planar Metal-Organic Framework.....	96
4.1. Abstract.....	98
4.2. Introduction.....	98
4.3. Results and Discussions.....	101
4.3.1. Single-Crystal X-Ray Diffraction.....	101
4.3.2. Variable-Temperature Powder Neutron Diffraction (VT-PND).....	103
4.3.3. Magnetic Susceptibility (DC).....	103
4.3.4. Quantum Monte-Carlo Simulation (QMC).....	107
4.3.5. Specific Heat.....	113
4.3.6. INS at 0 T.....	113
4.3.7. HFESR.....	116
4.3.8. Phonon Spectrum from INS and Comparison with the DFT Calculated INS Spectrum.....	120
4.4. Experimental Methods.....	122
4.4.1. Single-Crystal X-Ray Diffraction.....	122
4.4.2. Magnetic Susceptibility (DC) and Specific Heat.....	122
4.4.3. HFESR.....	123
4.4.4. Powder Neutron Diffraction (PND).....	123
4.4.5. INS.....	124

4.4.6. <i>DFT Calculations of Phonons and Spin Density</i>	124
4.5. Conclusions.....	125
 5. Chapter 5. Advanced Magnetic Resonance Studies of	
Tetraphenylporphyrinatoiron(III) Halides	127
5.1. Abstract.....	128
5.2. Introduction.....	130
5.3. Results.....	134
5.3.1. <i>HFEPR</i>	134
5.3.2. <i>FIRMS</i>	139
5.4. Discussion.....	144
5.4.1. <i>Spin-Hamiltonian and an Overview of the ZFS in Fe(TPP)X</i>	144
5.4.2. <i>Understanding the ZFS in Fe(TPP)X</i>	149
5.5. Experimental.....	153
5.5.1. <i>HFEPR</i>	154
5.5.2. <i>FIRMS</i>	154
5.6. Conclusions.....	155
 6. Chapter 6. Concluding Remarks	157
 References	161

Appendices.....	211
Appendix A. Supporting Information for Chapter 2.....	212
A1. <i>Synthesis of Co-TODA</i>	212
A2. <i>Additional Results from the Electronic Structure Calculations Using</i> <i>CASPT2/RASSI-SO with MOLCAS 8.4</i>	213
A3. <i>Crystal Structure of Co-TODA at 15(2) K and a Comparison of</i> <i>Selected Bond Lengths and Angles at 15(2) K and 123(2) K</i>	223
A4. <i>Additional Results from Pulsed X-Band EPR Experiments</i>	231
A5. <i>Calculated Spin Densities in Co-TODA</i>	231
A6. <i>Additional Calculated INS and Experimental INS Results</i>	251
Appendix B. Supporting Information for Chapter 3.....	252
B1. <i>Synthesis of $[\text{Co}(\mu\text{-bpeb})_2(\text{NCS})_2]_n \bullet n\text{G}$ (Co-BEBN), Growth of Its</i> <i>Single Crystals, and Synthesis of Co-BEBN_{0.05}</i>	252
B2. <i>Additional Crystal Structural Data for $[\text{Co}(\mu\text{-bpeb})_2(\text{NCS})_2]_n \bullet n\text{G}$</i> <i>(Co-BEBN)</i>	254
B3. <i>Magnetic Susceptibility (AC and DC) Data</i>	259
B4. <i>Additional Inelastic Neutron Scattering (INS) Data and Phonon</i> <i>Calculations</i>	261
B5. <i>Additional Data from the Electronic Structure Calculations</i>	265
B6. <i>Phonon Symmetries</i>	275
B7. <i>Spin Densities</i>	293

Appendix C. Supporting Information for Chapter 4.....	295
<i>C1. Synthesis of NiBO and NiBO-d₈ and Characterization by Powder X-ray Diffraction and IR.....</i>	<i>295</i>
<i>C2. Additional Discussion of the Crystal Structure of NiBO-d₈.....</i>	<i>301</i>
<i>C3. Additional Magnetic Susceptibility (DC) Data.....</i>	<i>311</i>
<i>C4. Additional Quantum Monte Carlo (QMC) Results.....</i>	<i>315</i>
<i>C5. Additional Specific Heat Data.....</i>	<i>326</i>
<i>C6. Additional Inelastic Neutron Scattering (INS) Data of NiBO and Tables of Calculated Phonons and Spin Densities.....</i>	<i>328</i>
Appendix D. Supporting Information for Chapter 5.....	334
Vita.....	344

LIST OF TABLES

Table 2.1. Calculated spin densities for atoms in a unit cell of Co-TODA . Ranges of spin densities are listed for O, N, C, and H atoms due to the large number of atoms existed in the unit cell.....	47
Table 2.2. Correlation between calculated spin densities on the Co^{II} ions and ZFS parameters of the Co^{II} complexes/CP.....	49
Table 3.1. Selected examples of single-ion Co^{II} complexes with $2D' > 250 \text{ cm}^{-1}$	65
Table 3.2. Comparison of experimental and calculated ZFS parameters D , E , and g [g_x , g_y , g_z] tensors of Co-BEBN using CASPT2 and NEVPT2 with MOLCAS 8.4 and ORCA 4.2, respectively.....	83
Table 4.1. Magnetic parameters obtained from the QMC simulations.....	112
Table 5.1. Spin-Hamiltonian parameters of $\text{Fe}^{\text{III}}(\text{TPP})\text{X}$	135

LIST OF FIGURES

Figure 1.1. Energy splitting diagram for $S = 3/2$ complexes when $D > 0$, where $D' = (D^2 + 3E^2)^{1/2}$	4
Figure 1.2. Double energy well scheme of an $S = 3/2$ system with $D < 0$ showing the energy barrier (U) and the transition between the low energy state to the high energy.....	6
Figure 1.3. Energy diagram of a Haldane spin-1 chain system and the Zeeman effect on the magnetic states.....	10
Figure 1.4. (Top) AKLT model representation of the Ni^{II} spin-1 Haldane chain showing the antiferromagnetic coupling (gray oval) between two unpaired electrons (red and blue arrows) in the middle of the chain, leaving unpaired electrons (orange arrows) at ends of the chain.....	11
Figure 2.1. (Top-Left) $[\text{Co}^{\text{III}}(\text{CN})_6]_2[\text{Co}^{\text{II}}(\text{TODA})]_3 \cdot n\text{H}_2\text{O}$ (Co-TODA).....	28
Figure 2.2. (Top) Transmittance line plot of FIRMS data at 5.3(3) K. (Bottom) 2-D FIRMS plot showing the zero-field magnetic transition originating from 80.4(1.0) cm^{-1} and its evolution at applied high magnetic fields.....	33
Figure 2.3. (Left) HFEPR spectrum of Co-TODA at 10(1) K and 321 GHz (black trace) and its simulation (red trace) using the following SH parameters: $D = 38.3(1.0) \text{ cm}^{-1}$, $E = 7.3(1.0) \text{ cm}^{-1}$, $\mathbf{g} = [2.33(6), 2.33(6), 2.06(6)]$. (Right) 2-D map (magnetic field vs. frequency/energy) of turning points in HFEPR spectra of Co-TODA at 10(1) K.....	36

Figure 2.4. VT HFEPR spectra at 273 GHz with temperatures ranging from 5(1) K to 150(1) K. The narrow resonance at ca. 9.8 T is due to an unidentified $S = 1/2$ impurity.....	39
Figure 2.5. Bose-corrected INS spectra collected at VISION. (Top) Forward scattering. (Bottom) Back scattering.....	42
Figure 2.6. Graphs of the echo intensity from pulsed X-band EPR at 5(1) K vs. time: (Top) Echo inversion recovery experiment; (Bottom) Hahn echo decay experiment.....	52
Figure 3.1. (Left) Truncated structure of Co-BEBN showing the Co^{II} local symmetry. (Right) Monolayer crystal structure of Co-BEBN	68
Figure 3.2. (Top) Far-IR transmission plot of Co-BEBN at 5.5 K at 0 and 17 T. (Bottom) FIRMS map revealing the origination of the ZFS energy gap.....	70
Figure 3.3. Fitting of the spin-phonon coupling in the FIRMS data using <i>Maple</i> , as black lines. The red solid line is a linear fit between the magnetic peak at zero-field and the phonon peak at 17 T corresponding to the slopes of the black lines, which is the transition energy in ZFS, E_{sp} , used in the spin-phonon fit.....	72
Figure 3.4. (Left) A derivative HFEPR graph of Co-BEBN showing three turning points corresponding to the transition $M_s = -1/2 \rightarrow M_s = +1/2$ at 10 K and 203 GHz (black trace) and its simulation (red trace) using the following SH parameters: $D = 127.3 \text{ cm}^{-1}$, $E = 17.8 \text{ cm}^{-1}$, $g = [2.54, 2.54, 2.59]$. (Right) 2-D graph showing the turning point as a function of frequency/energy.....	76

Figure 3.5. Variable-temperature INS spectra of Co-BEBN . (Top) Forward scattering data; (Bottom) Back scattering data.....	79
Figure 3.6. Comparison between the experimental INS data at 5.0(5) K and the calculated INS spectrum in the 200-400 cm^{-1} region.....	81
Figure 3.7. Echo inversion recovery plot of Co-BEBN at 10(1) K with external applied magnetic field of 3.300(1) T.....	87
Figure 3.8. Hahn echo decay plots: (Top) Co-BEBN ; (Bottom) Co-BEBN _{0.05} at 10(1) K with external applied magnetic field of 3.300(1) T and 3.450(1) T, respectively....	89
Figure 3.9. Rabi oscillation plots at 10(1) K. (Top) Co-BEBN . (Bottom) Co-BEBN _{0.05}	90
Figure 4.1. (Left) 2-D schematic of NiBO-d₈ showing the bonding around three Ni^{II} ions within the chain. Blue arrows show intra- and inter-chain directions. (Right) Structure of NiBO-d₈ along the crystallographic <i>a</i> -axis.....	102
Figure 4.2. (Top) PND pattern of NiBO at 1.70 and 100 K. (Bottom) Rietveld refinement of the PND data at 1.8 K.....	104
Figure 4.3. Temperature dependence of the DC magnetic susceptibility of NiBO at 0.1 T. Inset: magnetic susceptibility plot of $\ln[\chi(T) - \chi(0)]$ vs. $1/T$ for data below 11.5 K.....	105
Figure 4.4. Temperature dependence of the DC magnetization of NiBO	108
Figure 4.5. Quantum Monte Carlo results for the magnetic susceptibility as a function of temperature.....	111
Figure 4.6. Magnetic field-dependent specific heats of NiBO from 1.92 to 6.00 K.....	114
Figure 4.7. Expected transitions A , B at 0 T and C inside magnetic fields for NiBO	115

Figure 4.8. Temperature-dependent INS data for NiBO-<i>d</i>₈	117
Figure 4.9. HFESR spectrum of NiBO at 4.5 K and 511 GHz.....	118
Figure 4.10. Frequency dependence of the resonance observed by HFESR.....	119
Figure 4.11. The calculated phonon spectrum compares to the experimental INS spectrum of NiBO at 5 K.....	121
Figure 5.1. Structures of Fe(TPP)X	131
Figure 5.2. The effect of spin-Hamiltonian on an $S = 5/2$ wavefunction.....	133
Figure 5.3. Experimental HFEPR spectra at 5-10 K of the Fe(TPP)X series of compounds (black traces) and their powder-pattern simulations (red traces).....	136
Figure 5.4. 2-D field vs. energy (frequency) HFEPR maps of the Fe(TPP)X series of compounds.....	137
Figure 5.5. (Top left) 2-D map of FIRMS in Fe(TPP)Br at 4.6 K with HFEPR data points added as black squares.....	141

LIST OF ABBREVIATIONS

1-D	One-dimensional
2-D	Two-dimensional
3-D	Three-dimensional
4-D	Four-dimensional
AC	Alternate current
AF	Antiferromagnetic
AKLT	Affleck, Kennedy, Lieb, and Tasaki
AO	Atomic orbital
CASPT2	Complete-active-space second-order multiconfigurational perturbation theory
CASSCF	Complete-active-space self-consistent field
CP	Coordination polymer
CShM	Continuous Shape Measures
DC	Direct current
DCS	Disk chopper spectrometer
DFT	Density functional theory
FD	Frequency-domain
FIRMS	Far-IR magneto-spectroscopy
FT	Fourier transform
GGA	Generalized gradient approximation
HFEPR	High-field/-frequency electron paramagnetic resonance

HFESR	High-field/-frequency electron spin resonance
INS	Inelastic neutron scattering
IR	Infrared
iso	isotropic
KD	Kramers doublet
LFT	Ligand field theory
MCD	Magnetic circular dichroism
MOF	Metal-organic framework
NEVPT2	N-electron valence second-order perturbation theory
NMR	Nuclear magnetic resonance
NIR	Near-infrared
PAW	Projector Augmented Wave
PBE	Perdew-Burke Ernzerhof
PND	Powder neutron diffraction
QMC	Quantum Monte Carlo
Qubit	Quantum bit
SCXRD	Single-crystal X-ray diffraction
SH	Spin-Hamiltonian
SIM	Single-ion magnet
SMM	Single-molecule magnet
SOC	Spin-orbit coupling
SOMF	Spin-orbit mean-field

SSC	Spin-spin contribution
SSE	Stochastic series expansion
STM-IETS	Scanning tunneling microscopy-inelastic electron tunneling spectroscopy
VASP	Vienna ab-initio simulation package
UV	Ultra-violet
VH	Variable-field
VT	Variable-temperature
ZFS	Zero-field splitting

LIST OF SYMBOLS

χ	Magnetic susceptibility
B	Magnetic field
D	Single-ion axial anisotropy
E	Transverse or rhombic anisotropy
g	g -factor
J	Magnetic coupling constant
k_i	Momenta of incoming neutrons
k_f	Momenta of outgoing neutrons
m_l	Magnetic quantum number
M_s or m_s	Spin quantum number
M_{xy}	Transverse magnetization
M_z	Axial magnetization
Q	Momentum transfer
S	Spin
T_1	Spin-lattice relaxation time
T_2	Spin-spin relaxation time
T	Temperature
t	Time
T_B	Blocking temperature
T_m	Phase memory time
U_{eff}	Effective energy barrier

LIST OF COMPOUNDS, METAL-ORGANIC FRAMEWORKS (MOFs), AND COORDINATION POLYMERS (CPs)

Co-TODA	$[\text{Co}(\text{CN})_6]_2[\text{Co}(\text{TODA})]_3 \cdot 7\text{H}_2\text{O}$ (TODA = 1,4,10-trioxa-7,13-diazacyclopentadecane)
Co-BEBN	$[\text{Co}(\mu\text{-bpeb})_2(\text{NCS})_2]_n \cdot n\text{G}$ [bpeb = 1,4-bis(pyridine-4-ylethynyl)benzene]
Fe(TPP)X	$\text{Fe}(\text{TPP})\text{X}$ (X = F, Cl, Br, I; TPP^{2-} = <i>meso</i> -tetraphenylporphyrinate)
NDMAZ	$\text{Ni}(\text{dmpn})_2(\mu\text{-N}_3)(\text{ClO}_4)$ (dmpn = 1,3-diamino-2,2-dimethylpropane)
NENB	$[\text{Ni}(\text{en})_2(\mu\text{-NO}_2)](\text{BF}_4)$ (en = ethylenediamine)
NENP	$[\text{Ni}(\text{en})_2(\mu\text{-NO}_2)](\text{ClO}_4)$ (en = ethylenediamine)
NiBO	$[\text{Ni}(\mu\text{-4,4'-bpy})(\mu\text{-ox})]_n$ (bpy = bipyridine; ox^{2-} = oxalate)
NiBO-d_8	$[\text{Ni}(\mu\text{-4,4'-bpy-}d_8)(\mu\text{-ox})]_n$ (bpy- d_8 = bipyridine- d_8 ; ox^{2-} = oxalate)
NINO	$[\text{Ni}(1,3\text{-propanediamine})_2(\mu\text{-NO}_2)](\text{ClO}_4)$

Chapter 1

Introduction

1.1. Magnetic Systems

1.1.1. Single-Molecule Magnets (SMMs) or Single-Ion Magnets (SIMs)

Molecular-based magnets are at the forefront of magnetic materials with applications in magnetic memory storage devices and quantum computation.^{1, 2} One of the first molecules to be identified as an SMM in 1980 was a manganese oxide cluster with acetate ligands, $\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4$.³ In 1993, Sessoli and coworkers reported studies of the magnetic properties of $\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CPh})_{16}(\text{H}_2\text{O})_4$ (known as Mn_{12}) and its solvates, establishing the compounds as the first known SMMs.⁴ They observed spontaneous magnetization and a hysteresis loop, which are indications of the SMM characteristics. The origin of the hysteresis loop stems from the slow relaxation of magnetization between the two magnetic ground states of the spin.⁵ Subsequent studies into SMMs/SIMs have focused on improving the effectiveness of the relaxation of magnetization of the molecules through molecular designs.^{1, 2}

The process of slow relaxation of magnetization is important for SIMs due to its major impact on the effectiveness and stability of the magnetic spin states. The magnetic ground states consist of degenerate spin states that split without magnetic field through the effect of zero-field splitting (ZFS), which originates from the second-order spin-orbit coupling (SOC).⁶ The nature of the ZFS can be described by the spin-Hamiltonian ($\hat{H}$) in Eq. 1.1:^{1, 6}

$$\hat{H} = D \left[\hat{S}_z^2 - \frac{S(S+1)}{3} \right] + E (\hat{S}_x^2 - \hat{S}_y^2) + \mu_B g \hat{S} \cdot \hat{B} \quad (\text{Eq. 1.1})$$

where D is the axial single-ion anisotropy, E is the transverse or rhombic anisotropy, μ_B is the Bohr magneton, g is the electron spin g -tensor, $\hat{S}$ is the spin operator, and $\hat{B}$ is the magnetic induction vector.

In the half-integer spin system, the spin states exist as Kramers doublets (KDs) or degenerate states from $M_S = \pm 1/2$ to $\pm S$ that split by the ZFS. In the integer spin system, the spin states split from $M_S = 0$ to $\pm S$. The presence of the D and E magnetic anisotropy effectively lifts degeneracy of the spin states, causing the formation of the KDs in the half-integer spin system. For negative D values, the total spin is in the z -axis (easy-axis of magnetization along the z -axis known as easy-axis anisotropy), placing the largest M_S states at the lowest energy. For positive D values, the total spin is in the xy -plane (easy-plane of magnetization along the x, y -directions known as easy-plane or rhombic anisotropy), placing the smallest M_S states at the lowest energy. For $S = 3/2$ complexes such as those of Co^{II} ions with easy-axis anisotropy ($D > 0$), the energy splitting diagram is given in Figure 1.1 as an example. When the crystallographic point group symmetry of the metal site (i.e., paramagnetic center) is 3-fold or higher ($x = y \neq z$), $E = 0$. When $D > 0$ (easy plane), the $M_S = \pm 1/2$ KD is the ground state, giving the separation between the ground and excited KDs $= 2D$. When the crystallographic point group symmetry of the metal site is lower than 3-fold ($x \neq y \neq z$), $E \neq 0$.⁷ The mixing of the $M_S = \pm 1/2$ and $\pm 3/2$ KDs^{8,9} gives $2D' = 2(D^2 + 3E^2)^{1/2}$ for the separation between the KDs.^{6,10} Here, the $M_S = +1/2$ and $-3/2$ states mix with each other, as the $-1/2$ and $+3/2$ states (Figure 1.1). The mixed states are labeled ϕ_1 and ϕ_2 for the ground KD and ϕ_3 and ϕ_4 for the excited KD.

With negative anisotropy values, the unpaired electrons can transition from the ground spin states to the first excited spin states over an energy barrier (U). Though, there are external perturbations that can cause the relaxation faster and effectively cross over an effective energy barrier (U_{eff}). For half-integer and integer spin, the U_{eff} can be calculated using D in Eqs. 1.2 and 1.3, respectively.¹

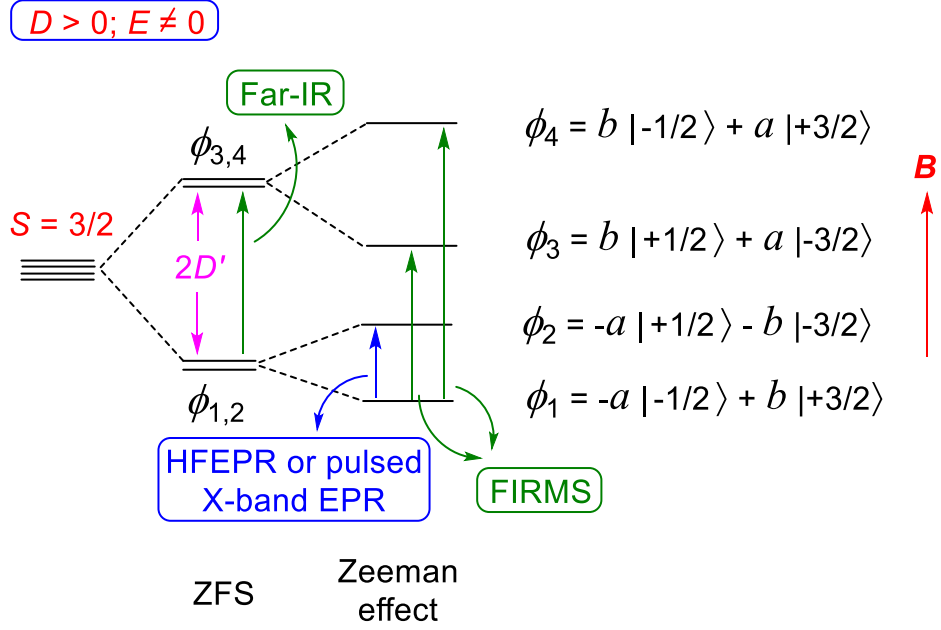


Figure 1.1. Energy splitting diagram for $S = 3/2$ complexes when $D > 0$, where $D' = (D^2 + 3E^2)^{1/2}$. The $M_S = \pm 1/2$ and $M_S = \pm 3/2$ are nominal labels for the levels due to the mixing of the two spin states when $E \neq 0$.¹¹ Here, the $M_S = +1/2$ and $-3/2$ states mix with each other, as the $-1/2$ and $+3/2$ states. The mixed states are labeled ϕ_1 and ϕ_2 for the ground KD and ϕ_3 and ϕ_4 for the excited KD. Mixing coefficients $a = \cos \beta$ and $b = \sin \beta$ are described by the mixing angle β obtained from the spin-Hamiltonian ($S = 3/2$).^{8,9} Mixing is a function of the rhombicity, since $\tan 2\beta = \sqrt{3} (E/D)$. In the absence of the external magnetic field $\mathbf{B}$, the excitation from the $M_S = \pm 1/2$ KD to the $M_S = \pm 3/2$ KD may be observed in far-IR spectroscopy. In the presence of the external magnetic field, Zeeman effect leads to the splittings of the two doublets (KDs). Electronic paramagnetic resonance (EPR), including high-field/-frequency EPR (HFEPR) and pulsed EPR, and far-IR magneto-spectroscopy (FIRMS), may be used to probe transitions from the ground to excited states, as discussed below in Section 1.3.

$$U_{eff} = \left(S^2 - \frac{1}{4}\right) |D| \quad (Eq. 1.2)$$

$$U_{eff} = S^2 |D| \quad (Eq. 1.3)$$

where S is the total spin of the system.

Having negative anisotropy values for SIMs is desirable due to the energy barrier to magnetization relaxation of the spin, as shown in Figure 1.2. Though, there are SIMs with positive anisotropy values exhibiting slow relaxation characteristics as effective SIMs.¹² The relaxation process of magnetization is governed by multiple mechanisms. Those relaxation mechanisms include the direct, Raman, and Orbach processes. Direct process occurs when there is an energy exchange between the excited spin and the phonon of the lattice. In a Raman process, the spin is excited to a virtual state and relaxes down to the ground state. Orbach process involves the excited spin transition to a higher energy spin state and relax back to the ground state. All three relaxation mechanisms can be describe by *Eq. 1.4*.¹

$$\tau^{-1} = AH^{n_1}T + CT^{n_2} + \tau_0^{-1}\exp\left(\frac{-U_{eff}}{kT}\right) \quad (Eq. 1.4)$$

where A , C , and τ_0^{-1} are constant and the three terms correspond to the direct, Raman, and Orbach processes, respectively, that contribute simultaneously to τ^{-1} , T is the temperature, H is the magnetic field, U_{eff} is the effective energy barrier, and k is the Boltzmann constant.

We can experimentally examine the relaxation mechanisms using AC susceptibility measurement. Fitting of the AC data can determine the mechanisms governing the relaxation process of a SIM. Spin-phonon coupling is a factor impacting the relaxation process. How the

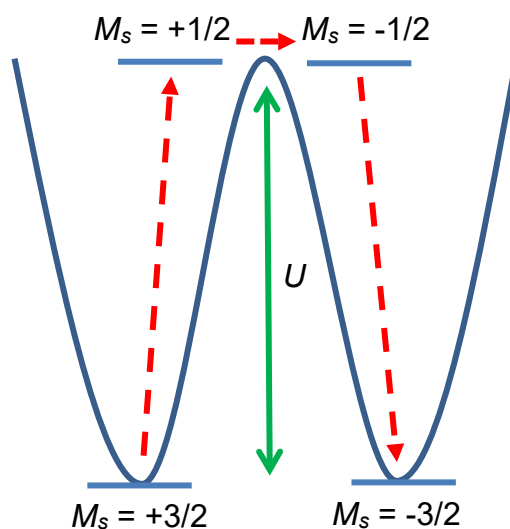


Figure 1.2. Double energy well scheme of an $S = 3/2$ system with $D < 0$ showing the energy barrier (U) and the transition between the low energy state to the high energy state while relaxing back down to the low energy state across U . The dashed red arrows are the transitions and relaxation pathways through the magnetic states. The solid green double arrow is the energy barrier to relaxation of magnetization.

spin-phonon coupling affects the relaxation process in SMMs is an actively area of experimental research, using, e.g., terahertz (THz) spectroscopy,¹³⁻¹⁵ resonant inelastic X-ray scattering (RIXS),¹⁶ far-IR magneto-spectroscopy (FIRMS),¹⁷⁻²⁰ and Raman spectroscopy.^{11, 19} Computational studies have also been performed to understand spin-phonon couplings in molecular magnets.²¹⁻²⁴ Phonon structures of SMMs have also been studied by inelastic neutron scattering (INS).^{17-19, 25-30} Works in the areas of probing phonon structures and spin-phonon coupling in molecular magnets have been recently reviewed.^{31, 32} Studies have shown that large anisotropy led to an increase in spin-phonon relaxation.³³ Methods such as FIRMS and high-field/-frequency electron paramagnetic resonance (HFEPN) can be used to directly determine the energy barrier to relaxation of the spin in SIMs as well as spin-phonon coupling.

1.1.2. Quantum Bits (Qubits)

Qubit, just like a classical bit, is the basic building block of computation. While the classical bit is the cornerstone of classical computers and supercomputers, the qubit is the elementary unit of the quantum computer. Unlike a classical bit, which can exist in one of the two classical states, $|1\rangle$ or $|0\rangle$, qubit exhibits the property of superposition. Superposition allows a qubit to simultaneously be in both states of a classical bit. The ability for a qubit to be concurrently in multiple states at one time can be observed in the increased processing speed of a quantum computer relative to a classical computer. Quantum computers can perform calculations 100 million times faster than classical computer.³⁴⁻³⁶

There are many methods in the literature that, when implemented successfully in different qubit systems, lengthened coherence (or spin-spin relaxation) time T_2 . Chemical

systems without nuclear spin, such as ^{12}O and ^{32}S atoms in the ligands bound to the V atoms in $[\text{V}(\text{C}_8\text{S}_8)_3]^{2-}$ and $[\text{VO}(\beta\text{-C}_3\text{S}_5)_2]^{2-}$, were found to lengthen T_2 of the unpaired electron on V^{IV} ion relative to chemical systems which exhibit nuclear spin.^{37, 38} The results further demonstrated that nuclear spins are associated with the decoherence of the electron spin. The potential of transition metal complexes in the application of qubit and quantum computation through the use of pulsed EPR and other magnetic spectroscopic methods such as FIRMS also highlighted in this dissertation.³⁶

One example of a spin qubit based on the structure of low-spin Co^{II} metal-organic framework (MOF) is $[(\text{TCPP})\text{Co}_{0.07}\text{Zn}_{0.93}]_3[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{H}_2\text{O})_6]_2$ [$\text{TCPP}^{2-} = \text{meso-tetra}(4\text{-carboxyphenyl})\text{porphyrinate}$].³⁹ The porphyrin ligand in the compound provides an isolated environment for the Co^{II} ions in the structure. The isolation, in turn, makes the compound a more promising SIM. The deuteration of the compound with diamagnetic Zn^{II} ions was employed in the experiment with pulsed EPR. To increase the signal-to-noise ratio in the spectra, the interactions between the Co^{II} ions must be minimized. This was accomplished by diluting the compound with diamagnetic Zn^{II} ions, increasing the distance between the individual Co^{II} ions. The structure of this compound provides an opportunity to study the qubit property of a spin 1/2 system consisting of an EPR clock transition in the hyperfine region. The Hahn echo experiment was performed as a function of temperature. T_2 of the system increases as the temperature decreases. At 5 K, T_2 is 13.74(9) μs . The relaxation time of this compound was an improvement compared to a previously reported qubit system of $[\text{Ho}(\text{W}_5\text{O}_{18})_2]^{9-}$ which has a reported $T_2 = 8.4 \mu\text{s}$.^{40, 41} These preliminary results imply promising potential in using MOFs to contribute to advancements in the field of chemical qubits.

1.1.3. Haldane One-Dimensional (1-D) Spin-1 Chains

Haldane indicated in 1983 that antiferromagnetic (AF) Heisenberg chains of integer spin exhibit a quantum disordered ground state and a finite energy gap, whereas the half-integer spin chains are gapless, based on effective-field theory and topological considerations.^{42, 43} Figure 1.3 shows the energy diagram in a Haldane spin-1 chain system, including the anisotropic (zero-field splitting or ZFS) and Zeeman effect. The topological Haldane phase of the AF spin-1 chain is regarded as the most fundamental example of symmetry-protected topological states.⁴⁴⁻⁴⁹ Following Haldane's work, Affleck, Kennedy, Lieb, and Tasaki (AKLT) identified an extended spin-1 model Hamiltonian describing the ground state of the Haldane phase with one unpaired electron at each end of the chain ($S = 1/2$),⁵⁰⁻⁵⁴ as visualized in Figure 1.4-Top. The two electrons at the ends of the chain lead to singlet or triplet as the edge states. The topological Haldane phase is unique due to the existence of the finite energy gap that is symmetry-protected.⁴⁵⁻⁴⁸ As long as symmetries are preserved, the Haldane phase is stable and can withstand external perturbations.^{47, 49} The Haldane materials are in contrast to typical antiferromagnetic materials such as NiO with long-range magnetic ordering in Figure 1.4-Bottom.⁵⁵ In NiO, a magnetic unit cell forms in addition to its crystal unit cell, leading to the observation of Bragg reflections from the magnetic unit cell together with peaks from the nuclear diffraction of its crystal unit cell.⁵⁵

1.2. Metal-Organic Frameworks (MOFs)

The term MOF was first coined by Omar Yaghi in 1995.⁵⁶ His contributions to the synthesis of different MOFs have demonstrated the advantages of using MOF in various applications. MOF or coordination polymer (CP) is a crystalline porous material which consists

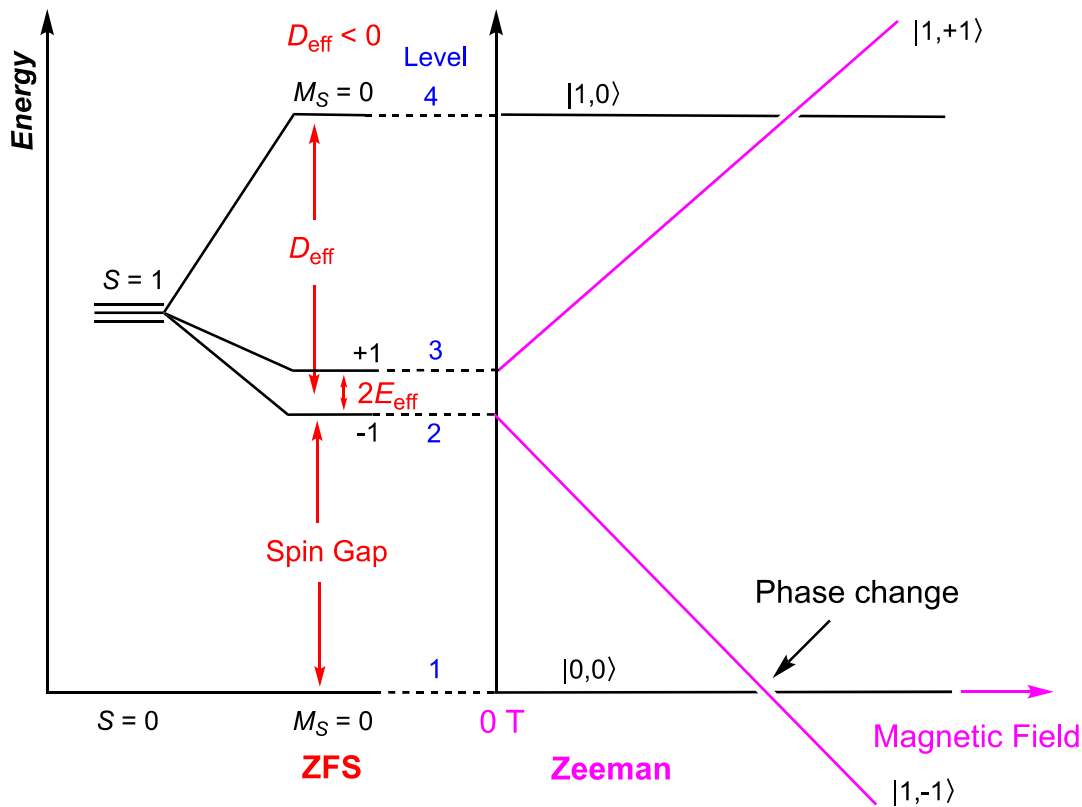


Figure 1.3. Energy diagram of a Haldane spin-1 chain system and the Zeeman effect on the magnetic states in, e.g., $[\text{Ni}(\mu\text{-}4,4'\text{-bpy})(\mu\text{-ox})]_n$ (bpy = bipyridine; ox^{2-} = oxalate; **NiBO**). Here, D_{eff} and E_{eff} are axial and rhombic (or transverse) ZFS parameters for the lowest spin excitation, respectively. The right panel illustrates the Zeeman effect on the states, leading to a magnetic phase transition at about 9 T for **NiBO**. The labels “+1” and “-1” represent $M_S = +1$ (or $|1,+1\rangle$) and -1 (or $|1,-1\rangle$) states, respectively, of the excited triplet state. The energy splitting diagram is based on the z direction [i.e., along the $\text{Ni}(\text{ox})$ chains as shown in Figure 1.4] aligned parallel to the magnetic field.

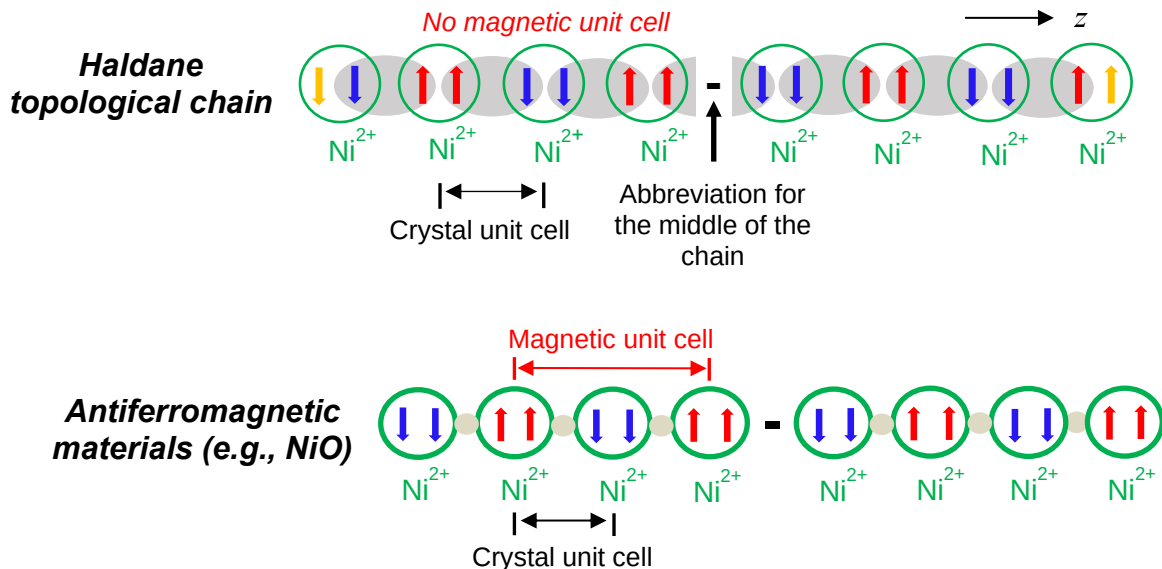


Figure 1.4. (Top) AKLT model representation of the Ni^{II} spin-1 Haldane chain showing the antiferromagnetic coupling (gray oval) between two unpaired electrons (red and blue arrows) in the middle of the chain, leaving unpaired electrons (orange arrows) at ends of the chain. These two unpaired electrons may have antiparallel (shown) or parallel spins, giving singlet and triplet states, respectively, in Figure 1.3. There is *no* magnetic unit cell in the Haldane system. (Bottom) Schematic of the antiferromagnetic structure in NiO below its Néel temperature. The magnetic unit cell has twice the linear dimension of the crystal unit cell, as revealed by powder neutron diffraction (PND).⁵⁵ In the crystal unit cell, Ni^{II} ions form a face-centered cubic cell with ferromagnetically coupled sheets that are anti-parallel with adjacent sheets. O^{2-} ions are shown as small grey cycles.

of organic ligands and metal centers. Organic ligands are used to connect one metal center to another forming a two-dimensional (2-D) or three-dimensional (3-D) structure. It should be pointed out that MOFs with voids are considered to be a subclass of CPs.⁵⁷ In subsequent discussions, MOFs and CPs are sometimes used interchangeably. MOF is known to be a rigid porous building block which can contain external molecules, such as solvent molecules.⁵⁸ The high porosity and surface area of MOFs provide an opportunity for many applications such as gas separation and storage, catalysis, and drug delivery.⁵⁸ Recently, MOFs have been a candidate for the potential use in quantum data processing and storage.⁵⁹⁻⁶³ The rigidity of the structure and the organized crystalline pattern of MOFs provide a straightforward route to scaling up qubit assemblies.³⁴ The choice of the organic spacers can greatly impact the nature of the qubit interactions between each metal node.

In SIMs, each metal ion center behaves as an isolated magnetic center. Thus, SIM in the form of MOF can be achieved by using the long organic spacers to separate the metal nodes and lower their interactions in space. SIMs studied in this dissertation are in the form of MOFs. There are certain advantages, such as definitive qubit separation distance, in arranging ion magnets in a perfect repeating array. MOFs provide the necessary structure for scaling the magnets to the macroscopic level.³⁴ The certainty in the connectivity of the structure grants SIMs the ability to be distanced from one another at a specific length. SIMs benefit from the large degree of isolation that the local environment around the ion can provide to avoid decoherence as a qubit. Furthermore, the nature of solvent molecules in the pores of the MOF can be directly responsible for changes in the topography or the structure of the MOF. Different solvents will morph the framework into different unit cells, thus changing the magnetic properties of the

compound.

Haldane spin-1 chains based on MOFs with oxalate-based ligands, $[\text{Ni}(\mu\text{-bpa})(\mu\text{-ox})]_n$ [bpa = 1,2-bis(4-pyridyl)ethane; ox^{2-} = oxalate],⁶⁴ $[\text{Ni}(\mu\text{-bpe})(\mu\text{-ox})]_n$ [bpe = 1,2-di(4-pyridyl)ethylene],⁶⁴ $[\text{Ni}(\mu\text{-en})(\mu\text{-ox})]_n$,⁶⁵ and $[\text{Ni}(\mu\text{-pip})(\mu\text{-ox})]_n$ (pip = piperazine),⁶⁶ have been reported to show the presence of a finite spin gap through DC magnetic susceptibility measurements. Unlike Haldane spin-1 chains $[\text{Ni}(\text{en})_2(\mu\text{-NO}_2)](\text{ClO}_4)$ (NENP; en = ethylenediamine),⁶⁷⁻⁷² $[\text{Ni}(1,3\text{-propanediamine})_2(\mu\text{-NO}_2)](\text{ClO}_4)$ (NINO),^{72, 73} and $[\text{Ni}(\text{en})_2(\mu\text{-NO}_2)](\text{BF}_4)$ (NENB),⁷⁴⁻⁷⁶ the MOF-based compounds exhibit stacked 2-D planar structures with decoupled magnetic 1-D chains. The ox-bridged Haldane chains in the MOFs are linked by N-containing ligands. From DC magnetic susceptibility data, García-Couceiro and coworkers found that the spin gap = 7.32 and 10.29 cm^{-1} for $[\text{Ni}(\mu\text{-bpa})(\mu\text{-ox})]_n$ and $[\text{Ni}(\mu\text{-bpe})(\mu\text{-ox})]_n$, respectively.⁶⁴ Similarly, Keene and coworkers obtained spin gap = 11.5 cm^{-1} for $[\text{Ni}(\mu\text{-en})(\mu\text{-ox})]_n$ from DC susceptibility data.⁶⁵ The spin gaps are comparable to those of other spin-1 chain systems such as NENP and NENB.^{67, 74} It should be noted that the presence of Haldane gaps in these MOFs is essentially based on DC susceptibility data fit.^{64, 65} However, the results show that 2-D MOFs containing inter-chain ligands that form planar structures have the potential to exhibit Haldane spin-chain properties, as long as the inter-chain magnetic couplings is negligible.

Moreover, 2-D MOFs can be exfoliated by overcoming the relatively weak Van der Waals force between the layers. Exfoliation of the 2-D MOFs may yield 2-D nanosheets with interesting low-dimensional properties. Several exfoliation methods have been established to be effective in synthesizing the 2-D MOF nanosheets.⁷⁷⁻⁷⁹ A review article by Zhao *et al.* shows various chemical and mechanical exfoliation methods to create 2-D nanosheets of MOFs.⁷⁷

Synthetic methods for the 2-D MOFs include the top-down and bottom-up methods, which encompass techniques like two-/three-layer synthesis and surfactant-assisted synthesis.

Mechanical exfoliation methods consist of sonication and the tape technique (used to exfoliate layers of graphene from graphite). Sonication yields different amounts of the exfoliated 2-D MOF based on the nature of the solvent used. Exfoliation methods for the crystals or powder samples are needed in various microscopy experiments, such as scanning tunneling electron microscopy.

1.3. Experimental Methods

The most common method used to determine the ZFS parameters (D , E , and g) is the magnetic susceptibility measurement. However, many previous studies have shown that the method is largely inaccurate due to the indirect determination of ZFS parameters using best fit analysis of the susceptibility data. Therefore, direct methods of measurements are needed to accurately and effectively yield the ZFS parameters. Several optical and neutron spectroscopy methods were used to elucidate the ZFS parameters including the far-IR magneto-spectroscopy (FIRMS), high-field/-frequency electron paramagnetic/spin resonance (HFEPR or HFESR), and the inelastic neutron scattering (INS).¹² FIRMS can be used to observe the magnetic transition between the ground state and the excited state. For example, the transition energy between the ground state and the excited state in an $S = 3/2$ compound is $2D'$ where $D' = (D^2 + 3E^2)^{1/2}$. When the magnetic separation is large ($>30 \text{ cm}^{-1}$ for the user facilities at the National High Magnetic Field Laboratory or NHMFL), combined use of FIRMS and HFEPR can lead to the determination of the $2D'$ value and its deconvolution into D and E values. Furthermore, HFEPR

gives the g -tensors, rhombicity ratio (E/D), and the sign of the D value. The ZFS diagram for $D > 0$, $S = 3/2$ complexes is given in Figure 1.1,^{10, 11} showing that the crystal field anisotropy split the four $(2S + 1)$ degenerate states into $M_S = \pm 1/2$ and $\pm 3/2$ Kramers doublets (KDs). The selection rules dictate the allowed and forbidden spin transitions in the system. Only transition with $\Delta M_S = 0, \pm 1$ is allowed, while the rest are forbidden transitions.

Inelastic neutron scattering (INS) can be used separately to determine the magnetic transition as well as the phonon properties of the system. Pulsed EPR is a spectroscopic method to extract spin-lattice relaxation time T_1 and coherence time T_2 as well as the Rabi oscillation for the qubit system.⁸⁰ T_1 and T_2 are relaxation times essential to understanding the effectiveness of a qubit candidate, while Rabi oscillation shows the ability of the system to exist in the superposition of the $|1\rangle$ and $|0\rangle$ state.

1.3.1. Far-IR Magneto-Spectroscopy (FIRMS)

According to Brackett and Richards, the magnetic transition in ZFS of transition metal compounds is governed by the magnetic dipole transition, therefore making the transitions allowed in the far-IR range.^{81, 82} Eq. 1.5 can be used to describe absorption cross-section of the transition between the initial ($|i_n\rangle$) and final ($|f_n\rangle$) state.⁸²

$$\alpha_n(\nu) = \frac{4\pi^2 e^2 N_o}{\hbar m_e^2 c^3} \nu \rho(\nu - \nu_n) |\langle f_n | \hat{k} \times \hat{n} \cdot \hat{S} | i_n \rangle|^2 \quad (Eq. 1.5)$$

where N_o is the paramagnetic ions concentration, m_e is the electron mass, c is the speed of light, ρ is the line-shape function, ν_n is the difference in energy between the eigenvalues of the initial and final state, $\hat{k}$ is the vector for the directions of propagation and the electric field polarization

of the incident light, $\hat{\pi}$ is the vector for the electric field polarization of the incident light, and $\hat{S}$ is the spin operator.

Furthermore, the Boltzmann distribution of the electron spin population in each state is determined at a given temperature by *Eq. 1.6*.⁸²

$$P_n(T) = \frac{\exp\left(-\frac{E_{i_n}}{kT}\right) - \exp\left(-\frac{E_{f_n}}{kT}\right)}{\sum_i \exp\left(-\frac{E_i}{kT}\right)} \quad (\text{Eq. 1.6})$$

where E_i is the solution to the spin-Hamiltonian of the initial state.

With the thermal distribution of the electron populations accounted for in each state. *Eq. 1.7* can be used to describe the total absorption $[\alpha(\nu)]$ with the sum over all possible magnetic transitions in ZFS.⁸²

$$\alpha(\nu) = \sum_n \alpha_n(\nu) P_n(T) \quad (\text{Eq. 1.7})$$

All the FIRMS experiments in the current dissertation were conducted using powder samples. The results from powder samples are the average over all orientations (x, y, z). Further studies using simulations can give the components of the magnetic transition in the x, y , and z direction parallel to the magnetic field (B). Detailed methods of the FIRMS experiments, and the analysis of the data can be found in Chapters 2 and 3.

1.3.2. *High-Field/-Frequency Electron Paramagnetic/Spin Resonance (HFEPR or HFESR)*

The HFEPR/HFESR experiments were performed under magnetic fields to understand the Zeeman effect on the magnetic transition as well as to directly determine the ZFS parameters. The Zeeman effect is the interaction between the unpaired electrons in the metal ions and the externally applied magnetic field. Since unpaired electrons have their own magnetic moment, degenerate levels of the up-spin and down-spin electrons will split inside a magnetic field. The magnetic transition in HFEPR can be described by *Eq. 1.8*.⁸³

$$\Delta E = \hbar\nu = g\mu_B B_0 \quad (\text{Eq. 1.8})$$

where ν is the applied frequency, g is the g -tensor, μ_B is the Bohr magneton, and B_0 is the applied magnetic field.

The g -tensor is a proportionality constant that is approximately in the range of 2 to 2.5 for most transition metal complexes. For a free electron, the g -tensor is equal to 2.002. In the absence of the Zeeman effect, the unpaired electrons are in the same spin states. Therefore, there is no energy difference to measure. With an applied magnetic field, the spin states are separated into a low- and a high-spin state with an energy difference. The energies of the spin states diverge linearly as the magnetic field increases. For $g = 2$, the slope of the linear separation is 2.8 MHz/G. Therefore, the energy difference between the two states depends linearly on the magnetic field.⁸³

There are two methods of measurements to determine the energy difference. For a conventional spectroscopy, a constant magnetic field is applied to the system and the frequency

is scanned. On the other hand, the frequency is constant, and the magnetic field can be scanned. The method used in this dissertation is the latter. A peak in the absorption can be detected when the magnetic field matches the energy difference, or the energy of the transition set by the radiation frequency. The resonance peak observed in the HFEPR experiments in these studies is the first derivative of the absorption peak. Detailed experimental methods can be found in Chapters 2 and 3.

1.3.3. Inelastic Neutron Scattering (INS)

Neutron carries magnetic moment due to its 1/2 spin, as electron. The magnetic moment of the neutron can interact with the magnetic moment of the unpaired electron in the paramagnetic ions, leading to the scattering of the incident neutrons from the magnetization density of the paramagnetic ions.²⁸ The scattering interactions result in a difference in energy of the incident neutron (E_i) and the scattered neutron (E_f). The difference in energy allows for the magnetic transition to occur in samples with unpaired electrons. At a low temperature, the sample is likely to gain the energy from the incident neutrons, allowing an excitation to occur between a low energy state to a high energy state.²⁵ There are three types of INS instruments: (1) Direct-geometry time-of-flight (TOF) spectrometer; (2) Indirect-geometry TOF spectrometer; (3) Triple-axis spectrometer.²⁵ In this dissertation, we have used the indirect-geometry TOF vibrational spectrometer (VISION) at the Spallation Neutron Source (SNS) in Oak Ridge National Laboratory (ORNL) to study the magnetic transitions and phonon properties.

For the indirect-geometry TOF spectrometer, the incident neutrons are from a “white” (i.e., many wavelengths/energies) neutron beam where E_i is determined in part by the time for

the neutrons to reach the detectors using TOF. E_f of the scattered neutrons is fixed to a certain value. VISION can detect magnetic transitions and phonon energies between 10 and 8000 cm^{-1} . The spectrometer contains two banks of analyzers with two different scattering angles at 45° (forward scattering) and 135° (backward scattering).²⁵ Analysis of the neutron data were conducted using a software in the ORNL internal computational system called *Mantid workbench*. The background data were subtracted from the whole data and Bose-correction were performed. Bose-correction is a data processing method that accounts for the phonon population (boson) dependency on the temperature. To clearly reveal the magnetic transition of the unpaired electron (fermion), temperature-dependence measurements were performed. While fermions follow the Boltzmann distribution, bosons follow the Bose-Einstein distribution. The Bose-correction allows the intensities of phonon peaks to stay about the same as the temperatures are changed, while intensities of the magnetic transitions change with temperature due to Boltzmann distribution. Further discussions of the phonon nature in the INS experiments can be found in Chapters 2 and 3.

1.3.4. Pulsed Electron Paramagnetic Resonance (Pulsed EPR)

Pulsed EPR has been used to study the magnetization property of the qubit system. There are two important properties of qubits that can be obtained from pulsed EPR, spin-lattice relaxation time (T_1) and coherence (spin-spin relaxation) time (T_2). T_1 is the time for the magnetization of the electron to go back to the initial state in a magnetic field. T_2 is the decay of the magnetization time from the transverse plane and is used to determine the dephasing of the qubit from the superposition state.⁸⁰ The ideal condition for quantum calculations is for the qubit

to be in the superposition state as long as possible. Therefore, a long T_2 is desirable. The realization of a qubit system with long T_2 is challenging, as the interaction with the local environment causes the rapid collapse of the superposition state through a process called decoherence. Effects such as nuclear spin diffusion coupling to nearby electrons, methyl rotation, and spin diffusion barrier are major obstacles to prolonging T_2 .³⁴ In order to avoid short T_2 , minimizing or eliminating factors affecting T_2 is vital. Further detailed discussion of the pulsed EPR in the current dissertation can be found in Chapters 2 and 3.

1.4. Current Dissertation

In this dissertation, first row transition metal complexes and MOFs have been studied to understand magnetic properties such as anisotropies, magnetic transitions, qubit properties, and Haldane properties. Three types of systems have been studied: (1) Two different Co^{II} MOFs displacing SIM properties; (2) A topological Ni^{II} MOF with Haldane gaps; (3) Molecular Fe^{III} complexes. The studies comprise of the following goals: (1) Determination of ZFS parameters and the Haldane spin gap using optical and neutron spectroscopic methods such as FIRMS, HFEPR/HFESR, and INS; (2) Probing the qubit properties of the Co^{II} MOFs using pulsed EPR; (3) Investigation of phonon properties of the MOFs; (4) Elucidating the Haldane properties of the Ni^{II} MOF.

1.4.1. Chapter 2

Magnetic and phonon properties of two-dimensional (2-D) MOF/CP $[\text{Co}^{\text{III}}(\text{CN})_6]_2[\text{Co}^{\text{II}}(\text{TODA})]_3 \cdot 9\text{H}_2\text{O}$ (**Co-TODA**) have been studied by advanced

spectroscopies and computations. Combined use of FIRMS and variable-temperature (VT) HFEPR gives spin-Hamiltonian (SH)/ZFS parameters, D and E , revealing that **Co-TODA** has the easy-plane magnetic anisotropy. Two Co^{II} centers in **Co-TODA**, as determined by synchrotron single-crystal X-ray diffraction at 15(2) K, show similar magnetic properties indistinguishable in FIRMS at 5.3(3) K or in HFEPR at 5-150 K. *Ab initio* calculations explore the origin of the magnetic anisotropy and magnetostructural correlations. VT inelastic neutron scattering (INS) spectra show the phonon properties of the CP. Spin distributions in **Co-TODA** from density functional theory (DFT) calculations demonstrate that, when compared with other high-spin Co^{II} complexes, the larger spin density on a metal ion, the larger ZFS in the complex. Pulsed X-band EPR studies probe relaxations of the Co^{II} ions in **Co-TODA** from the $M_S = +1/2$ to $-1/2$ state in the ground Kramers doublet (KD), yielding spin-lattice (T_1) and spin-spin relaxation (T_2) times.

1.4.2. Chapter 3

Synthesis and characterization of the 2-D MOF, $[\text{Co}(\mu\text{-bpeb})_2(\text{NCS})_2]_n \cdot n\text{G}$ [**Co-BEBN**; bpeb = 1,4-bis(pyridine-4-ylethynyl)benzene; G = 1,2-dichlorobenzene], are reported, including an in-depth analysis of the magnetic properties of **Co-BEBN** using a combination of optical and neutron spectroscopies in conjunction with *ab initio* calculations. Our studies demonstrate that **Co-BEBN** is a SIM with, to our knowledge, the largest ZFS among six-coordinated Co^{II} systems. In addition, among those with very large ZFS ($>250 \text{ cm}^{-1}$), it is the only one determined by spectroscopies rather than by fitting DC susceptibility data. **Co-BEBN** also displays qubit properties. *Ab initio* electronic structure calculations help understand the origin of the anisotropy

and the magneto-structural nature of **Co-BEBN**.

1.4.3. Chapter 4

We report that $[\text{Ni}(\mu\text{-}4,4'\text{-bpy})(\mu\text{-ox})]_n$ (bpy = bipyridine; ox^{2-} = oxalate; **NiBO**) is a Haldane spin-1 chain material. It has been comprehensively probed by a variety of techniques, including variable-temperature (VT) powder neutron diffraction (PND), magnetization measurements (DC magnetic susceptibility at different fields), high-field EPR (HFEPR), inelastic neutron scattering (INS), and specific heat measurements. In addition, quantum Monte Carlo (QMC) simulations of the spin-1 chains in **NiBO** have been performed, revealing remarkable agreements with the results from DC magnetic susceptibility measurements. VT-PND data, showing no long-range antiferromagnetic ordering down to 1.7 K, further support that **NiBO** is a Haldane material. Both the magnetic susceptibility data and specific-heat data reveal a field-induced phase transition in **NiBO** for magnetic field beyond 9 T and temperatures below 5 K. X-ray single-crystal diffraction of deuterated $[\text{Ni}(\mu\text{-}4,4'\text{-bpy-}d_8)(\mu\text{-ox})]_n$ (**NiBO- d_8**) at 100 K shows a non-planar structure of the 4,4'-bpy- d_8 ligand.

1.4.4. Chapter 5

Magnetic properties study of five-coordinate tetraphenylporphyrinatoiron complexes in **Fe^{III}(TPP)X** (**X** = **F**, **Cl**, **Br**, **I**; TPP^{2-} = *meso*-tetraphenylporphyrinate) is presented. The series of **Fe(TPP)X** complexes presented in this work offers a specific case allowing the following: (1) Comparison of diverse experimental techniques, including relatively new and advanced magnetic resonance methods such as HFEPR and FIRMS, in terms of accuracy and precision of

measurement; (2) From a scientific viewpoint, methodically tracking the influence of the axial halide ligand on the resulting ZFS of the given complex.

Chapter 2

Advanced Spectroscopic and Computational Studies of a Cobalt(II) Coordination Polymer with Single-Ion-Magnet Properties

This chapter is based on the following paper:

Pagnareach Tin, Alexandria N. Bone, Nhat N. Bui, Yi-Quan Zhang, Tieyan Chang, Duncan H. Moseley, Mykhaylo Ozerov, J. Krzystek, Yongqiang Cheng, Luke L. Daemen, Xiaoping Wang, Likai Song, Yu-Sheng Chen, Dong Shao, Xin-Yi Wang, Xue-Tai Chen, Zi-Ling Xue, Advance Spectroscopic and Computational Studies of a Cobalt(II) Coordination Polymer with Single-Ion-Magnet Properties. *J. Phys. Chem. C* **2022**, *126*, 13268. <https://doi.org/10.1021/acs.jpcc.2c03083>

Author contributions:

P. Tin, D.H. Moseley, and M. Ozerov performed the FIRMS experiments. PT and MO interpreted FIRMS results and conducted simulations of transitions using *EasySpin* package. J. Krzystek performed HFEPR experiments, analyzed, and interpreted the results. N.N. Bui and L. Song performed pulsed X-band EPR experiments and helped interpret the results. PT processed the pulsed X-band EPR data and interpreted the results. Y.-Q. Zhang performed the electronic structure calculations and interpreted the results. L.L. Daemen, Y. Cheng, and PT collected VT INS spectra. PT analyzed the INS data and interpreted the results. Cheng conducted VASP calculations of the INS spectra and spin density. PT processed data from the calculations and interpreted results. T. Chang and Y.-S. Chen collected single-crystal X-ray diffraction data at 15 K and helped process the data. A.N. Bone processed the X-ray diffraction data and solved the structure. X. Wang resolved the disorder in the structure. D. Shao and X.-Y. Wang prepared the **Co-TODA** sample. X.-T. Chen initiated parts of the project and helped interpret the results. Z.-L. Xue initiated parts of the project, supervised the research, including data analyses, and interpreted the results of VASP calculations. Tin, Bone, Krzystek, Zhang, and Xue wrote the

manuscript with input from all authors.

2.1. Abstract

Two-dimensional (2-D) coordination polymer $[\text{Co}^{\text{III}}(\text{CN})_6]_2[\text{Co}^{\text{II}}(\text{TODA})]_3 \cdot 7\text{H}_2\text{O}$ (TODA = 1,4,10-trioxa-7,13-diazacyclopentadecane, **Co-TODA**) was reported earlier to show field-induced slow magnetic relaxation, displaying single-ion magnet (SIM) behaviors. Most SIMs are molecular compounds with fewer adopting coordination polymer (CP) or metal-organic framework (MOF) structures. In the current work, magnetic and phonon properties of **Co-TODA** have been studied by advanced spectroscopies and computations. A combined use of far-IR magneto-spectroscopy (FIRMS) and variable-temperature (VT) high-field/-frequency electron paramagnetic resonance (HFEPR) gives spin-Hamiltonian (SH) parameters: Axial zero-field splitting (ZFS) parameter D as $+38.0(1.0) \leq D \ll +40.2(1.0) \text{ cm}^{-1}$ and rhombic ZFS parameter E as $0 \ll |E| \leq 7.3(1.0) \text{ cm}^{-1}$, showing that **Co-TODA** has the easy-plane magnetic anisotropy. Two Co^{II} centers in the CP, as determined by synchrotron single-crystal X-ray diffraction at 15(2) K, show similar magnetic properties indistinguishable in FIRMS at 5.3(3) K or in HFEPR at 5-150 K. *Ab initio* calculations explore the origin of the magnetic anisotropy and magnetostructural correlations. VT inelastic neutron scattering (INS) spectra of **Co-TODA** have been obtained to show the phonon properties of the CP. Density functional theory (DFT) calculations, giving both a calculated INS spectrum and spin distributions in **Co-TODA**, demonstrate that, when compared with other high-spin Co^{II} complexes, the larger spin density on a metal ion, the larger ZFS in the complex. Pulsed X-band EPR studies probe relaxations of the Co^{II} ions from the $M_S = +1/2$ to $-1/2$ state in the ground Kramers doublet (KD), yielding spin-

lattice (T_1) and spin-spin relaxation (T_2) times. The work reported here highlights the versatility and power of the spectroscopic techniques and computations in the characterization of magnetic and phonon properties of a CP and the understanding of its magnetic anisotropy.

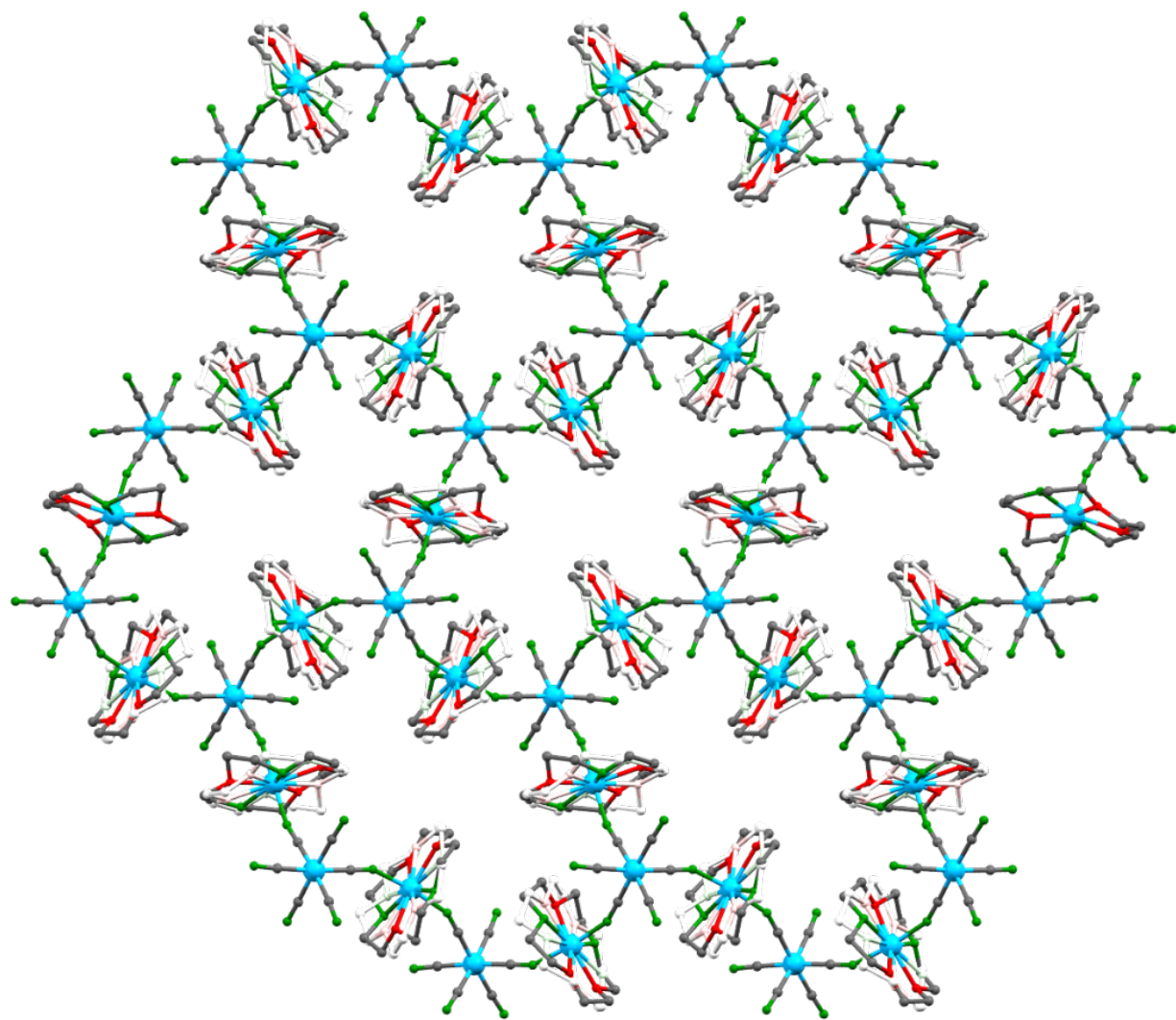
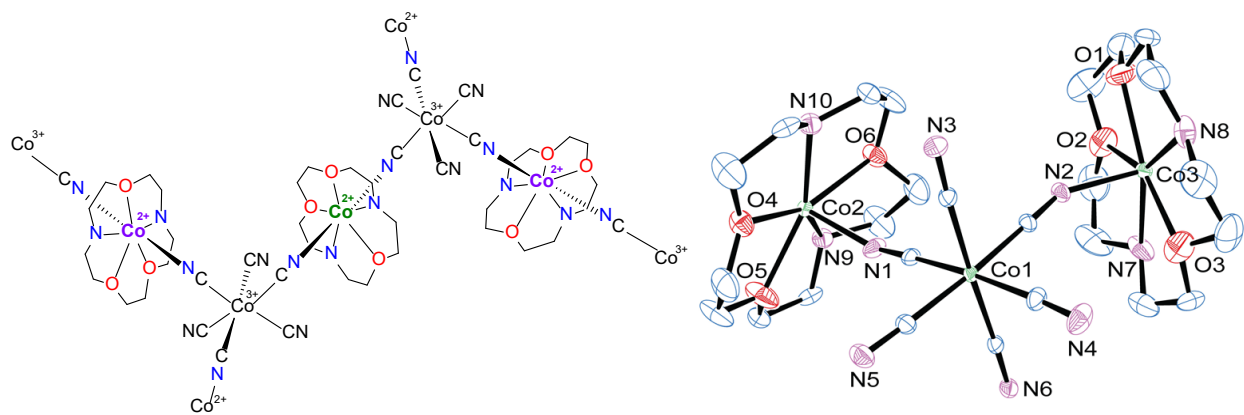
2.2. Introduction

Introduction of single-molecule magnets (SMMs), including zero-field splitting (ZFS) in high-spin Co^{II} complexes and the energy splitting diagram for $S = 3/2$ complexes when $D > 0$ in Figure 1.1, and qubits is given in Chapter 1, Subsections 1.1.1 and 1.1.2, respectively. Overviews of MOFs and experimental methods to probe magnetism are provided in Chapter 1, Sections 1.2 and 1.3, respectively.

Reported SIMs are mostly molecular compounds. There are fewer SIMs as coordination polymers (CPs) or metal-organic frameworks (MOFs) which provide the necessary structures for scaling the magnets to the macroscopic level,⁸⁴ although MOFs and CPs,⁸⁵⁻⁸⁷ including cyanometallate CPs,^{85, 86} are of intense current interest with many applications. SIMs with CP structures can be achieved by using long organic spacers to separate the metal nodes and lower their interactions in space.

Two-dimensional (2-D) CP **Co-TODA**, $[\text{Co}^{\text{III}}(\text{CN})_6]_2[\text{Co}^{\text{II}}(\text{TODA})]_3 \cdot 9\text{H}_2\text{O}$ (Structure in Figure 2.1), was recently synthesized and found to have SIM properties by Shao and coworkers.⁸⁸ In the CP, there are two slightly different high-spin seven-coordinated Co^{II} ions, each coordinated by a TODA and two CN^- ligands, in addition to a low-spin (diamagnetic) six-coordinated Co^{III} ion. Cyanometallates have been widely used as building blocks to give magnetic materials.⁸⁸⁻⁹³ Fitting of direct current (DC) magnetic

Figure 2.1. (Top-Left) $[\text{Co}^{\text{III}}(\text{CN})_6]_2[\text{Co}^{\text{II}}(\text{TODA})]_3 \cdot n\text{H}_2\text{O}$ (**Co-TODA**). There are two different Co^{II} ions (purple and green color) in the structure. The lattice water molecules are omitted. (Top-Right) Crystal structure of **Co-TODA** at 15(2) K. Colors: red = O, purple = N, green = Co, blue = C. H-atoms and the disordered components of the structure were omitted for clarity. Selected bond lengths and angles are given in Figure A.6. (Bottom) Packing structure of **Co-TODA** at 15(2) K, showing the interconnected network with pores in the MOF structure. H atoms and lattice water molecules are omitted for clarity.



susceptibility data of **Co-TODA** yielded $D = 29.9 \text{ cm}^{-1}$ and 26.5 cm^{-1} by the PHI and Anisofit2.0 programs, respectively.⁸⁸ AC (alternating current) susceptibility data under 5500 Oe external dc field at 2.0-3.0 K gave the effective energy barrier $U_{\text{eff}} = 12.6 \text{ cm}^{-1}$ and the relaxation time of, e.g., 130 μs at 3.0 K.⁸⁸

We are interested in an in-depth understanding of the magnetic properties of **Co-TODA** with the following: (1) Determination of the CP structure at 15(2) K (near 1.8-3.0 K in which **Co-TODA** reveals the SIM properties) through single-crystal X-ray diffraction to see if there is any phase change from the reported crystal structure at 123 K;⁸⁸ (2) Spectroscopic observations of *inter*- and *intra*-KD transitions of **Co-TODA** to determine spin-Hamiltonian parameters (D , E , and g) of the CP by a combined use of HFER and FIRMS; (3) Probe of the *inter*-KD magnetic transition and phonons by INS with the help of a DFT-calculated INS spectrum; (4) Study of the magnetic anisotropy through electronic structure calculations by complete active space second-order multiconfigurational perturbation theory (CASPT2) and N-electron valence second-order perturbation theory (NEVPT2); (5) Calculations of spin densities in **Co-TODA** to see, when compared with other high-spin Co^{II} compounds, whether there is a correlation between the axial anisotropy (D) values in the compounds (or the CP) and spin densities on the Co^{II} ions; (6) Determination of spin-lattice (T_1) and spin-spin (T_2) relaxation times for the *intra*-Kramers $\phi_2 \rightarrow \phi_1$ relaxation by pulsed EPR. Our studies are reported.

2.3. Results and Discussions

2.3.1. *Single-Crystal Structure of Co-TODA at 15(2) K*

Determination of the crystal structure of **Co-TODA** at 15(2) K by X-ray diffraction was prompted by the following two considerations: (1) Reported SIM behaviors of **Co-TODA** (and many other SMMs) are displayed at 15(2) K or below, while its reported crystal structure was determined at 123 K.⁸⁸ (2) While the structure at 123(2) K shows two Co^{II} centers, neither FIRMS nor HFEPR, discussed below, resolved the transitions from the two Co^{II} centers in **Co-TODA**. Thus, it is desirable to rule out a phase change between 123(2) K and 15(2) K.

The structure at 15(2) K determined by synchrotron X-ray diffraction is similar to that at 123 K. The shortest Co^{II}...Co^{II} distance is 7.52 Å, while the longest Co^{II}...Co^{II} distance is 15.4 Å with an interlayer separation of 9.18 Å between the Co^{II} ions. Each diamagnetic Co^{III} ion acts as a spacer between the Co^{II} ions, making each Co^{II} unit as a SIM. Both Co^{II} ions, **Co2** and **Co3**, are coordinated by the five atoms (three N and two O atoms) of a TODA ligand and two N atoms of the CN⁻ ligands in similar pentagonal bipyramidal geometries. The Continuous Shape Measures (CShM) were performed on the two Co^{II} centers in the 15(2) K structure to determine their deviations from the ideal (D_{5h}) geometry. The CShM values of **Co2** and **Co3** show deviations of 0.791 and 0.410 from 0, respectively. With similar geometries, the magnetic properties of the two different Co are expected to be comparable.

Additional plots of the 15(2) K crystal structure in **Co-TODA**, showing its CP features, are given in Appendix A. Variable-temperature (VT) HFEPR was performed to observe potential changes to the magnetic properties between 5 K and 150 K due to the potential phase change. The VT-HFEPR results will be discussed below.

2.3.2. *Studies of the Magnetic Transitions by FIRMS and HFEPR to Determine Spin-Hamiltonian Parameters*

2.3.2.1. FIRMS

As indicated earlier, the FIRMS experiment was used to probe dominant *inter*-Kramers transitions from ϕ_1 to ϕ_3 and ϕ_4 (Figure 1.1). The experiments were performed several times at 5.3(3) K under magnetic field ranging from 0.000(2) T to 17.000(2) T with a 1 T step. Figure 2.2-Top shows a transmittance plot of the FIRMS data. The data were collected at each magnetic field separately and then normalized to a reference, which is an average of all transmission spectra. The purpose of normalization is to eliminate instrumental arbitrations or artifacts as well as the non-magnetic spectrum background. A comparison of the 0 and 17 T transmittance plots (Figure 2.2-Top) did not clearly reveal a magnetic peak in the 0 T plot. However, a major change of $\sim 2\%$ in intensity between the 0 and 17 T spectra (Figure 2.2-Top) is observed around $80.4(1.0) \text{ cm}^{-1}$, while spectra match each other beyond this spectral range. In Figure 2.2-Bottom, a colored two-dimensional (2-D) FIRMS plot was obtained through a normalization process. In this plot, the intensity in the blue region reveals the magnetic transitions. The FIRMS and HFEPR (discussed below) do not have enough resolution to resolve the magnetic transitions from the two Co^{II} centers in the CP in the powder form. The blue region at $\sim 78\text{-}83 \text{ cm}^{-1}$ is broad, suggesting that transitions from both Co^{II} centers are in the 2 cm^{-1} -wide range. The transitions from two different Co^{II} centers in **Co-TODA** cannot be distinguished in Figure 2.2-Bottom in part because the transition is weak. Repeated FIRMS experiments to resolve the transitions from the two Co^{II} centers did not work. The energy separation between the two Kramers doublets is $2D' = 80.4(1.0) \text{ cm}^{-1}$. The result from FIRMS, combined with those from HFEPR, give the SH

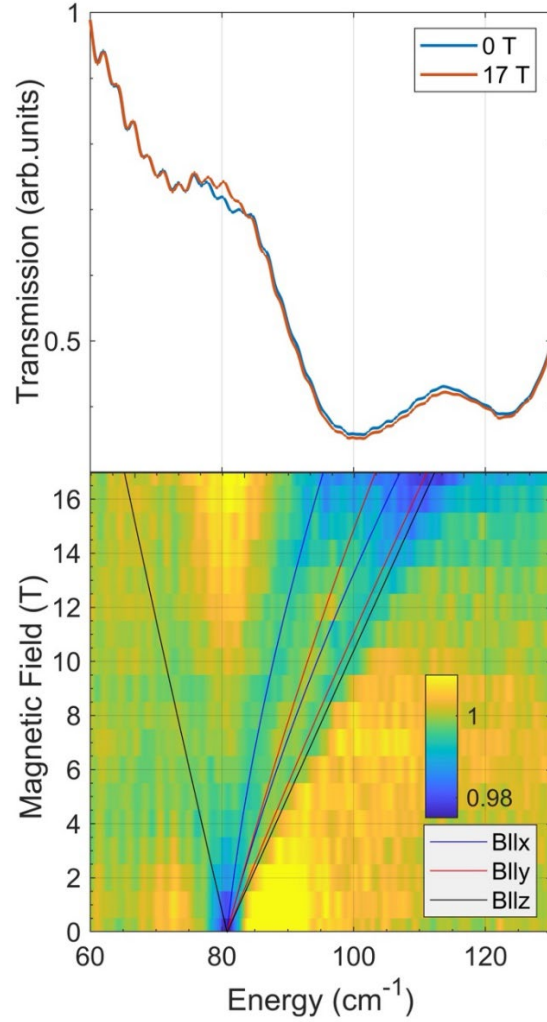


Figure 2.2. (Top) Transmittance line plot of FIRMS data at 5.3(3) K. (Bottom) 2-D FIRMS plot showing the zero-field magnetic transition originating from 80.4(1.0) cm⁻¹ and its evolution at applied high magnetic fields. The blue, red, and black lines are simulated transitions, using *EasySpin* on MATLAB,⁹⁴ when the magnetic field is applied along the x -, y -, and z -axes of the $[D,E]$ tensor, respectively. The ZFS parameters used in the simulations are $D = 38.3(1.0)$ cm⁻¹, $E = 7.3(1.0)$ cm⁻¹, and $g = [2.33(6), 2.33(6), 2.06(6)]$, as discussed below in the HFEPR section. The 2-D FIRMS plot was obtained from data normalized to the reference spectrum, which is the average spectrum for all magnetic fields.

parameters discussed below.

For $S = 3/2$ compounds (or CPs) with rhombic $E (\neq 0)$ parameters, such as **Co-TODA** here, mixing of the two spin states (Figure 1.1) makes both inter-KD transitions from ϕ_1 , $\phi_1 \rightarrow \phi_3$ and $\phi_1 \rightarrow \phi_4$, allowed inside a magnetic field. The zero-field splitting is directly observed at 80.4 cm^{-1} (Figure 2.2-Bottom). The simulated transitions in Figure 2.2-Bottom were generated using *EasySpin*⁹⁴ on MATLAB and $D = 38.3(1.0) \text{ cm}^{-1}$, $E = 7.3(1.0) \text{ cm}^{-1}$, and $g = [2.33(6), 2.33(6), 2.06(6)]$. As the magnetic field increases, the two transitions from ground state $\phi_1 \rightarrow \phi_3$ and $\phi_1 \rightarrow \phi_4$ split, each along the $\mathbf{B}\parallel x$, $\mathbf{B}\parallel y$ and $\mathbf{B}\parallel z$ directions of the magnetic anisotropy tensor. One $\mathbf{B}\parallel z$ transition is red-shifted to lower energy (Figure 2.2-Bottom). The other $\mathbf{B}\parallel z$ transition and two $\mathbf{B}\parallel x$ and $\mathbf{B}\parallel y$ transitions each are blue-shifted with increasing field. One $\mathbf{B}\parallel x$ transition matches an observed trace in Figure 2.2-Bottom well. Another observed trace appears to follow one simulated $\mathbf{B}\parallel y$ and $\mathbf{B}\parallel z$ transitions. These lines restrict the area of the resonance frequencies, which are smeared in the magnetic field due to the arbitrary orientation of the microcrystalline in the powder sample. The FIRMS spectra and *EasySpin* simulations are similar to the reported FIRMS spectra of $\text{Co}(\text{acac})_2(\text{H}_2\text{O})_2$ and simulations of the spectra, which also give one red-shift and five blue-shift traces for the $\phi_1 \rightarrow \phi_3$ and $\phi_1 \rightarrow \phi_4$ transitions.¹¹ The simulations in the current work gave reasonable fits to the experimental data, which further support the direct observation of the zero-field splitting at 80.4(1.0) cm^{-1} as well as the Zeeman splitting that occurs at a higher magnetic field.

No spin-phonon coupling was observed in FIRMS involving the magnetic transitions from 80.4(1.0) cm^{-1} , although there is a strong far-IR peak at $\sim 98 \text{ cm}^{-1}$ which may be too far from 80.4(1.0) cm^{-1} to show spin-phonon coupling at 0 T. The magnetic

transition at $80.4(1.0) \text{ cm}^{-1}$ in FIRMS is not strong. In addition, the CP structure leads to unique vibrational/phonon features (which appear to be different from those of molecular compounds).⁹⁵ For example, rotations of organic linkers in MOFs may be hindered. Trampoline-like motions were observed recently in a low-symmetry MOF, which was believed to be a potential source of negative thermal expansion of the MOF.⁹⁵ However, to understand why spin-phonon coupling in **Co-TODA** was not observed in FIRMS requires separate studies including computations similar to those reported recently for ionic and molecular compounds.^{31, 32, 96-98}

INS was also performed to determine the *inter*-Kramers transition and phonon features in **Co-TODA** that are discussed below.

2.3.2.2. HFEPR

The HFEPR experiment was used to probe *intra*-Kramers transition ϕ_1 to ϕ_2 , as shown in Figure 1.1. For each frequency used for a powder sample of **Co-TODA**, three peaks at different magnetic fields: $\mathbf{B}||x$, $\mathbf{B}||y$ and $\mathbf{B}||z$, are expected.

The experiment was conducted at 10(1) K with various set frequencies and variable magnetic fields. **Co-TODA** produced a clear HFEPR pattern at any frequency, showing three peaks (turning points) when pressed into a pellet with *n*-eicosane. The spectrum was simulated using the SH parameters in the caption of Figure 2.3 with the assumption of powder distribution of crystallites in the sample. The simulated spectrum agrees very well with the experimental one. It is characteristic of a high-spin Co^{II} ion with positive D , i.e., easy-plane anisotropy, and pronounced rhombicity (E) of the ZFS tensor. Figure 2.3-Left shows a spectrum at 10(1) K and

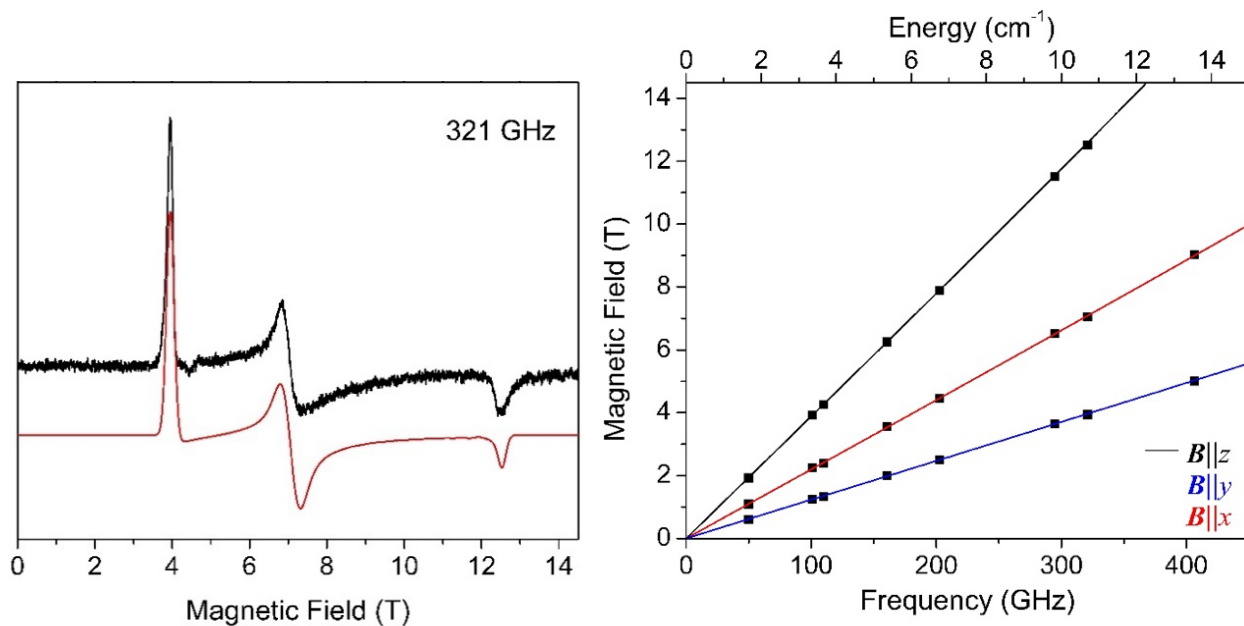


Figure 2.3. (Left) HFEPR spectrum of **Co-TODA** at 10(1) K and 321 GHz (black trace) and its simulation (red trace) using the following SH parameters: $D = 38.3(1.0) \text{ cm}^{-1}$, $E = 7.3(1.0) \text{ cm}^{-1}$, $\mathbf{g} = [2.33(6), 2.33(6), 2.06(6)]$. (Right) 2-D map (magnetic field vs. frequency/energy) of turning points in HFEPR spectra of **Co-TODA** at 10(1) K. The squares are experimental points while the lines were simulated using best-fit SH parameters. (The D and E values were chosen such that $2D'$ agrees with the ZFS transition at that was found in FIRMS).

321 [or 321.000(2)] GHz with its simulation. The separation of B_x and B_y turning points in the HFEPR spectra could also be a result of the g -anisotropy (g_x not equal to g_y). However, simulations show that, in order for the g -anisotropy to reproduce that separation, the g -values would have to be physically unrealistic. The actual E parameter should thus be understood as being $0 \ll E \leq 7.3(1.0) \text{ cm}^{-1}$ and D as $38.0(1.0) \leq D \ll 40.2(1.0) \text{ cm}^{-1}$. That is, the E and D values are much closer to $7.3(1.0) \text{ cm}^{-1}$ and $38.0(1.0) \text{ cm}^{-1}$, respectively, than to 0 and $40.2(1.0) \text{ cm}^{-1}$.

Due to the large rhombicity ($E \gg 0$) in **Co-TODA**, there is a significant mixing of the $M_S = \pm 1/2$ and $M_S = \pm 3/2$ spin states, giving, e.g., $\phi_1 = -a|-1/2\rangle + b|+3/2\rangle$ and $\phi_2 = -a|+1/2\rangle - b|-3/2\rangle$ for the lower energy KD [Mixing coefficients: $a = \cos \beta$, $b = \sin \beta$, $\tan 2\beta = \sqrt{3} (E/D)$], as shown in Figure 1.1. Thus, the Zeeman splitting is a function of both g and the mixed spin states. Using the $D' = (D^2 + 3E^2)^{1/2}$ value from FIRMS, a simulation to the 2-D map of turning points in Figure 2.3-Right gave the values of the spin-Hamiltonian (SH) parameters D , E , and $\mathbf{g}$ [g_x , g_y , g_z]. The simulations assume that the g -tensor is axial, which we do not know since E and g -rhombicity are interrelated. We can only state that the $E/D = 0.19$ ratio represents the maximum value. With the combined data from FIRMS and HFEPR, we were able to quantify the values of D , E , and g in the spin-Hamiltonian as well as determine the *inter*-Kramers transition energy of the CP.

The single-crystal structure of **Co-TODA** at 123(2) K shows two different Co^{II} centers, while both FIRMS and HFEPR data at 5-10 K, *using powder samples*, did not resolve the transitions from the two Co^{II} centers in **Co-TODA**. Repeated attempts to synthesize the CP only yielded powders or small crystals not large enough for single-

crystal FIRMS and HFEPR studies. The single-crystal structure of **Co-TODA** at 15(2) K, discussed earlier, is similar to that at 123(2) K, ruling out a phase change between the two temperatures. In other words, the two different Co^{II} centers exist at both 15(2) K and 123(2) K. We have decided to conduct VT HFEPR at several temperatures between 5(1) K and 150(1) K to reveal potential changes in the magnetic properties of the molecule at the different temperatures. Figure 2.4 shows the VT HFEPR graph at a set frequency of 273 [or 273.000(2)] GHz. The characteristics of all three visible EPR patterns did not change as the temperature decreased. The VT HFEPR results are consistent with the single-crystal X-ray diffraction results, which showed no phase transition between 5(1) K and 150(1) K. Therefore, there are no changes to the magnetic characteristics of **Co-TODA** at the low temperature.

It is noted that both the current FIRMS/HFEPR spectroscopies and earlier DC susceptibility data fitting⁸⁸ show that **Co-TODA** has the easy-plane anisotropy, although the current spectroscopic studies give direct determination of the D and E values. The easy-plane anisotropy ($D > 0$) obtained from HFEPR here is supported by the *ab initio* calculations discussed below. Easy-axis anisotropy ($D < 0$) was considered to be an important criterion for SIMs because it favors high $|M_S|$ states energetically.⁹⁹ In a classical picture, for molecules with the easy-plane anisotropy, there is no (when $E = 0$) or a small (when $E \neq 0$) barrier for spin reversal because of the condition $|E| = D/3$.⁹⁹ In addition, spin tunnelling rates are expected to be high.⁹⁹ Both factors contribute to the loss of magnetic memory. However, many complexes with the easy-plane anisotropy,¹⁰⁰⁻¹¹¹ including **Co-TODA** here,⁸⁸ have shown SIM behaviors with slow magnetic relaxation. Using Co(acac)₂(H₂O)₂ (acac⁻ = acetylacetonate) as a model, Gomez-Coca and coworkers have found that the slow relaxation in such systems is a general

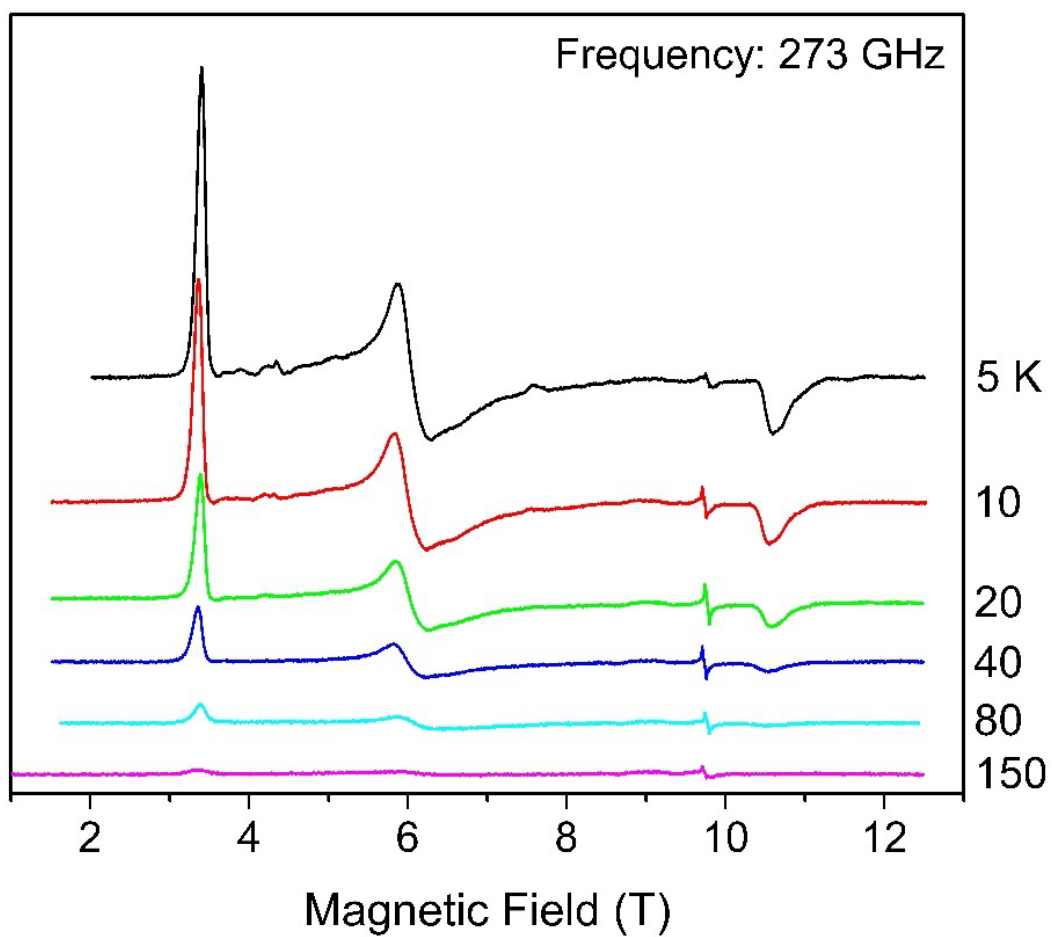


Figure 2.4. VT HFEPR spectra at 273 GHz with temperatures ranging from 5(1) K to 150(1) K.

The narrow resonance at ca. 9.8 T is due to an unidentified $S = 1/2$ impurity.

consequence of time-reversal symmetry that hinders direct spin–phonon processes regardless whether the complexes have the easy-plane or easy-axis anisotropy.⁹⁹ It is also noted that the reported AC susceptibility measurements of **Co-TODA** at 2.0-3.0 K give $U_{\text{eff}} = 11 \text{ cm}^{-1}$,⁸⁸ which significantly lower than $+38.0(1.0) \leq D < +40.2(1.0) \text{ cm}^{-1}$ determined spectroscopically here.

2.3.3. INS Studies of the Inter-KD Transition and Phonon Properties

INS spectra give complete phonon spectra of the sample, which may help understand phonon properties of the CP. In addition, INS may show magnetic transitions in the sample. There are generally two types of interactions between incident neutrons and a sample in the INS process. The neutrons interact with the atomic nuclei of the sample, leading to the excitation of phonons. The neutrons (spin = 1/2) also interact with the magnetic field of the sample created by its unpaired electrons, leading to the magnetic excitations.

Phonons of molecular crystals include both internal and external modes.^{29, 112} Internal mode or (intramolecular) vibration is caused by the distortion of atoms in a molecule as well as a slight shift in the molecular center of mass. External mode (or lattice vibration) is that of the lattice with little to no internal distortion of the molecule. All phonon modes, however, exhibit features of both internal and external modes. Phonons in this study refer to both external and internal modes in the solid. Variable-temperature (VT) INS may be used to differentiate the magnetic and phonon transitions. Because electrons and phonons are fermions and bosons, respectively, they will have different temperature profiles, making it possible to use Bose-corrected VT INS to distinguish magnetic transitions from those of phonons.

Current INS studies were conducted using vibrational spectrometer (VISION) at ORNL.

The INS work was performed by sealing 0.5 g of sample in an aluminum container under helium. The spectra were measured at 5.0(5), 25.0(5), 50.0(5), 75.0(5), 100.0(5), 125.0(5), and 150.0(5) K for one hour at each temperature. Bose-corrected INS spectra of forward scattering data and back scattering data are given in Figure 2.5. Since phonons are bosons following Bose-Einstein statistics,^{17, 26, 27, 102, 113-115} the Bose correction applies a frequency- and temperature-dependent normalization factor such that INS spectra measured at different temperatures are brought to a similar level for comparison. In other words, the spectrum is divided by the phonon population factor, which facilitates the comparison of the various spectra collected at different temperatures. Phonon features at different temperatures in Bose-corrected spectra are expected to have similar profile and baseline intensity. The magnetic transition from electrons, which are fermions, does not follow the expected temperature dependence for phonons. A broad peak was observed at $\sim 75(2) \text{ cm}^{-1}$ in the INS spectrum at 5.0(5) K, which is more intense in the forward scattering (Figure 2.5-Top) than in the back scattering spectrum at 5.0(5) K (Figure 2.5-Bottom), when, e.g., compared with the peak to its right [at $\sim 94(1) \text{ cm}^{-1}$]. In INS, magnetic transitions are stronger in the forward scattering (with smaller magnitudes of the momentum transfers, $|\mathbf{Q}| = |\mathbf{k}_i - \mathbf{k}_f|$; $\mathbf{k}_i$ and $\mathbf{k}_f$ refer to the momenta of the incoming and outgoing neutrons, respectively) than in the back scattering spectra, while phonon transitions are weaker in the forward scattering than in the back scattering spectra.²⁵ Thus, it is likely that the broad peak at $\sim 75(2) \text{ cm}^{-1}$, extending to $>82 \text{ cm}^{-1}$, contains the contribution from the magnetic transition. That is, overlapping peaks of magnetic and phonon transitions at $\sim 75(2) \text{ cm}^{-1}$ make the peaks more intense in the forward scattering spectrum at 5.0(5) K than that in the back scattering spectrum. However, the broad, likely overlapping peaks at $\sim 75(2) \text{ cm}^{-1}$ from a powder sample of **Co-TODA** prevents definitive

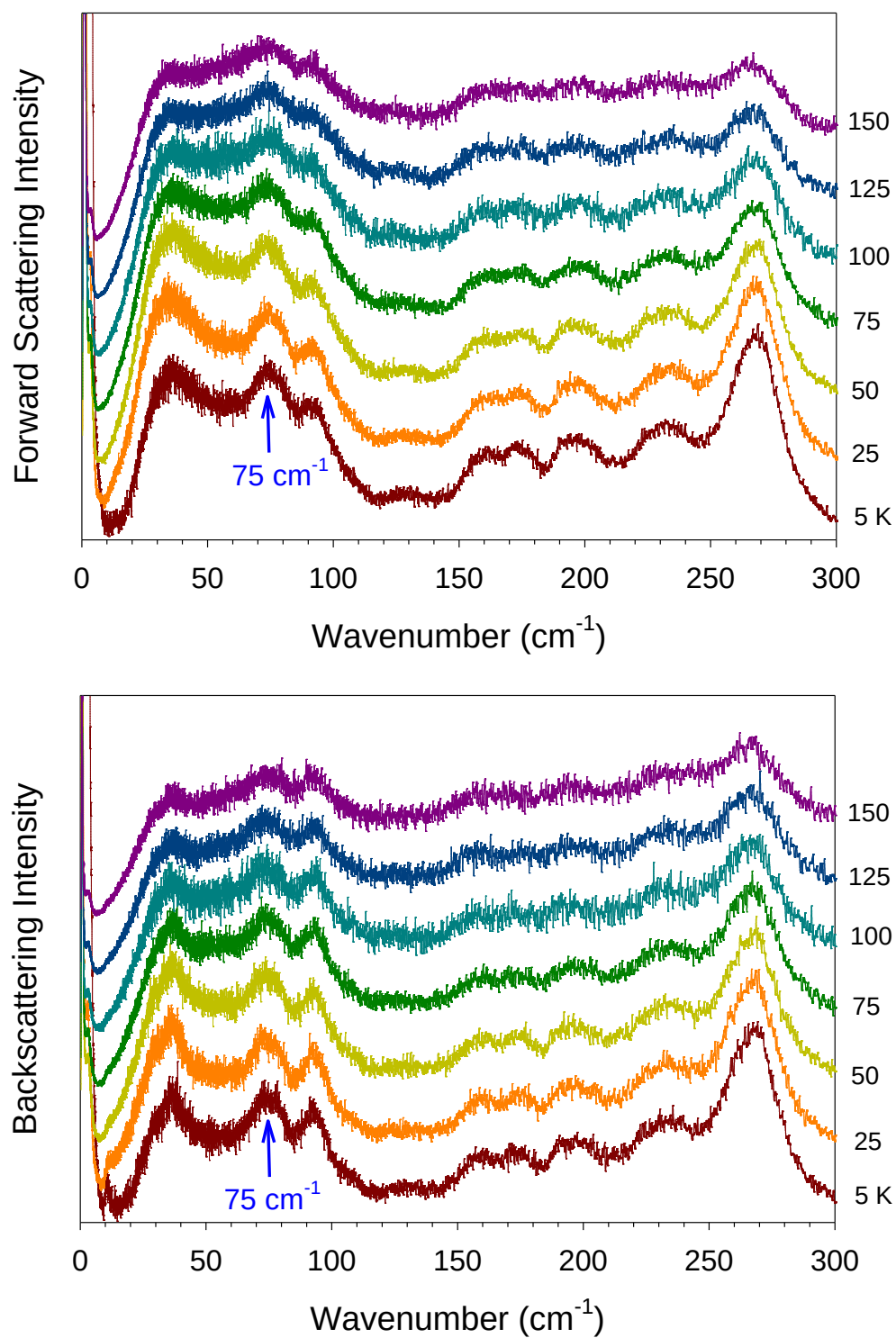


Figure 2.5. Bose-corrected INS spectra collected at VISION. (Top) Forward scattering. (Bottom) Back scattering.

assignment of the magnetic contribution to the peaks. The spectrum shows two phonon features between 70 cm^{-1} and 100 cm^{-1} . The phonon features around the region of the observed magnetic transition [$80.4(1.0)\text{ cm}^{-1}$ from FIRMS] can potentially lower the relaxation time of the spins due to the phonon acting as an external perturbation to the system. Even though phonons are found around the region of the magnetic transition, no phonon couplings were observed in FIRMS.

DFT (density functional theory) calculations of the phonon INS spectrum of **Co-TODA** were conducted using VASP. The goal of the calculations is to compare the calculated phonon INS spectrum to the experimental one so a magnetic transition in the experimental INS spectra, which is not in the calculated phonon INS spectrum, *may* be revealed. Due to the complexity of the crystal structure of the **Co-TODA** and the disorder of the TODA ligands, the symmetry of the CP was lowered to *P1* in the calculations. Since the calculations were not conducted in the original, higher symmetry of *P2₁/c* (No. 14), phonon modes were not assigned symmetries. The calculated INS spectrum in the range of $10\text{-}4000\text{ cm}^{-1}$ is given in Figure A.17, in comparison with the experimental INS at 5 K. The calculated and experimental INS spectra match fairly well, considering that the magnetic transition at $80.4(1.0)\text{ cm}^{-1}$ overlaps with phonon peaks around $75(2)\text{ cm}^{-1}$.

2.3.4. Computational Studies of the Magnetic Anisotropy in Co-TODA

With the determination of the easy-plane anisotropy in **Co-TODA** by both FIRMS/HFEPR spectroscopies and DC susceptibility data fit, we have conducted *ab initio* studies to understand the anisotropy.

There are two Co^{II} ions, **Co2** and **Co3**, in the crystal structure of **Co-TODA**, both

coordinated by TODA ligands (Figure 2.1). The calculated molecular structures of individual Co^{II} fragments are given in Figure A.1. The energy differences between the lowest two spin-free states (Table A.1) of **Co2** and **Co3** are both much larger than those between the lowest two spin-orbit states (Table A.2), and the compositions of the ground spin-orbit states are almost entirely from the ground spin-free states. Thus, we can use ZFS parameters D and E to depict their magnetic anisotropies.

The calculated D , E (cm^{-1}) and $\mathbf{g}$ (g_x, g_y, g_z) tensors for **Co2** and **Co3** using CASPT2 and NEVPT2 with MOLCAS 8.4¹¹⁶ and ORCA 4.2,¹¹⁷ respectively, are shown in Table A.3, where the D values obtained from NEVPT2 are more consistent with the experiments when compared with those from CASPT2. Figure A.2 shows calculated orientations of the local magnetic axes (g_x, g_y, g_z) on **Co2** and **Co3** in their ground spin-orbit states using CASPT2/RASSI-SO with MOLCAS 8.4. To analyze magnetic anisotropies deeply, we gave the contributions of the excited states to D values for **Co2** and **Co3** in Table A.4 using NEVPT2 with ORCA 4.2. The dominant contributions to the positive D values were from the two close quartet states, particularly the third and the fourth quartet states for both **Co2** and **Co3**. The calculations yield positive D values, which are consistent with the geometries around the Co^{II} ions and easy-plane anisotropies ($g_x, g_y > g_z$). Molecular coordination frame was chosen so that the Z axis is along the numerically largest eigenvalue of the D -tensor and the X and Y axes accordingly to the other two. The following discussion of Co d -atomic orbitals (d -AOs) is classified in accordance with this frame. The calculated relative energies (cm^{-1}) of ligand field one-electron states (in the basis of d -AOs) for **Co2** and **Co3** using NEVPT2 with ORCA4.2 are shown in Table A.5 according to the *ab initio* ligand field theory (AILFT)^{118, 119} analysis. The CASPT2

calculations gave the D values for **Co2** and **Co3** as 30.5 cm⁻¹ and 43.0 cm⁻¹, respectively. The experimental value of D from HFEPR [$38.0(1.0) \leq D \ll 40.2(1.0)$ cm⁻¹] is between the calculated D values of **Co2** and **Co3** from CASPT2.

The magnetic susceptibility of **Co-TODA** was calculated using CASPT2/RASSI-SO with MOLCAS 8.4. The calculated plots of magnetic susceptibilities vs. temperatures for both **Co2** and **Co3** are shown in Figure A.3, giving the susceptibility value of 1.5-1.7 cm³ mol⁻¹ K near 0 K that plateaus around 2.5 cm³ mol⁻¹ K at 300 K. The calculated magnetic susceptibilities of **Co2** and **Co3** are alike, supporting that the two Co^{II} centers have close characteristics. The calculated plots are similar to those from the earlier experiments.⁸⁸ For example, the experimental magnetic susceptibility value, which does not distinguish the contributions from **Co2** or **Co3**, is 1.37 cm³ mol⁻¹ K at 2 K, while plateauing around 2.48 cm³ mol⁻¹ K at room temperature. Therefore, the calculated magnetic susceptibility values are agreeable with the experimental data.⁸⁸

For **Co2** and **Co3**, the most destabilized by ligand field is the singly occupied state composed of practically pure d_z^2 AOs. The orbital energies computed for the ground states are shown in Figure A.4, where the ground states for **Co2** and **Co3** are both multideterminant with prevailing (62.2% and 84.1%, respectively) contribution of $(d_{yz})^1(d_{xz})^2(d_{xy})^1(d_{x^2-y^2})^2(d_z^2)^1$ and $(d_{yz})^1(d_{xz})^2(d_{xy})^1(d_{x^2-y^2})^2(d_z^2)^1$, and are mixed with another with the weightage of 13.3% and 12.1%, respectively. For **Co2**, the major contributions to D are from the ground to the third and the fourth excited states transitions ($d_{xz} \rightarrow d_z^2$ and $d_{x^2-y^2} \rightarrow d_z^2$, respectively). The positive sign of the D parameter is attributed to these transitions which occur between orbitals with the different magnetic quantum number (m_l) values.^{120, 121} In the case of **Co3**, as it is similar to **Co2**, the largest contributions to D are also from the ground to the third and the fourth excited states

transitions ($d_{x^2-y^2} \rightarrow d_{yz}$ and $d_{x^2-y^2} \rightarrow d_{z^2}$, respectively). Since these orbitals also have different m_l value, the contributions to the D value are positive in complete agreement with the experiments.

The multideterminantal wavefunctions of the selected excited states having important contributions to D tensor are shown in Figure A.5, where all the excited states are composed by several configurations indicating the presence of the unquenched orbital angular momentum. The calculated $\chi_M T$ versus T plots are shown in Figure A.2. The calculated orientations of the g_x , g_y and g_z in the ground spin-orbit states on Co^{II} ions of **Co2** and **Co3** are shown in Figure A.3.

2.3.5. Calculated Spin Densities and a Correlation with the D Parameter

Spin density calculations were performed using VASP (Vienna Ab initio Simulation Package) with the Projector Augmented Wave (PAW)¹²²⁻¹²⁵ method and the local density approximation (GGA)¹²⁶ + U ($U = 4.4$ eV)^{127, 128} exchange correlation functional. Spin density calculation is used to study the localization of spin in the metal ions as well as the ligands. The calculations do not include the spin densities that reside in the bonds, but rather just the densities in individual atoms. The range of spin densities for each atom type is presented in Table 2.1. Detailed spin densities are given in Table A.9.

The results show that the spin densities are mostly concentrated on the Co^{II} ions, containing 2.68-2.69 (89.3-89.7%) of the 3 unpaired electrons on the metal ions, while the rest are dispersed on the ligands and the diamagnetic Co^{III} ions. We recently found that, among four Co^{II} complexes $\text{Co}(\text{PPh}_3)_2\text{X}_2$ ($\text{X} = \text{I}, \text{Br}, \text{Cl}$) and $\text{Co}(\text{acac})_2(\text{H}_2\text{O})_2$ ($\text{acac}^- = \text{acetylacetonate}$), the

Table 2.1. Calculated spin densities for atoms in a unit cell of **Co-TODA**. Ranges of spin densities are listed for O, N, C, and H atoms due to the large number of atoms existing in the unit cell.

Atoms	Ranges of Spin Densities
Co ^{II}	2.69
Co ^{III}	0.01
O	2.15×10^{-2} to 3.57×10^{-2}
N of TODA	4.31×10^{-2} to 4.33×10^{-2}
N of CN ⁻	-1.14×10^{-4} to -1.02×10^{-4} 2.11×10^{-4} to 1.92×10^{-2}
C of CN ⁻	-2.03×10^{-4} to -1.18×10^{-4} 7.89×10^{-5} to 7.23×10^{-3}
C of TODA	-8.96×10^{-4} to -2.89×10^{-4} 7.62×10^{-5} to 1.81×10^{-3}
H	-3.14×10^{-4} to -1.2×10^{-7} 2.00×10^{-8} to 2.04×10^{-3}
Total	17.616 (2.936 per SBU*)

*SBU = Secondary Building Unit

larger the spin density on a metal ion, the larger the ZFS is in the complex,¹⁸ as summarized in Table 2.2. **Co-TODA** in the current work [$D' = 40.2(1.0)$] follows the trend (Table 2.2). Its spin densities of 2.68-2.69 on the Co^{II} ions and $D' = 40.2(1.0)$ are both lower than those of $\text{Co}(\text{acac})_2(\text{H}_2\text{O})_2$ but higher than those of $\text{Co}(\text{PPh}_3)_2\text{X}_2$ ($\text{X} = \text{I}, \text{Br}, \text{Cl}$) (Table 2.2).

In both $\text{Co}(\text{acac})_2(\text{H}_2\text{O})_2$ and **Co-TODA**, only light N and O atoms (in the 2nd row of the periodic table) are bound to the Co^{II} ions with 6- and 7-coordination, respectively. For **Co-TODA**, seven N,O atoms (and other atoms in the ligands) share the spin densities from the three unpaired electrons, while in $\text{Co}(\text{acac})_2(\text{H}_2\text{O})_2$, six O atoms bound to the Co^{II} ion (and other atoms of the ligands) share the spin densities. Perhaps the different coordination numbers in $\text{Co}(\text{acac})_2(\text{H}_2\text{O})_2$ and **Co-TODA** are one contributor to the spin density differences between the two. In $\text{Co}(\text{PPh}_3)_2\text{X}_2$ ($\text{X} = \text{I}, \text{Br}, \text{Cl}$), the halogen atoms in the 3rd, 4th and 5th-rows of the periodic table have higher spin densities [6.69×10^{-2} (Cl), 6.85×10^{-2} (Br) and 6.01×10^{-2} to 6.39×10^{-2} (I) in the three complexes¹⁸] than, e.g., those on N and O atoms in **Co-TODA**.

It should be pointed out that the number of complexes here (five in Table 2.2) is limited, and different DFT programs may give different calculated spin densities. Additional studies are needed to see if there is a correlation between the spin densities and magnitudes of ZFS.

2.3.6. Studies of Spin-Lattice (T_1) and Spin-Spin (T_2) Relaxation Times in the Ground KD by Pulsed X-band EPR

Pulsed X-band EPR was used to probe the spin-lattice and spin-spin relaxation times T_1 and T_2 after the Co^{II} centers are excited from ϕ_1 to ϕ_2 (Figure 1.1). In other words, pulsed EPR here provides relaxation times for the *intra*-KD transition inside a magnetic field. The two

Table 2.2. Correlation between calculated spin densities on the Co^{II} Ions and ZFS parameters of the Co^{II} complexes/CP

Complexes	Spin Densities on the Co^{II} Ions (and Percentage of 3 Unpaired Electrons)	<i>D'</i> Values (cm⁻¹)
Co(PPh ₃) ₂ I ₂	2.553 (85.1%)	13.63(10)
Co(PPh ₃) ₂ Br ₂	2.570 (85.7%)	13.83(2)
Co(PPh ₃) ₂ Cl ₂	2.585 (86.2%)	14.89(2)
Co-TODA	2.68-2.69 (89.3%-89.7%)	40.2
Co(acac) ₂ (H ₂ O) ₂	2.81 (93.7%)	57.0

relaxation times are intrinsic magnetic properties of **Co-TODA**.

T_1 quantifies the time of energy transfer from the molecular spin to the lattice.⁸⁰ Using the technique of echo inversion recovery, a pulsed wave at 180° is applied inside a field,^{129, 130} leading to the flipping of the magnetization (M_z) from $+z$ to $-z$ with higher energy. Afterwards, the flipped spin will undergo spin-lattice relaxation to return to $+z$, releasing energy to the environment through spin-lattice relaxation. $M_z(t)$, magnetization along z at different times (t) after the 180° pulse, is measured. T_1 is the time for $M_z(t)$ to reach 63% of its maximum value, $M_z(0)$, as shown in *Eq. 2.1*.^{131, 132} T_1 is also the time at which the spins relax back to the Boltzmann equilibrium state at a given temperature after the removal of the external magnetic field. T_1 is an important magnetic property of a compound or CP, e.g., for the relaxation from ϕ to ϕ_1 in **Co-TODA**.

$$M_z(t) = M_z(0)[1 - 2\exp(-t/T_1)] \quad (\text{Eq. 2.1})$$

where $M_z(0)$ and $M_z(t)$ are the axial component of the magnetization vector at time = 0 and t , respectively; T_1 is the spin-lattice relaxation time.

Spin-spin relaxation is the process where the transverse component of the magnetization (M_{xy}) dephases or decays. According to Bloch, this process follows first-order kinetics resulting in the exponential decay.¹³¹ T_2 is the time it takes for the traverse magnetization to fall to 37% of its initial value, as shown in *Eq. 2.2*.¹³¹ Hahn echo decay is typically used to study the spin-spin relaxation, quantifying T_2 .³¹ A 90° pulse inside magnetic field flips the magnetization to the x - y plane. Then, spins in different environments begin to dephase at different speeds due to the local

magnetic field inhomogeneities. Next, a 180° pulse is used to flip the spin dephasing direction to remove the inhomogeneous dephasing so to detect the magnetization. The process is repeated with different periods (t) of dephasing before the echo.^{80, 131}

$$M_{xy}(t) = M_{xy}(0)\exp(-t/T_2) \quad (\text{Eq. 2.2})$$

where $M_{xy}(0)$ and $M_{xy}(t)$ are the transverse components of the magnetization vector at time = 0 and t , respectively; T_2 is the spin-spin relaxation time.

T_2 reflects the coherence time of the two spin states and thus the effectiveness of qubits. Metal complexes with long T_2 have been actively investigated as qubit candidates.^{31, 34-36, 133-136} Finding a compound with long T_2 is challenging, as interactions of unpaired electron spins in a compound with the local environment causes the rapid collapse of the superposition state through decoherence. Effects such as nuclear spin diffusion coupling to nearby electron, methyl rotation, and spin diffusion barrier are major obstacles when it comes to prolonging the T_2 . Zadrozny and coworkers have quantified μs -length T_2 of various $d^1 \text{V}^{\text{IV}}$ compounds and compare the spin-spin relaxation times with those of other well-known qubits such as the nitrogen-vacancy (NV) center. For example, $T_2 = \sim 1 \text{ ms}$ for $(\text{Ph}_4\text{P}-d_{20})_2[\text{V}(\text{C}_8\text{S}_8)_3]$ in CS_2 at 10 K, eclipsing the nitrogen vacancy center in non-isotopically enriched diamond.³⁷

Pulsed X-band EPR experiments of a powder sample of **Co-TODA** (with *no* magnetic dilution of the Co^{II} ions) were performed at 5(1) K to give T_1 and T_2 times. Figure 2.6-Top gives the echo inversion recovery graph, giving the T_1 value of 235(4) μs at 5 K. It is interesting to note that, for **Co-TODA**, $T_1 = 235(4) \mu\text{s}$ at 5(1) K, the lowest temperature

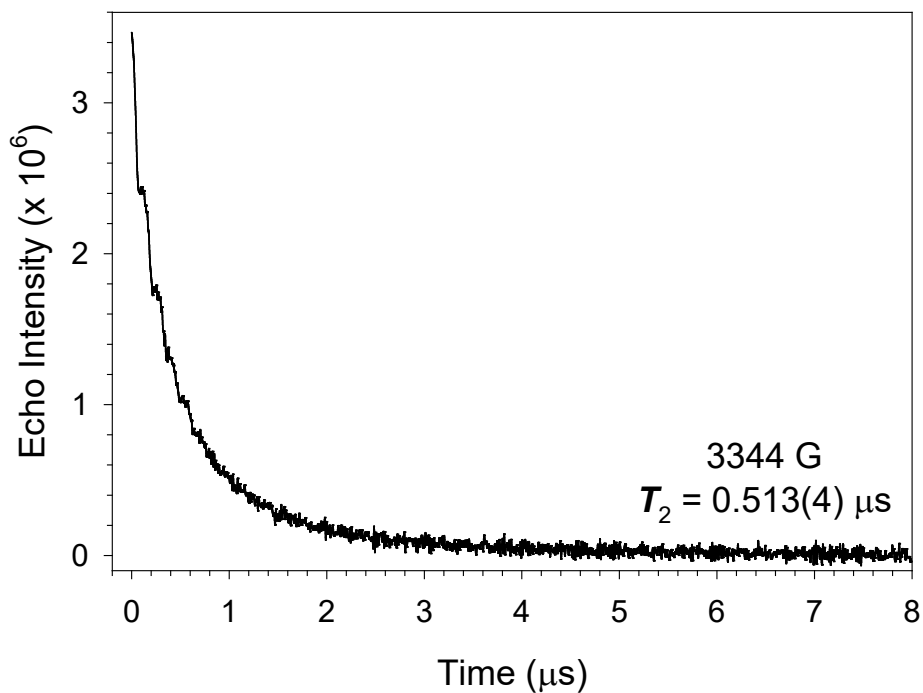
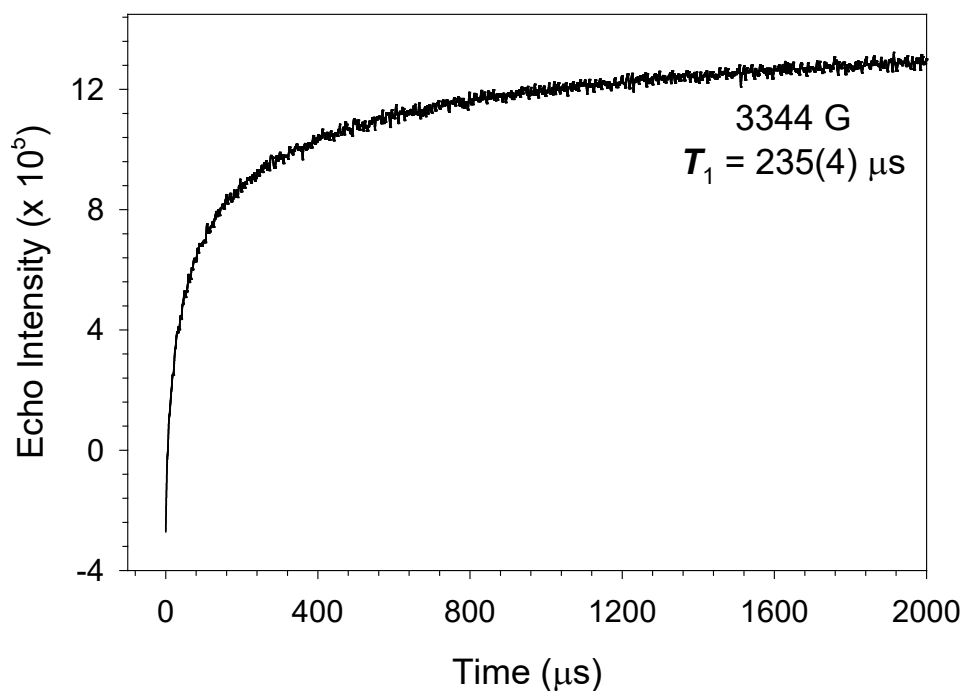


Figure 2.6. Graphs of the echo intensity from pulsed X-band EPR at 5(1) K vs. time: (Top) Echo inversion recovery experiment; (Bottom) Hahn echo decay experiment. External magnetic field = 3344(1) Gauss.

measured in the current work, is at the same order as the relaxation time $\tau = 130 \mu\text{s}$ at 3.0 K, the highest temperature probed by AC (alternating current) susceptibility studies.⁸⁸ Figure 2.6-Bottom shows the Hahn echo decay graph with the T_2 value of $0.513(4) \mu\text{s}$ at 5(1) K. It should be noted that the **Co-TODA** sample used here for the pulsed X-band EPR studies is 100% Co. The relatively short T_2 value suggests the presence of inter- Co^{II} magnetic interactions in **Co-TODA** that may be reduced with the use of diamagnetic Zn^{II} dilution. The field swept echo graphs in Figures A.14 and A.15 show one feature at 3344(1) G or approximately 0.33 T. The feature suggested an EPR observable *intra*-Kramers transition from ϕ_1 to ϕ_2 . Due to the excitation bandwidth limitations, a pulsed X-band EPR sequence can only excite a portion of the spin populations. Moreover, not all spins can be flipped by a pulse in the same angle. Therefore, only one such transition can be seen in the spectra. T_1 and T_2 times at 10(1) K, 20(1) K and 30(1) K were also measured. The echo inversion recovery and the Hahn echo decay graphs of the temperatures as well as the field swept echo graphs are given in Appendix A.

The T_2 time for **Co-TODA** is fairly long considering that there is no magnetic dilution in the CP and that the shortest $\text{Co}^{\text{II}} \cdots \text{Co}^{\text{II}}$ distance is 7.52 Å in the CP, making Zn^{II} -diluted **Co-TODA** potential qubit candidates. The rigid and sturdy structure of a CP and its unique phonon properties may provide an environment for the qubit centers in the CP, potentially prolonging T_2 times. Previous studies of the spin coherence times of qubit candidates were reported for Cu^{II} , Co^{II} , and V^{IV} CPs.^{34, 137-139} Yu, Freedman and coworkers have shown that a magnetically diluted Cu^{II} porphyrin MOF at the 10%, 40%, and 100% levels has the phase memory time (T_m) values of 0.645, 0.121, and $0.046 \mu\text{s}$, respectively.¹³⁸

T_m is the measure of all processes contributing to the spin decoherence, including T_2 . In the non-diluted CP, the distance between two nearest Cu^{II} centers is 13.595 Å. T_2 of 0.467 μs for **Co-TODA** is thus comparable to T_m of the 100% Cu^{II} porphyrin MOF, showing that **Co-TODA** is a promising qubit candidate. Another notable example is a Co^{II} porphyrin-based MOF investigated by Zadrozny, Freedman and coworkers.³⁴ In the non-magnetically diluted MOF, the distance between the two nearest Co^{II} neighbor is 13.643 Å. Once magnetically diluted to 7% of Co^{II} (with 93% of Zn^{II}), the T_2 time was found to be 13.74(9) μs .³⁴ The T_2 time is considerably longer than that of **Co-TODA** that is likely a result of the dilution of the Co^{II} magnetic centers as well as longer distances between the nearest Co^{II} neighbor in the structure. Further studies with Zn^{II} -diluted **Co-TODA** are needed to see if the diluted CP has qubit properties.

2.4. Experimental Section

Polycrystalline sample of **Co-TODA** was prepared as reported in the literature.⁸⁸

2.4.1. FIRMS

FIRMS spectra were collected at the NHMFL (Tallahassee, Florida, USA) using a Bruker Vertex 80v Fourier-transform infrared (FT-IR) spectrometer coupled with a 17.5 T vertical-bore superconducting magnet. The experimental setup is equipped with a mercury lamp and a composite silicon bolometer (Infrared Laboratories), as an incoherent (sub)-THz radiation source and detector, respectively. The THz radiation is free-space propagating inside the optical beamline, connecting the output of the spectrometer and top of the sample probe. The radiation is

then passed through the brass light pipe over a distance of 2.5 m from room temperature to the field center. The probe and beamline are evacuated to eliminate strong parasitic absorptions of the air. The studied samples are the mulls of *n*-eicosane and powder (~ 2 mg) of each complex. Both the sample and the bolometer were cooled by low-pressure helium gas to 5.3(3) K. The spectrum of the THz radiation transmitted through the samples was measured in the spectroscopic between 10 and 720 cm^{-1} (0.3–21.6 THz) with a resolution of 0.3 cm^{-1} (9 GHz), acquisition time of 3 min and 5 kHz scanner speed. FIRMS spectra of **Co-TODA** were collected a total of four times with different samples, yielding similar results.

2.4.2. HFEPR

HFEPR spectra were obtained at the NHMFL using the home-built spectrometer based on a 17-T superconducting magnet described previously,¹⁴⁰ and differs from that description only by the use of a low-frequency (8-20 GHz) microwave source complemented by a cascade of amplifiers and multipliers (Virginia Diodes, Charlottesville, VA, USA) to produce higher frequency harmonics.

2.4.3. INS

For variable-temperature INS at VISION, the sample (0.5 g) was sealed in an aluminum container and placed inside the neutron beam at Vibrational Spectrometer (VISION) at Spallation Neutron Source (SNS), ORNL. INS spectra of **Co-TODA** were measured at 10.0(5), 25.0(5), 50.0(5), 100.0(5) and 125.0(5) K. The design at VISION offers two banks of detectors for both forward (low $|Q|$) and back (high $|Q|$) scattering of neutrons.¹⁴¹ The phonon population

effect was corrected by normalizing the INS intensity at energy transfer ω with $\coth\left(\frac{\hbar\omega}{2k_B T}\right)$.¹⁴²

2.4.4. *Electronic Structure Calculations*

Electronic structure calculations were conducted by extracting two types of three-core units from the 2-D framework complex. For each unit, there are two individual Co^{II} fragments (**Co2** and **Co3** in Figure A.1) needed to be calculated while the neighboring Co^{III} ions are diamagnetic. Complete active space second-order multiconfigurational perturbation theory (CASPT2) considering the effect of the dynamic electron correlation based on complete-active-space self-consistent field (CASSCF) method with MOLCAS 8.4 program package¹¹⁶ was performed on the basis of single-crystal X-ray determined geometries of the complex.

For the first CASSCF calculation, the basis sets for atoms are atomic natural orbitals from the MOLCAS ANO-RCC library: ANO-RCC-VTZP for magnetic center ion Co^{II}; VTZ for close N and O atoms; VDZ for distant atoms. The calculations employed the second order Douglas-Kroll-Hess Hamiltonian, where scalar relativistic contractions were taken into account in the basis set. The effect of the dynamical electronic correlation was applied using CASPT2 based on the first CASSCF calculation. After that, the spin-orbit coupling was handled separately in the restricted active space state interaction (RASSI-SO) procedure. The active electrons in 5+5' active spaces considering 3d double shell effect include all d electrons [CAS(7 in 5+5')] in the CASSCF calculations. To exclude all the doubts, we calculated all the roots in the active space. We have mixed the maximum number of spin-free state which was possible with our hardware (all from 10 quadruplets and 20 from 40 doublets). SINGLE_ANISO¹⁴³⁻¹⁴⁵ program was used to obtain zero-field splitting parameters $D(E)$ (cm⁻¹), g tensors, energy levels, and

magnetic axes based on the above CASPT2/RASSI-SO calculations.

To deeply analyze the magnetic anisotropies, ORCA 4.2 calculations¹¹⁷ were performed with complete active space self-consistent field calculations (CASSCF), followed by N-electron valence second-order perturbation theory (NEVPT2). The spin-orbit coupling (SOC) operator used was the efficient implementation of the multicenter spin-orbit mean-field (SOMF) concept developed by Hess et al.¹⁴⁶ The spin-spin contributions (SSC) to the D values were also included although they are very small for our complex. The NEVPT2¹⁴⁷⁻¹⁵⁰ calculations with seven $3d$ electrons in five Co $3d$ -based orbitals [CAS(7, 5+5')] including $3d$ -double shell effects were performed on **Co2** and **Co3**. In the calculations, the orbitals were determined for the average of 10 $S = 3/2$ and 40 $S = 1/2$ roots. All calculations were performed with triple- ζ with one polarization function def2-TZVP¹⁵¹⁻¹⁵³ basis set for all atoms.

2.4.5. DFT Calculations of INS Spectrum and Spin Densities

Spin-polarized density functional theory (DFT) calculations of the **Co-TODA** compound were performed using the *Vienna Ab initio Simulation Package* (VASP).¹⁵⁴ The calculation used Projector Augmented Wave (PAW) method^{122, 123} to describe the effects of core electrons, and Perdew-Burke-Ernzerhof (PBE)¹²⁶ implementation of the Generalized Gradient Approximation (GGA) for the exchange-correlation functional. Energy cutoff was 600 eV for the plane-wave basis of the valence electrons. The lattice parameters and atomic coordinates from the original paper⁸⁸ were used as the initial structure. Ideally, the partial occupancy and structure disorder should be accounted for by creating a supercell and assigning the ligands to each possible configuration according to the occupancy probability. This is however too costly for the already

large unit cell (volume $>3500 \text{ \AA}^3$). As an approximation, this procedure was done within the unit cell, resulting in the same periodicity with internal disorder (loss of symmetry). The electronic structure was calculated at the Γ point only. The total energy tolerance for electronic energy minimization was 10^{-8} eV , and for structure optimization, it was 10^{-7} eV . The maximum interatomic force after relaxation was below $0.001 \text{ eV/\AA}$. The optB86b-vdW functional¹⁵⁵ for dispersion corrections was applied, and a Hubbard U term of 3.32 eV ¹⁵⁶ was applied to account for the localized $3d$ orbitals of Co. The interatomic force constants were calculated by finite displacement method, and the vibrational eigen-frequencies and modes were then calculated using Phonopy.¹⁵⁷ The OCLIMAX software¹⁵⁸ was used to convert the DFT-calculated phonon results to the simulated INS spectra.

2.4.6. Pulsed X-Band EPR

Pulsed X-band EPR experiments were performed on a Bruker E680 spectrometer (Billerica, MA) operating at a microwave frequency of 9.5 GHz at the NHMFL. Echo detection and T_1 and T_2 relaxation times were collected using a dielectric ER4118X-MD-5 resonator equipped with an Oxford CF-935 helium flow cryostat. The temperature was controlled and monitored using an Oxford Instrument ITC503 temperature controller. The 4-mm outer-diameter EPR tubes were used to load samples. The experiments were conducted in the temperature range of 5(1)-30(1) K. Echo-detected field swept spectra were obtained by measuring the Hahn echo intensity ($\pi/2-\tau-\pi-\tau$ -echo) as a function of transverse field. The time delay (τ) between two detection pulses was 200 ns. Echo detection was swept from 100 Gauss (G) to 10000 G magnetic field. T_1 was measured using an echo-detected inversion recovery pulse sequence ($\pi-\tau_1-\pi/2-\tau-$

π - τ -echo). T_2 was measured using a standard two-pulse Hahn echo sequence ($\pi/2$ - τ - π - τ -echo). The lengths of the $\pi/2$ and π pulses were 16 and 32 ns for all experiments, respectively.

2.5. Conclusions

The versatility and power of the spectroscopic techniques in characterization of molecular magnetism, especially the determination of the SH parameters, are highlighted in the current studies of powder samples of **Co-TODA** with field-induced slow magnetic relaxation. From perspectives of physical chemistry, the current work demonstrates the power of advanced optical (FIRMS, HFEPR, pulsed EPR) and neutron (INS) spectroscopies in probing magnetic properties of a metal-containing network. Results from the spectroscopies, combined with single-crystal X-ray diffraction at 15(2) K and *ab initio* calculations, offer a rare opportunity to understand the structure and properties of the CP in detail. FIRMS has revealed the inter-KD magnetic transition, and, together with HFEPR, led to a direct determination of the SH parameters (D , E , and g). In other words, the combined use of FIRMS and HFEPR is critical here for the deconvolution of the D' into the D and E values. Due to the large value of the E parameter, **Co-TODA** exhibits significant mixing of states, as demonstrated in the simulations of the FIRMS and HFEPR spectra. The electronic structure calculations in the current work have pointed out the origin of the magnetic anisotropy and the magnetostructural correlations, giving calculated SH parameters. The calculated SH parameters as well as the calculated DC susceptibility data are in support of the experimental findings, showcasing the utilities of the *ab initio* calculations. INS studies have given calculated INS spectra, phonon properties, and spin densities in the CP. The current work has also showcased that pulsed EPR is a unique tool in

obtaining the magnetic relaxation times T_1 and T_2 for the intra-KD transition $\phi_1 \rightarrow \phi_2$. The T_2 time for the **Co-TODA** was found to be fairly long, with no magnetic dilution, compared to T_2 times of other transition metal MOFs. The evidence suggested **Co-TODA** to be a potential qubit candidate. The calculated spin densities on the Co^{II} ions in **Co-TODA** and other high-spin Co^{II} complexes reported earlier reveal that the larger spin density on a Co^{II} ion, the larger ZFS in the complex.

Chapter 3

Hexacoordinate Co(II)-MOF-Based Single-Molecule Magnet with Very Large Magnetic Anisotropy and Qubit Properties

This chapter is based on a manuscript that has yet to be submitted for publication.

List of authors and their contributions:

Pagnareach Tin, Alexandria N. Bone, Adam T. Hand, Phattananawee Nalaoh, Nhat N. Bui, Yi-Quan Zhang, Mykhaylo Ozerov, J. Krzystek, Zheng Gai, Likai Song, Yongqiang Cheng, Luke L. Daemen, Zi-Ling Xue

P. Tin performed syntheses and grew single crystals of **Co-BEBN**. He prepared all samples for the experiments indicated below and prepared the manuscript. PT also coordinated research using different methods. A.N. Bone and P. Nalaoh performed the single-crystal X-ray diffraction experiment and solved the crystal structure. AB, PN, and PT analyzed and interpreted the data. P. Tin, A.T. Hand, and M. Ozerov performed the FIRMS measurements. AH generated the transition simulations and performed the spin-phonon fitting. PT and AH analyzed and interpreted the data. J. Krzystek performed the HFEPR measurement. JK and PT analyzed the data and interpreted the results. L.L. Daemen performed INS experiments at VISION. PT analyzed and interpreted the data. Y.-Q. Zhang performed the electronic structure calculations. PT and YQZ analyzed and interpreted the data. Z. Gai performed the magnetic susceptibility measurements. PT analyzed and interpreted the data. Y. Cheng performed the VASP calculations. PT analyzed and interpreted the data. N.N. Bui and L. Song performed the pulsed EPR measurements. PT analyzed and interpreted the data. Z.-L. Xue initiated the project and supervised the research, including data analyses and interpretations.

3.1. Abstract

Search for transition metal complexes with large zero-field splitting (ZFS) from magnetic anisotropy is of intense interest for applications as single-molecule (or single-ion) magnets (SMMs or SIMs). Six-coordinated transition metal complexes with nearly O_h geometries typically have small anisotropy (and ZFS). We have found that a Co^{II} metal-organic framework (MOF), $[\text{Co}(\mu\text{-bpeb})_2(\text{NCS})_2]_n \cdot n\text{G}$ [**Co-BEBN**; bpeb = 1,4-bis(pyridine-4-ylethynyl)benzene; G = 1,2-dichlorobenzene], demonstrates SIM properties with rhombic ZFS of $262(1) \text{ cm}^{-1}$, the largest among reported six-coordinated Co^{II} complexes. Comprehensive studies have been performed on magnetic properties of the SIM-MOF, including the use of far-IR magneto-spectroscopy (FIRMS), high-field/-frequency electron paramagnetic resonance (HFEPR), inelastic neutron scattering (INS), and *ab initio* electronic structure calculations. **Co-BEBN** and Zn^{II} -diluted **Co-BEBN**_{0.05Co} (5% Co^{II} -95% Zn^{II}) show the abilities in the superposition of the $|0\rangle$ and $|1\rangle$ states between the ground doublet ($M_S = \pm 1/2$) with Rabi oscillations as pulsed X-band EPR has revealed, indicating their qubit behaviors. DFT phonon calculations give energies of phonons and their symmetries as well as a calculated INS spectrum of the phonons, helping identify the magnetic peak in the experimental INS spectra.

3.2. Introduction

Introduction of single-molecule magnets (SMMs), including zero-field splitting (ZFS) in high-spin Co^{II} complexes and the energy splitting diagram for $S = 3/2$ complexes when $D > 0$ in Figure 1.1, and qubits is given in Chapter 1, Subsections 1.1.1 and 1.1.2, respectively. Overviews of MOFs and experimental methods to probe magnetism are provided in Chapter 1, Sections 1.2

and 1.3, respectively.

Significant efforts have been made over the past few years to design and synthesize compounds with large magnetic anisotropies. Among transition metal-based SIMs, Co^{II} complexes are the most reported.¹⁵⁹ One approach is to use first-order SOC,^{125, 160, 161} leading to anisotropies typically much larger than the second-order ZFS. For Co^{II} complexes with ZFS, few have $2D' > 250 \text{ cm}^{-1}$,¹⁵⁹ as the list in Table 3.1 shows.

It should be pointed out that the SH theory is a simplification which may not work, especially for hexacoordinate Co^{II} complexes, as a recent analysis of 24 complexes by Boča, Rajnák, and Titiš clearly showed.¹⁶² The extended Griffith–Figgis model or the complete active space may need to be used to give more accurate description of magnetic properties of the complexes.¹⁶² In the discussion below, especially when comparing magnetic anisotropies of different reported compounds, the widely employed SH model will be used, including in the analysis of spectroscopically observed anisotropy in the current work.

Determination of the ZFS parameters (D , E , and g) in transition metal complexes has been challenging and the most common method used to make an indirect determination is the DC magnetic susceptibility measurements,¹⁶² as exemplified by the literature listed in Table 3.1.¹² Recently, direct quantification of the ZFS parameters has been employed by various optical and neutron spectroscopies such as FIRMS,^{11, 17, 18, 27, 30, 81, 82, 163-169} HFEPR,^{18, 169, 170} and INS.

Vallejo, Pardo, Cano, and coworkers reported the synthesis, structures and properties $[\text{Co}(\mu\text{-bpeb})_2(\text{NCS})_2]_n \cdot n\text{G}$, a polymorph of **Co-BEBN** (in the current studies) with a different crystal structure (called **Co-BEBN-polymorph**). **Co-BEBN-polymorph** shows a host structure

Table 3.1. Selected examples of single-ion Co^{II} complexes with $2D' > 250 \text{ cm}^{-1}$ ^a

Compound	Coord. No.	$2D'$ (cm^{-1})	D (cm^{-1})	E (cm^{-1})	Method	Ref.
(Ph ₄ P) ₂ [Co(C ₃ S ₅) ₂]	4	322	−161	0	DC	Fataftah et al. ¹⁷¹
CoL ¹ Cl ₂ L ¹ = 4-hept-1-ynyl-2,6- dipyrzazol-1-ylpyridine	5	305	151	11.6	DC	Rajnák et al. ¹⁷²
(HNEt ₃) ₂ [Co(L ²) ₂]·H ₂ O, H ₂ L ² = <i>N,N'</i> -bis(<i>p</i> - toluenesulfonyl)oxamide	4	288(1)	−144.1(3)	0.02(7)	DC	Cui et al. ¹⁷³
Co-BEBN	6	262(1)	127.3	17.8	FIRMS and HFEPR	Current work
(Bu ⁿ ₄ N) ₂ [Co(L ³) ₂]·H ₂ O, H ₂ L ³ = <i>N,N'</i> -diphenyloxamide	4	262(1)	−130.8(9)	−0.70(0)	DC	Cui et al. ¹⁷³
(HNEt ₃) ₂ [CoL ⁴] ₂ , H ₂ L ⁴ = <i>N,N'</i> - bis(methanesulfonyl)oxamide)	4	256	−128.2	−0.65	DC	Wang et al. ¹⁷⁴
[Co(L ⁵)](BF ₄) ₂ , L ⁵ = tris(pyridylhydrazonyl)- phosphorylsulfide	6	255 ^b	−127.6(8)	−0.22(6)	DC	Landart- Gereka et al. ¹⁷⁵

^a Complexes with two magnetic centers are not included in the table for single-ion magnets (SIMs). These include (CH₆N₃)₂[Co₂(citH)₂(H₂O)₄]·2H₂O (CH₆N₃⁺ = guanidinium; citH₄ = citric acid) with intramolecular ferromagnetic interactions [$D = -226(14) \text{ cm}^{-1}$]¹⁷⁶ and [Co(dppmo)₃](CoBr₄) [dppmo = bis(diphenylphosphan)methane oxide; $D = 147$ and 12.3 cm^{-1} for the octahedral and tetrahedral site, respectively].¹⁷⁷

^b From FIRMS and HFEPR experiments, $2D' = 201 \text{ cm}^{-1}$.

of the MOF containing solvents as guests.¹⁷⁸ Their work demonstrates that the **Co-BEBN-polymorph** exhibits SIM properties at low temperatures through magnetic susceptibility [alternating current (AC) and direct current (DC)] measurements. In addition, Co^{II} nodes in the square layers of the **Co-BEBN-polymorph** minimized intermolecular interactions between Co^{II} ions, thus improving the magnetic properties.¹⁷⁸

In this study, we report the synthesis and characterizations of the two-dimensional (2-D) MOF **Co-BEBN**. We are interested in an in-depth analysis of the magnetic properties of **Co-BEBN** using a combination of optical and neutron spectroscopies in conjunction with *ab initio* calculations. Our studies demonstrate that **Co-BEBN** is a SIM with, to our knowledge, the largest ZFS among six-coordinated Co^{II} systems. In addition, among those with very large ZFS (>250 cm⁻¹) in Table 3.1, it is the only one determined by spectroscopies rather than by fitting DC susceptibility data. **Co-BEBN** also displays qubit properties. *Ab initio* electronic structure calculations help understand the origin of the anisotropy and the magneto-structural nature of **Co-BEBN**.

3.3. Results and Discussions

The synthesis of **Co-BEBN** is given in Appendix B including the method to grow the single crystals for the single-crystal X-ray diffraction measurements. AC magnetic susceptibility data, presented in Figure B.2 and discussed in Appendix B, show that **Co-BEBN** exhibits an out-of-phase signal at low temperatures, indicating SIM behaviors. Moreover, DC magnetic susceptibility data, presented in Figure B.3 and discussed in Appendix B, confirms that the system consists of high-spin Co^{II} ions. Both the AC and DC magnetic susceptibility results are

similar to those previously reported.¹⁷⁸ The magnetic susceptibility data from the current studies are given in Appendix B.

Phonons here refer to both intra-molecular vibrations and lattice vibrations in the crystalline solid.^{17, 29, 112}

3.3.1. *Single-Crystal X-Ray Diffraction*

Single-crystal X-ray diffraction of **Co-BEBN** at 100(2) K showed the structural features of the MOF and solvent in the guest-host system. Comparisons of the structures of **Co-BEBN** to the reported **Co-BEBN-polymorph**¹⁷⁸ are given in Tables B.1 and B.2 in Appendix B. **Co-BEBN** crystallized in the monoclinic space group while **Co-BEBN-polymorph**¹⁷⁸ exhibits lower symmetry in the triclinic space group. The bpeb ligand in **Co-BEBN-polymorph** is fairly long (~20 Å), therefore bending of the ligand is possible inside the MOF. Figure 3.1-Right shows a monolayer crystal structure of **Co-BEBN**, where the bpeb ligand bends into an “S” shape. It is important to note that there are 4 solvent molecules in the pores of **Co-BEBN** but there are 7 solvents in **Co-BEBN-polymorph**.¹⁷⁸ The difference in the number of solvent molecules in the MOF pore may cause the ligand to bend.

The longest and shortest Co-Co ions distances are ~20.992 Å and ~20.515 Å, respectively, with an interlayer separation of ~8.984 Å between the Co^{II} ions. Each Co^{II} ion is bonded to four bpeb ligands in the *x-y* plane, while two NCS ligands bind the Co^{II} ion using their N atoms in the *z*-axis, making the **Co-BEBN** six-coordinated (Figure 3.1-Left). Continuous Shape Measure (CShM) analysis¹⁷⁹ was used on the Co^{II} ion to determine deviations from the octahedral symmetry (*O_h*), giving a value of 0.044 (while the value of a perfect octahedral is 0).

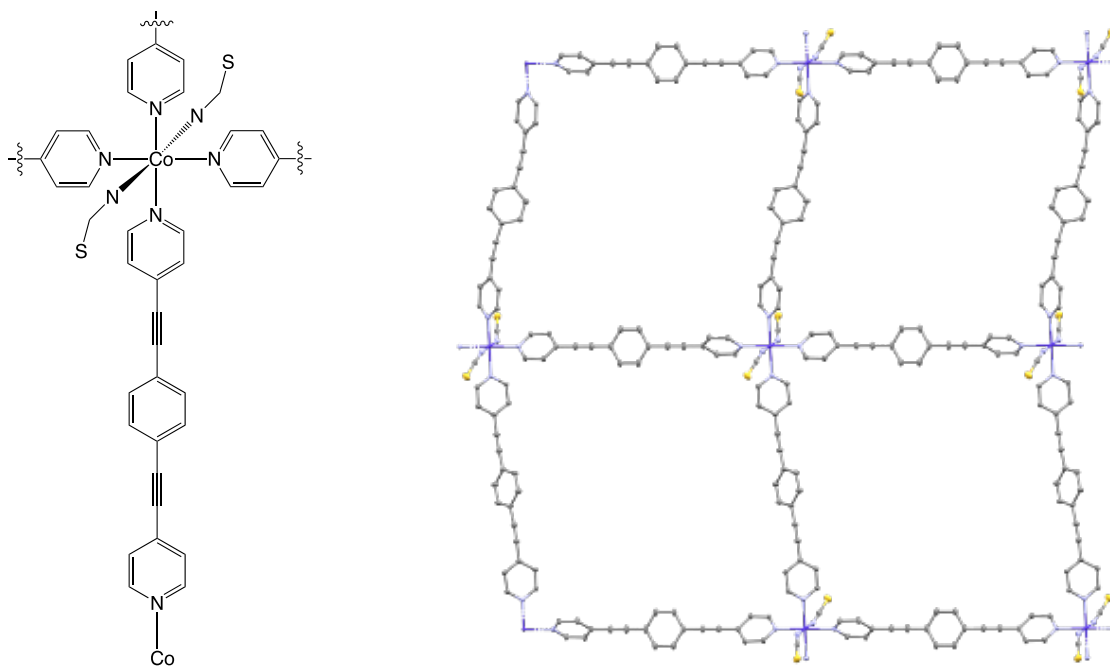


Figure 3.1. (Left) Truncated structure of **Co-BEBN** showing the Co^{II} local symmetry. (Right) Monolayer crystal structure of **Co-BEBN**. Hydrogens and solvent molecules are omitted for clarity.

The result shows that the Co^{II} ion local symmetry in **Co-BEBN** is close to an octahedral.

3.3.2. *Determination of Spin-Hamiltonian (SH) Parameters and Spin-Phonon Couplings through FIRMS and HFEPR*

3.3.2.1. FIRMS

FIRMS measurements were conducted to probe the inter-Kramers transition between the spin-1/2 state and the spin-3/2 state, where the energy gap is $2D'$ when $E \neq 0$ (Figure 1.1). The experiments were performed at about 5.5 K under the magnetic field between 0 and 17 T using powder samples of **Co-BEBN** mixed with a small amount of the solvent (1,2-dichlorobenzene) in eicosane. Figure 3.2-Top gives the transmission plots at 0 and 17 T, indicating a possible magnetic transition in the region of 250 and 270 cm⁻¹. To reveal the magnetic transition, Figure 3.2-Bottom shows the heatmap plot of the transmission spectra, normalized to an average of spectra for all magnetic fields. The normalization process eliminates instrumental artifacts, arbitrations, and non-magnetic background. The FIRMS map shows a broad spectral feature at 262(1) cm⁻¹ shifting to higher energies as the magnetic field increases. A large slope of ~0.9 cm⁻¹/Tesla indicates the magnetic origin of the feature. Therefore, we assigned the feature to the magnetic resonance of the inter-Kramers transition. Another feature at 283(1) cm⁻¹ stems from the phonon absorption coupled to the magnetic resonance transition, leading to the observed avoided crossing discussed below.

Figure 3.2-Bottom shows an overlay of the magnetic transition calculations onto the FIRMS map. The calculations are obtained from *EasySpin*⁹⁴ by the MATLAB software.¹⁸⁰ The SH parameters used in the calculations are $D = 127.3$ cm⁻¹, $E = 17.8$ cm⁻¹, $g = [g_x, g_y, g_z] = [2.54,$

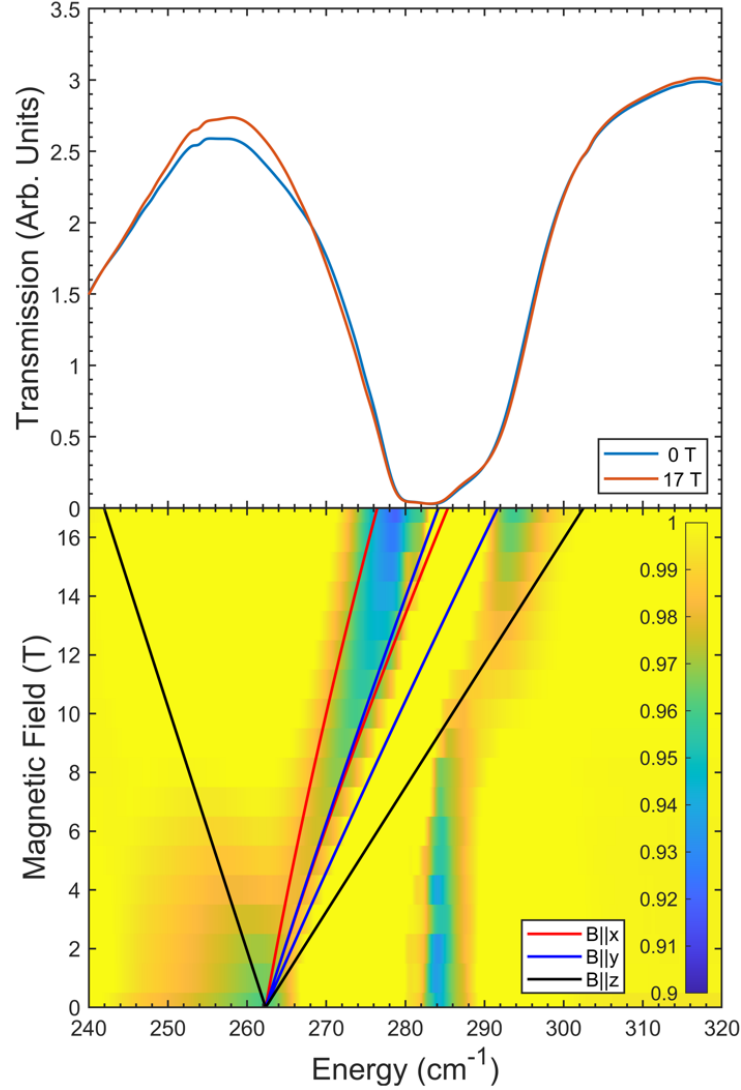


Figure 3.2. (Top) Far-IR transmission spectra of **Co-BEBN** at 5.5 K at 0 and 17 T. (Bottom) FIRMS map revealing the ZFS gap $2D' = 262(1) \text{ cm}^{-1}$ as well as its evolution in an external magnetic field, indicated with the blue color. The red, blue, and black lines are calculations from *EasySpin* on MATLAB.⁹⁴ The red, blue, and black lines are dependence of the transition energy on the magnetic field along the x , y , and z axis of the D tensor. SH parameters in the calculations are $D = 127.3 \text{ cm}^{-1}$, $E = 17.8 \text{ cm}^{-1}$, $g = [2.54, 2.54, 2.59]$, as discussed in the HFEPR section below.

2.54, 2.59] discussed below. There are six calculated lines corresponding to two transitions inside the magnetic field, one from the ground state ϕ_1 to the excited state ϕ_3 , and the other from ϕ_1 to the excited state ϕ_4 , respectively, in Figure 1.1. Each transition follows along the x , y , and z axis (from $D = [D_x, D_y, D_z]$), leading to a total of six calculated lines. The calculations reveal that the magnetic transitions, when $\mathbf{B} \parallel x$ and $\mathbf{B} \parallel y$, fit well with the observed blue spectral feature in the experimental FIRMS map. When $\mathbf{B} \parallel z$, the transition consists of one red-shifted transition and one blue-shifted transition. Overall, the calculations fit well with the experimental FIRMS.

Strong coupling is observed between the magnetic transition and a nearby phonon at $283(1) \text{ cm}^{-1}$ in Figure 3.2-Bottom as a deviation from the linear dependence of the magnetic feature and the declining of the phonon feature from the linear vertical position. The former behavior is anticipated from the Zeeman splitting, while the latter is attributed to the insensitivity of the phonon feature to the magnetic field. The avoided crossing was observed around 8 T when the magnetic transition energy, blue-shifted with increasing magnetic field, comes into proximity of the phonon feature. The magnetic and phonon features exchange during the avoided crossing, converting the magnetic feature into the phonon feature and vice versa. Such coupling between spin (magnetic feature) and phonon can influence the relaxation of the magnetic transition from the excited to the ground state and the relaxation pathways.^{96, 97, 181} The coupling can also impact the energy gap or the anisotropies in ZFS.³³ It is imperative to obtain spin-phonon coupling constants for a better understanding of the effect. Figure 3.3 shows spin-phonon fittings (two overlaying black lines) on the FIRMS map. The fittings were performed on *Maple*¹⁸² using matrix calculation methods. For the case of two coupled transitions with one magnetic feature and one phonon feature, we employed the Hamiltonian for the spin-phonon coupling model in

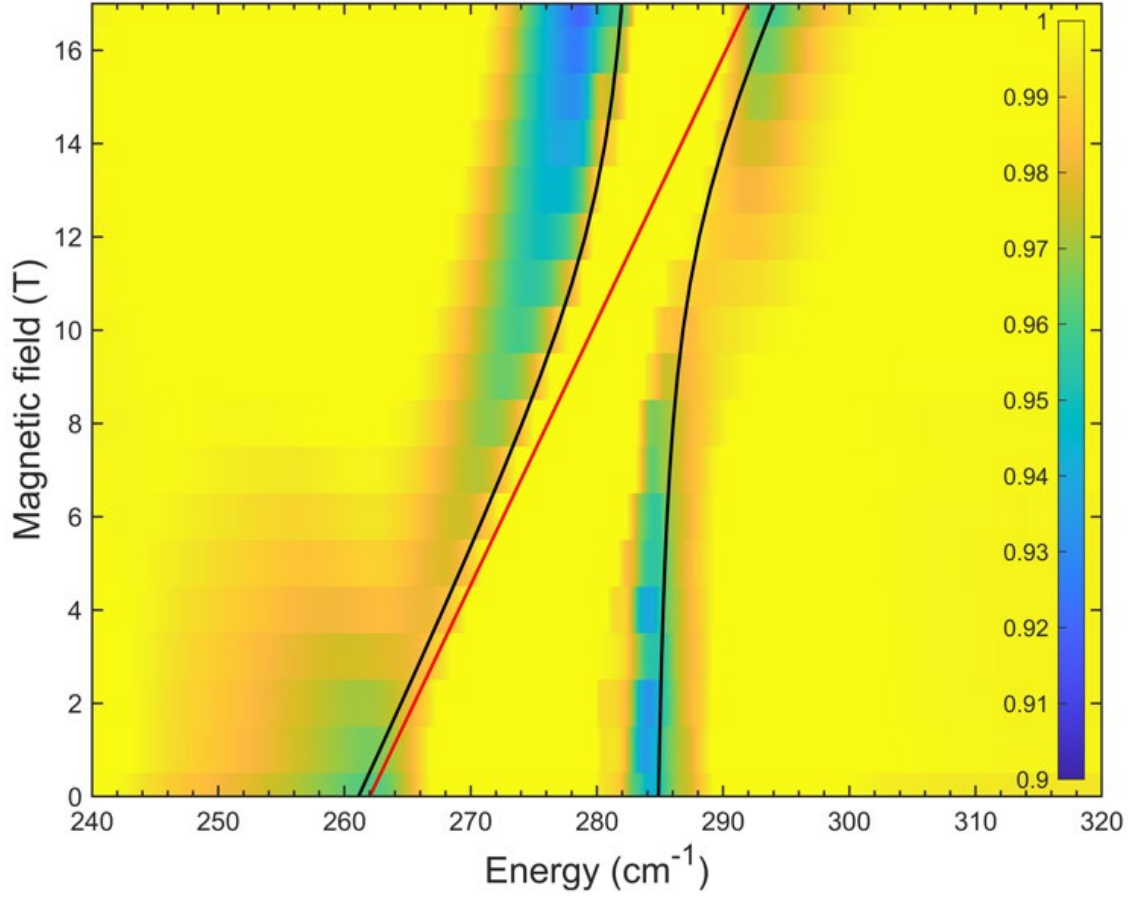


Figure 3.3. Fitting of the spin-phonon coupling in the FIRMS data using *Maple*¹⁸² as black lines. The red solid line is a linear fit between the magnetic peak at zero-field and the phonon peak at 17 T corresponding to the slopes of the black lines, which is the transition energy in ZFS, E_{sp} , used in the spin-phonon fit.

Eq. 3.1 to describe their behavior.^{11, 17, 183}

$$H = \begin{bmatrix} E_{sp} & \Lambda \\ \Lambda & E_{ph} \end{bmatrix} \quad (Eq. 3.1)$$

where E_{sp} [262 cm⁻¹] and E_{ph} [283.8 cm⁻¹] are energies of the magnetic and phonon feature, respectively. Λ is the coupling constant between the two magnetic and phonon transitions.

The solution to the Hamiltonian gives two energy eigenvalues ($E_{\pm}$) in Eq. 3.2.^{11, 17}

$$\begin{bmatrix} E_{sp} - E_{\pm} & \Lambda \\ \Lambda & E_{ph} - E_{\pm} \end{bmatrix} = 0 \quad (Eq. 3.2)$$

Results of the spin-phonon fittings rely on the visual examinations of how the black lines overlay the magnetic and phonon peaks in the FIRMS map.

The magnetic feature was modeled from 262 cm⁻¹ at zero-field to 292 cm⁻¹ at 17 T (red line in Figure 3.3), giving the coupling constant $\Lambda = 4.5$ cm⁻¹ from the best visual matching. The coupling constant is large compared to those previously reported SIMs.^{17, 18} The large coupling is also evident in the FIRMS map (Figure 3.3), showing avoided crossing even when the two features are fairly apart. Based on the work by Chakarawet, Neese, Long and workers, increase in anisotropy from the SOC effect contributes to the increase in the spin-phonon relaxation originated from spin-phonon coupling.³³ In the previously reported SIM-CP (coordination polymer) **Co-TODA**,³⁰ no spin-phonon coupling was observed and its ZFS is much smaller [2*D'*

= 80.4(1.0) cm⁻¹]. Even though the Co^{II} ion in **Co-BEBN** is nearly octahedral with six N-containing ligands, its $2D' = 262(1)$ cm⁻¹ is much larger. The results support the findings correlating anisotropy with spin-phonon coupling.³³ Even if the effect of spin-phonon coupling correlated to the increase in the anisotropy value of the system, it shortens the relaxation time of the magnetizations, which is undesirable in SIMs.

Spin-phonon coupling is an active area of research due to its effects on the relaxation process in SMMs. Various experimental techniques were utilized to probe the coupling effect such as, terahertz (THz) spectroscopy,¹³⁻¹⁵ resonant inelastic X-ray scattering (RIXS),¹⁶ FIRMS,¹⁷⁻²⁰ and Raman spectroscopy.^{11, 19} In addition to the experimental researches, computational studies have also been performed to understand spin-phonon couplings in molecular magnets.²¹⁻²⁴ Phonon structures of SMMs have been studied by inelastic neutron scattering (INS) to understand the nature of the phonon.^{17-19, 25-30} Works in the areas of probing phonon structures and spin-phonon coupling in molecular magnets have been recently reviewed.^{31, 32} Recent studies have shown that large anisotropy led to an increase in spin-phonon relaxation.³³ Methods such as FIRMS and HFEPR can be used to directly determine the energy barrier to relaxation of the spin in SIMs as well as spin-phonon coupling.

3.3.2.2. HFEPR

For HFEPR experiments, the powdered sample was stored in liquid 1,2-dichlorobenzene before being transferred into a sample holder and frozen with liquid nitrogen. The use of the liquid was to ensure that the voids in the MOF, **Co-BEBN**, were saturated with 1,2-dichlorobenzene. The resulting HFEPR spectra are frequency-limited to below ~215 GHz since

the liquid-soaked sample absorbs sub-THz wave power more strongly with increasing frequency than a dry powder. Measurements at 10 K produced spectra characteristic for an $S = 1/2$ spin state, and positive D . The three features visible in Figure 3.4-Left are turning points of the intra-Kramers transition within the $M_S = \pm 1/2$ doublet with the magnetic field along the x , y , and z axes of the ZFS tensor, respectively. A presence of three, rather than two, turning points indicates significant rhombicity of the ZFS and g -tensors.

HFEPR alone, observing a single intra-Kramers transition, cannot deliver the full set of SH parameters. However, it is possible to do so in conjunction with FIRMS. By fitting the parameters to the full set of experimental points (Figure 3.4-Right), we obtained the following values: $E/D = 0.14$, $g = [2.54, 2.54, 2.59]$. The D and E values were then chosen to be $D = 127.3 \text{ cm}^{-1}$, $E = 17.8 \text{ cm}^{-1}$ so that $2D' = 262 \text{ cm}^{-1}$ (the value obtained from FIRMS). The g -tensor was assumed axial, i.e., $g_x = g_y$, since the rhombic g anisotropy is intercorrelated with E . The reverse case, i.e., $E = 0$ and $g_x \neq g_y$, yields unphysical g -values $[2.0, 3.0, 2.45]$. Because of the intercorrelation, to be on the safe side, we can describe the ZFS parameters as: $127.3 \text{ cm}^{-1} \leq D \ll 131 \text{ cm}^{-1}$ and $0 \ll E \leq 17.8 \text{ cm}^{-1}$. The SH parameters above reproduce the experimental spectra very well, as seen in Figure 3.4-Left.

With the rhombicity of the ZFS tensor, there is a significant mixing of the spin states between $M_S = \pm 3/2$ and $M_S = \pm 1/2$ as represented by ϕ in Figure 1.1. The mixing may lead to a fast relaxation of magnetization as well as quantum tunneling. It is important to note that the D and E values found through FIRMS and HFEPR are directly determined in contrast to those from fittings of the magnetic susceptibility measurements, as often conducted. FIRMS and HFEPR indicate an easy-plane anisotropy ($D > 0$) for **Co-BEBN** as well as a large transverse anisotropy

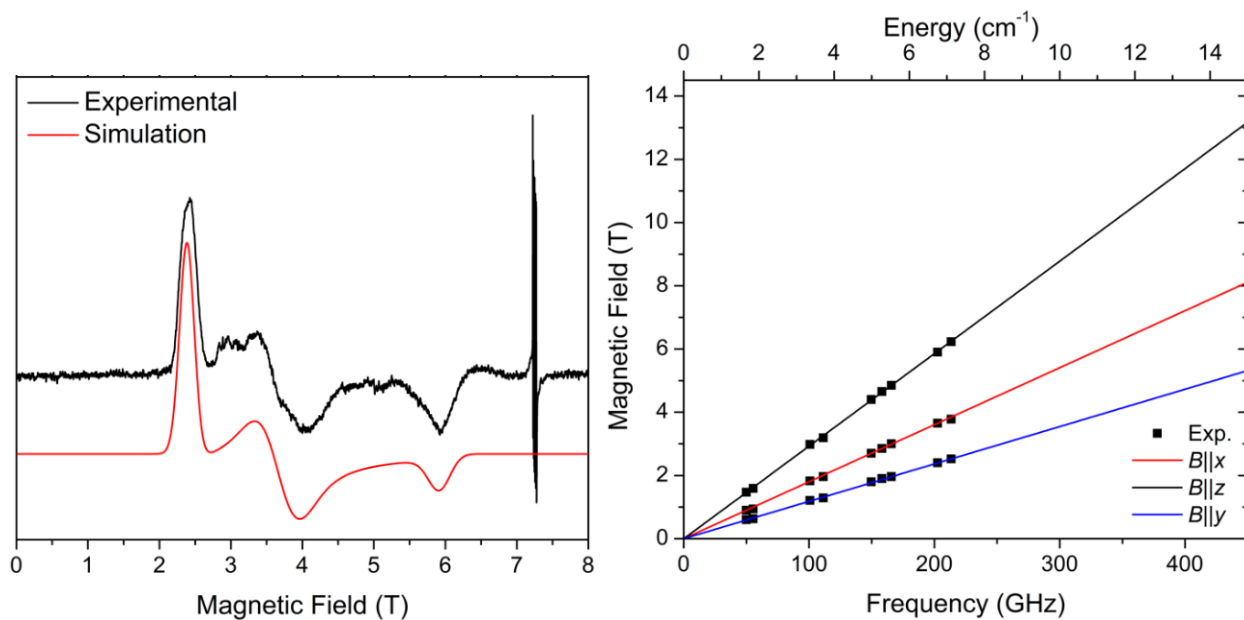


Figure 3.4. (Left) A derivative HFEPR spectrum of **Co-BEBN** showing three turning points corresponding of the transition $M_S = -1/2 \rightarrow M_S = +1/2$ at 10 K and 203 GHz (black trace) and its simulation (red trace) using the following SH parameters: $D = 127.3 \text{ cm}^{-1}$, $E = 17.8 \text{ cm}^{-1}$, $g = [2.54, 2.54, 2.59]$. The sextet of narrow lines at $\sim 7.25 \text{ T}$ ($g = 2.00$) originates from a Mn^{II} contaminant. (Right) A 2-D graph showing the position of the experimental turning points as a function of frequency/energy. The black squares are the experimental data. The lines are simulated using the best-fit SH parameters as above.

($E \gg 0$), which are supported by the *ab initio* electronic structure calculations discussed below. Most SIMs normally exhibit an easy-axis anisotropy ($D < 0$) with little-to-no transverse anisotropy ($E = 0$), giving an effective energy barrier to slow relaxation of magnetization and limiting quantum tunneling. Both characteristics are important for the application of magnetic memory storage. However, **Co-BEBN** is another example with easy-plane anisotropy ($D > 0$) but demonstrates SIM characteristics with slow magnetization relaxation.^{30, 88, 100-111, 178}

3.3.3. *Determination of the Inter-Kramers Magnetic Transition and Phonon Properties with INS and DFT Calculations*

INS is a powerful tool to probe the phonon properties as well as magnetic transitions in molecular system.^{17, 26, 27, 113, 115, 184-186} Applications of INS in coordination chemistry are recently reviewed.²⁵ Neutron spectroscopy is governed by the neutron kinetic energy transfer, therefore the symmetry-based selection rules for vibrations (or phonons) in optical spectroscopies (FIRMS and HFEPR) do not apply in neutron spectroscopy. All phonons observed in the INS experiments are a combination of both the internal and external vibrational modes.^{17, 29, 112} Furthermore, *ab initio* density functional theory (DFT) calculations using the Vienna Ab-Initio Simulation Package (VASP) were employed in conjunction with the INS experimental data to give a better insight into the phonon characteristics of the system as well as help reveal the magnetic transitions.^{11, 17, 18, 27, 29, 158, 187-189}

INS experiments using the Vibrational Spectrometer (VISION) at ORNL can reveal accurate phonon features of the solids in the energy range between 10 and 8000 cm^{-1} as well as any magnetic transition in the system. There are two types of interactions in INS that the

neutrons interact with: (1) Atomic nuclei of the sample, leading to phonon excitations; (2) Unpaired electrons through magnetic fields as both neutrons and electrons have 1/2 spins. Phonons observed in the INS experiments consist of both internal and external modes.^{17, 29, 112} INS experiments were performed on a powder sample of **Co-BEBN** in 1,2-dichlorobenzene liquid sealed in vanadium can under helium gas. The measurements were taken at 5.0(5), 20.0(5), 40.0(5), 60.0(5), 80.0(5), 100.0(5), 120.0(5), and 140.0(5) K. Bose-correction was applied by using a frequency- and temperature-dependence normalization factor such that the phonon intensities are not temperature-dependence.^{17, 26, 27, 102, 113-115} Bose-correction procedure mainly affects the low-energy region. The small separation between each spectra line is due to the Debye-Waller factor.¹⁹⁰ As the temperature increases, the intensity of the peak decreases into the background and the peak width increases. INS spectra of frozen 1,2-dichlorobenzene were also taken at 5.0(5) K so its peaks could be subtracted from the data of **Co-BEBN** in frozen 1,2-dichlorobenzene. Four different phonon peaks are observed in the range of 200-400 cm^{-1} from the data collected in both forward and backward detectors (Figure 3.5). The same four phonon peaks were also observed in the spectrum of frozen 1,2-dichlorobenzene at 5.0(5) K, indicating that they are from the organic compound. The intensities of all four phonon peaks do not change with temperature and the peaks are fairly sharp, indicating their phonon characteristics. The peak at 280(2) cm^{-1} seems to exhibit magnetic characteristics, as its intensity decreased with the temperature increase. Boltzmann distribution at a lower temperature allows for more unpaired electrons to be in the ground state. Therefore, the magnetic transition to the excited state is more intense compared to a higher temperature. It is also important to note that the intensity of the peak, as well as the peak's width, is larger in the forward scattering plot with lower momentum

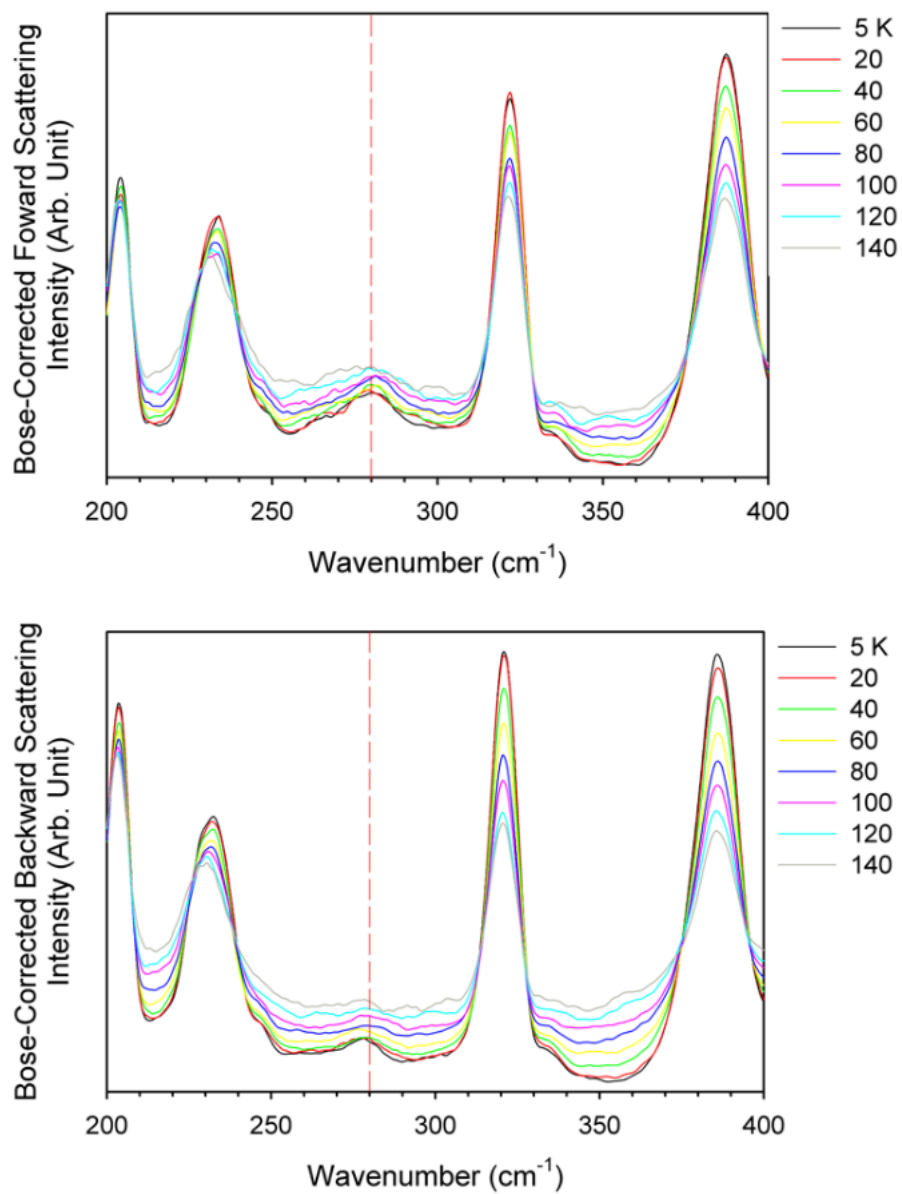


Figure 3.5. Variable-temperature INS spectra of **Co-BEBN**. (Top) Forward scattering data; (Bottom) Back scattering data. The red dotted vertical line is an eye-guide for the peak at 280(2) cm⁻¹.

transfer Q ($Q = |\mathbf{Q}| = |\mathbf{k}_i - \mathbf{k}_f|$; $\mathbf{k}_i$ and $\mathbf{k}_f$ are momenta of the incoming and outgoing neutrons, respectively).²⁵ In INS, the magnetic peaks are more intense in the forward scattering than in the back scattering spectra, while phonon peaks are more intense in the back scattering than in the forward scattering spectra.²⁵ The peak was not observed in the spectrum of the solvent 1,2-dichlorobenzene at 5.0(5) K. Therefore, the peak at 280(2) cm^{-1} has magnetic contributions and is likely an overlapping peak between the magnetic transition observed at 262(1) cm^{-1} in FIRMS and a larger phonon at 283(1) cm^{-1} in FIRMS (Figure 3.2-Bottom).

To further understand the phonon features of **Co-BEBN**, phonon calculations using DFT calculations by VASP were conducted based on the single-crystal X-ray diffraction data. Figure 3.6 shows a comparison between the experimental INS spectrum to 5.0(5) K and the calculated phonon spectrum at 200-400 cm^{-1} . The calculated phonon spectrum fits well with the experimental spectrum, including the four intense phonon peaks. In addition, phonon calculations give the mode of individual phonon features in the system at 16-3150 cm^{-1} , as listed in Table B.7. Around the region of the observed phonon at 280(2) cm^{-1} in far-IR (Figures 3.2-3.3), the calculated phonon spectrum shows three smaller INS peaks that potentially overlap giving the phonon in far-IR. Additional phonon information can be found in Appendix B.

3.3.4. *Studies of the Magnetic Anisotropy and the Magneto-Structure by Ab Initio*

Computations

Ab initio calculation was conducted to understand the electronic structure as well as the origin of the anisotropy for **Co-BEBN**. The calculated molecular structure is given in Figure B.6. The core unit of the grid-like structure was used in the calculations. The energy difference

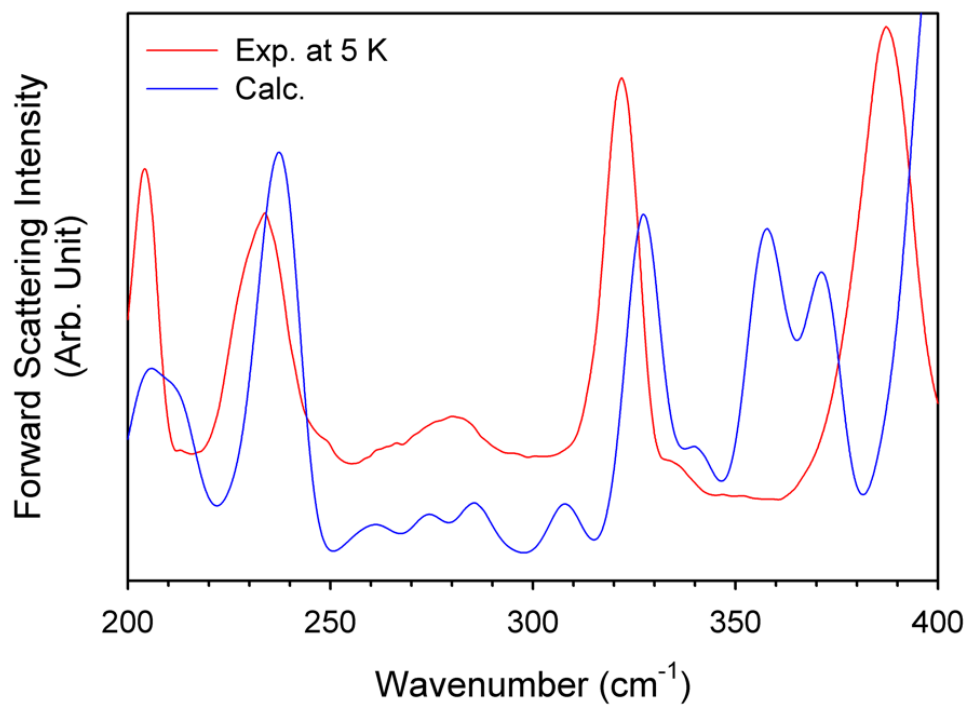


Figure 3.6. Comparison between the experimental INS data at 5.0(5) K and the calculated INS spectrum in the 200-400 cm⁻¹ region.

between the lowest two spin-free states of **Co-BEBN** is 163.3 cm⁻¹ (Table B.3). Therefore, we can use ZFS parameters D and E to depict the magnetic anisotropy. The calculated D , E , and g (g_x , g_y , g_z) tensors for **Co-BEBN** using CASPT2 and NEVPT2 with MOLCAS 8.4¹¹⁶ and ORCA 4.2¹¹⁷ are shown in Table 3.2. The calculated ZFS parameters extracted from both methods are similar. Calculated values from CASPT2 are agreeable with the experimental data from FIRMS and HFEPR. To deeply analyze magnetic anisotropy, we gave the contributions of the excited states to the D values for **Co-BEBN** in Table B.5 using NEVPT2 with ORCA 4.2. The dominant contributions to the positive D values are found to arise from the two close quartet states, particularly the first and the second quartet states. The calculations yield positive D values, which are consistent with the geometries around Co^{II} ions and easy-plane anisotropies ($g_{x,y} > g_z$). The results are also consistent with the experimental SH parameters (Table 3.2).

Molecular coordination frame was chosen in such a way that the z -axis goes along the numerically largest eigenvalue of the D -tensor and the x and y -axes accordingly to the other two in Figure B.6. The following discussions of Co d -atomic orbitals (d -AOs) are classified following this frame. The calculated relative energies (cm⁻¹) of ligand field one-electron states [in the basis of d -atomic orbitals (d -AOs)] for **Co-BEBN** using NEVPT2 with ORCA 4.2 are shown in Table B.6 according to the analysis by the *ab initio* ligand field theory (AILFT).^{118, 119} The orbital energies computed for the ground state are shown in Figure B.9, where the ground state for **Co-BEBN** has a dominant (91.1%) $(d_{yz})^1(d_{xz})^2(d_{xy})^1(d_{z^2})^2(d_{x^2-y^2})^1$ configuration. The largest contribution to D is from the ground to the first excited state transition ($d_{z^2} \rightarrow d_{yz}$; Figures B.9 and B.10). Since these orbitals also have different m_l values, the contributions to the D value are both positive.^{120, 121} The multideterminantal wavefunctions of the selected excited states

Table 3.2. Comparison of experimental and calculated ZFS parameters D , E , and g [g_x , g_y , g_z] tensors of **Co-BEBN** using CASPT2 and NEVPT2 with MOLCAS 8.4 and ORCA 4.2, respectively

Methods	D (cm⁻¹)	E (cm⁻¹)	g_x	g_y	g_z
FIRMS/HFEPR	127.3	17.8	2.54	2.54	2.59
CASPT2	114.0	23.7	3.000	2.197	1.715
NEVPT2	116.8	30.8	3.047	2.161	1.595

having important contributions to the D tensor (Figure B.10). The calculated orientations of g_x , g_y , and g_z in the ground spin-orbit states on Co^{II} ions are shown in Figure B.8.

The calculations were able to extract the χ_{MT} versus T plots (DC magnetic susceptibility) of **Co-BEBN** in Figure B.7. The magnetic susceptibility increases as the temperature increases. The magnetic susceptibility value plateaued around $3.3 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$. The increasing feature indicates an antiferromagnetic interaction in the system. The calculated DC magnetic susceptibility data is agreeable with the experimental data in Figure B.3 showing an $S = 3/2$ antiferromagnetic interacting system at low temperature.

3.3.5. *Determination of the Qubit Properties Using Pulsed X-band EPR*

Pulsed X-band EPR has previously been used to study the relaxation times or spin decoherence. Therefore, it is a crucial spectroscopy in understanding the quantum bit (qubit) properties of the system.^{31, 37, 80, 191-193} Qubit is a building block of quantum computers, and it is at the forefront of modern cutting-edge technology.^{34-36, 133-136} Three important qubit properties can be obtained from pulsed X-band EPR, including the spin-lattice relaxation time (T_1), spin-spin relaxation time (T_2), and the Rabi oscillation. T_1 reflects the time of energy transfer between the spin and its local environments. T_2 quantifies the time of spin dephasing of magnetizations in the x - y plane. Pulsed X-band EPR quantified T_1 and T_2 based on the transition between $M_S = -1/2$ and $M_S = +1/2$ state. Rabi oscillation measurements provide a unique insight into the quantum superposition state of the system and the probability of the system being in the $|1\rangle$ or the $|0\rangle$ state.

Pulsed X-band EPR measurements were conducted to probe the spin relaxation of **Co-**

BEEN as well as its qubit potentials based on the *intra*-Kramers transition of the $M_S = \pm 1/2$ state. Spin-lattice relaxation (T_1) and the spin-spin relaxation (T_2) times were measured as well as the Rabi-oscillation. The T_1 and T_2 are intrinsic magnetic properties of **Co-BEEN**, while the Rabi-oscillation shows qubit properties.

T_1 determines the rate of energy transfer between the spin and the crystal lattice.⁸⁰ Echo inversion recovery is a technique to probe T_1 by applying a 180° -pulse in an applied field, causing the magnetization to be flipped from $+z$ to $-z$ direction.^{129, 130} Then, the magnetization relaxes back to the $+z$ direction by releasing the energy to the crystal lattice. The time-dependent magnetization along the z direction, $M_z(t)$, is measured during the spin relaxation process. The process is repeated at different times (t). T_1 is the time for $M_z(t)$ to reach 63% of its maximum value. It is also considered as the time of magnetization relaxation across the energy barrier back to the thermal equilibrium. T_1 can be calculated using Eq. 3.3.^{131, 132}

$$M_z(t) = M_z(0)[1 - 2\exp(-t/T_1)] \quad (\text{Eq. 3.3})$$

where t is time and $M_z(0)$ is the magnetization when time is at 0.

T_2 is the rate at which the magnetizations are dephased in the x - y plane.⁸⁰ Bloch found that the T_2 relaxation process follows first-order kinetics, leading to exponential decay.¹³¹ Hahn echo decay is the technique used to quantify T_2 by first applying a 90° pulse to the sample. Then, the magnetization in the x - y plane begins dephasing at different speeds due to the inhomogeneities of the local magnetic field. Once the magnetization dephasing in the x - y plane is nearly complete, a 180° pulse is applied to change the spin dephasing direction and remove the

inhomogeneities, allowing for the magnetization measurement. The process is repeated at different times (t) before the echo. T_2 is the time the magnetization in the x - y plane is at 37% of its initial value (Eq. 3.4).

$$M_{xy}(t) = M_{xy}(0)\exp(-t/T_2) \quad (\text{Eq. 3.4})$$

where $M_{xy}(t)$ and $M_{xy}(0)$ are the magnetization vector at time t and 0, respectively.

The T_2 measurement is important for determining the effectiveness of a qubit. The dephasing time is related to the time it takes for the qubit to stay in its superposition state. The longer T_2 , the more effective the material as a qubit candidate. Though, finding materials exhibiting long T_2 is challenging due to many factors limiting the time through interactions of unpaired electron spins with local environments, leading to the collapse of the superposition state. Nuclear spin diffusion coupling to nearby electrons, methyl rotation, and spin diffusion barrier are just some of the main effects with strong correlations with the T_2 time. Graham, Freedman, and coworkers recently discussed how environmental effects can negatively affect T_2 time.³⁴

Pulsed X-band EPR measurements were conducted at 10 K on powders of two samples in frozen 1,2-dichlorobenzene: (1) **Co-BEBN** (100% Co^{II} ion); (2) **Co-BEBN_{0.05}** (5% Co^{II} ion with 95% diamagnetic Zn^{II}). Figure 3.7 is an echo inversion recovery plot that shows $T_1 = 329(4)$ μs for **Co-BEBN**. It is noted that T_1 here is longer than 235(4) μs of **Co-TODA**, a Co^{II}-based coordination polymer (CP).³⁰ The reason for the longer observed T_1 time can be attributed to the longer distance (20.515 Å) of Co^{II} ions in **Co-BEBN** in the same layer. For **Co-TODA**, the

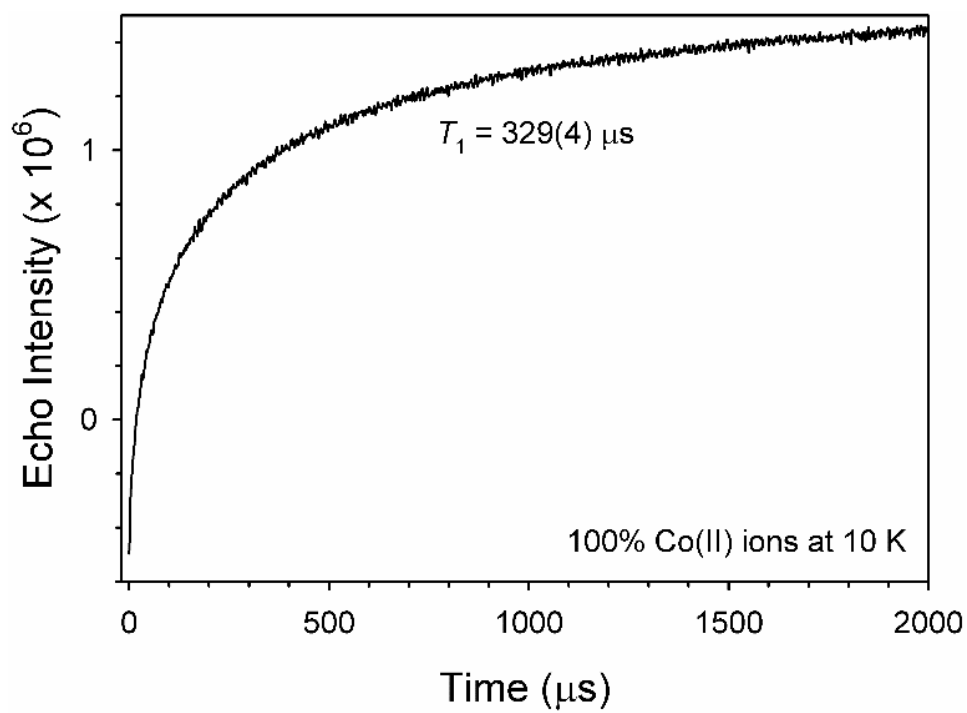


Figure 3.7. Echo inversion recovery plot of **Co-BEBN** at 10(1) K with external applied magnetic field of 0.33 T.

shortest distance between Co^{II} ions is only 7.52 Å. More isolated Co^{II} ions in **Co-BEBN** limit magnetic interactions between the neighboring Co^{II} ions, leading to a longer relaxation time of the magnetization. For **Co-BEBN**, $T_2 = 1.387(4) \mu\text{s}$ (Figure 3.8-Top), which is much longer than 0.513(4) μs of **Co-TODA**. The purpose of the diamagnetic Zn^{II} -dilution is to further limit the magnetic interactions between the Co^{II} ions through space, potentially improving relaxation times. For **Co-BEBN**_{0.05}, $T_2 = 1.450(4) \mu\text{s}$ (Figure 3.8-Bottom), longer than 1.387(4) μs of **Co-BEBN** with Zn^{II} dilution.

Rabi oscillation measurements were also performed on **Co-BEBN** and **Co-BEBN**_{0.05} to observe the ability of the systems to stay in the superposition state or exhibit quantum coherence as qubit candidates. Rabi oscillation is a procedure to observe the probability of a qubit system existing in the $|1\rangle$ or $|0\rangle$ states periodically.¹⁹⁴ By measuring the projection of the magnetization onto the z -axis with a Hahn echo as a function of time for the initial nutation pulse, Rabi oscillation is observed.^{138, 195-199} Rabi oscillation plots for **Co-BEBN** and **Co-BEBN**_{0.05} are given in Figure 3.9. The oscillating wave-like pattern in the plots suggests that the sample changes the states that it occupies periodically during the experiment. The results show that **Co-BEBN** is a viable option for a qubit candidate. It is important to note that the echo intensity of the wave seems to be slightly bigger for **Co-BEBN**_{0.05} compared **Co-BEBN**. The difference in intensity could be related to the inter-ion interactions between the Co^{II} ions. The stronger echo intensity of the Rabi oscillation in **Co-BEBN**_{0.05} means a more stable existence in the $|1\rangle$ or $|0\rangle$ states in that period.^{138, 194} The results further support that Zn^{II} -diluted **Co-BEBN**_{0.05} is a better qubit candidate than **Co-BEBN**.

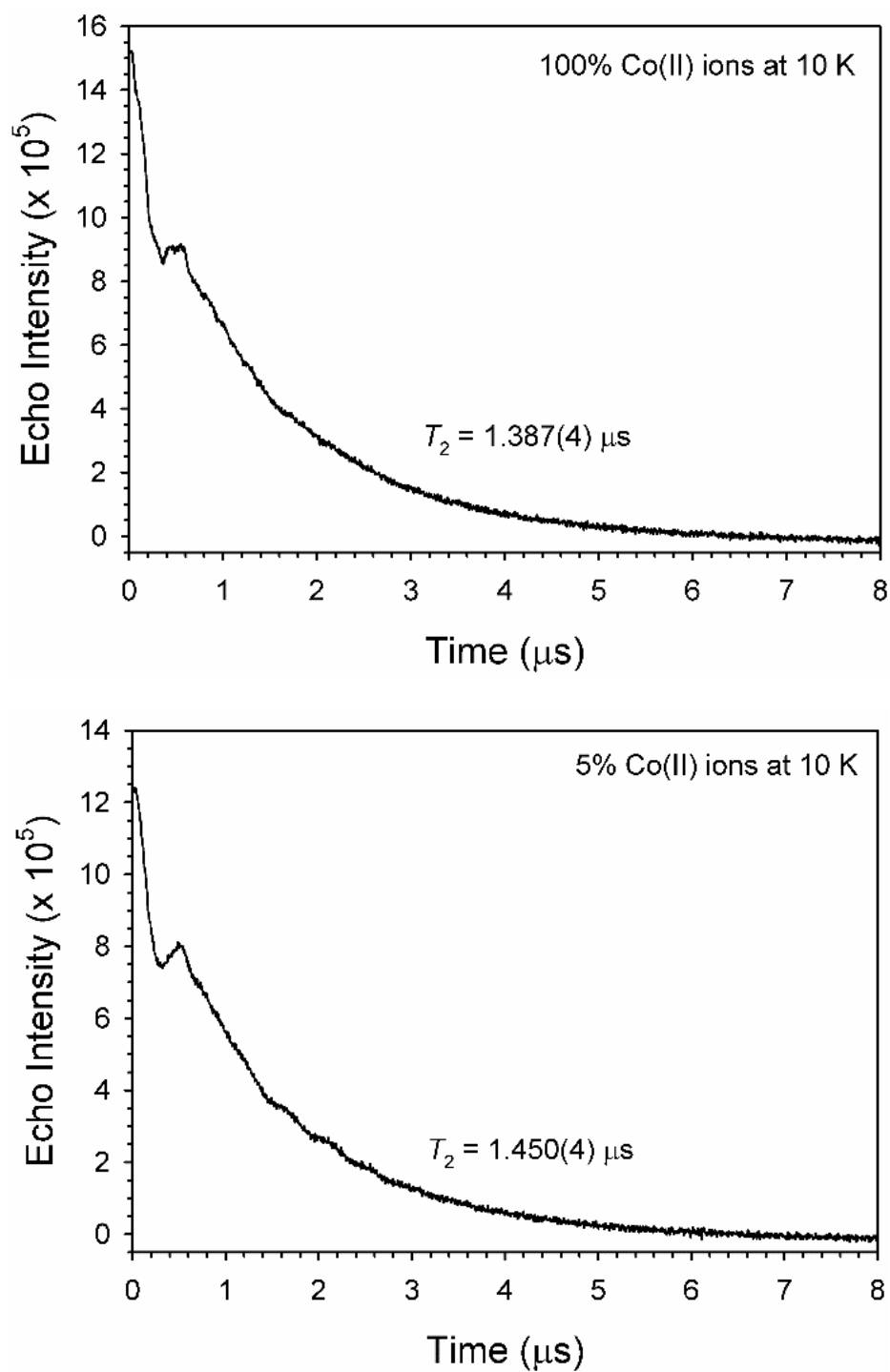


Figure 3.8. Hahn echo decay plots: (Top) **Co-BEBN**; (Bottom) **Co-BEBN_{0.05}** at 10(1) K with external applied magnetic field of 0.33 T and 0.34 T, respectively.

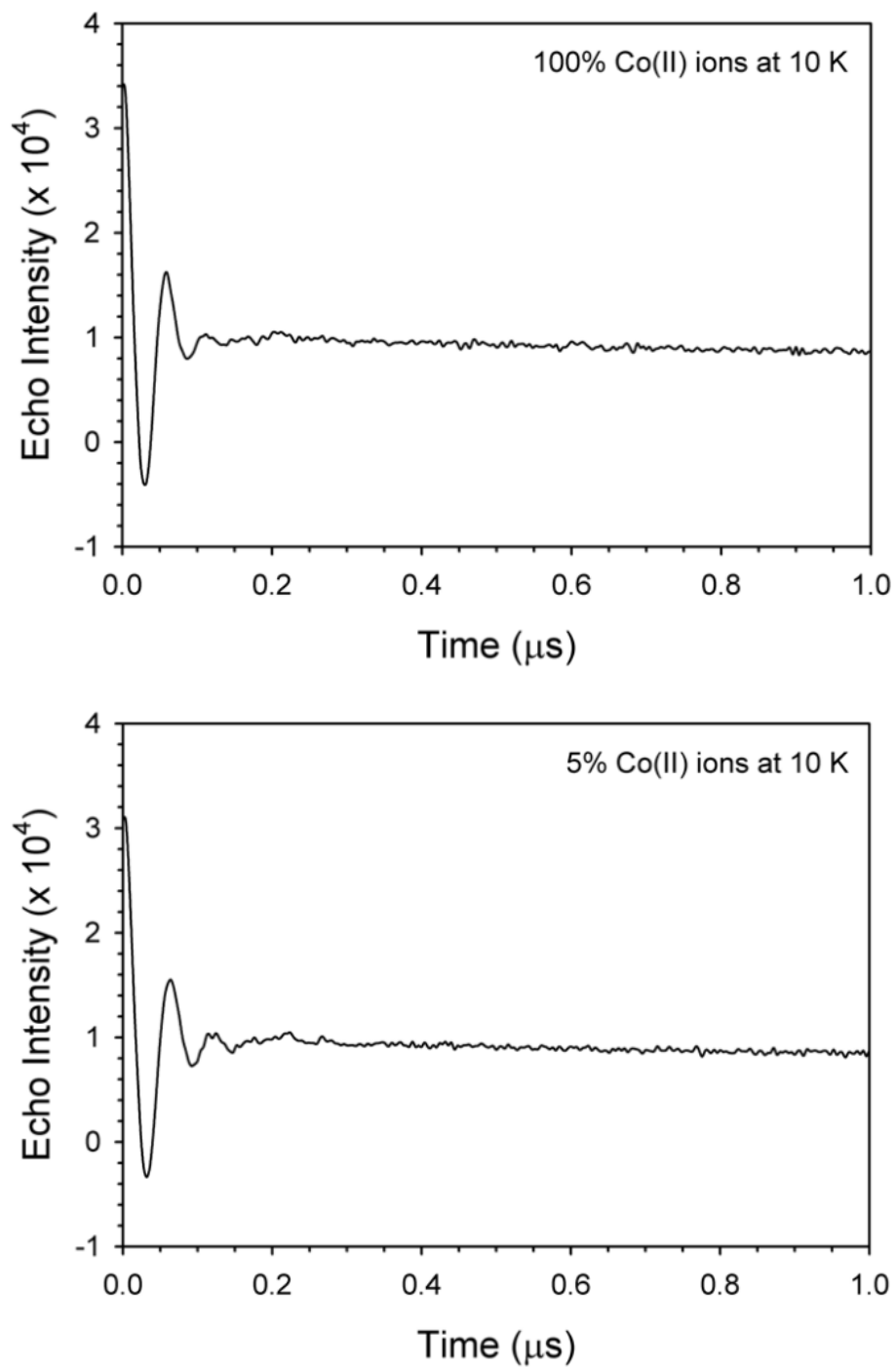


Figure 3.9. Rabi oscillation plots at 10(1) K. (Top) **Co-BEBN**. (Bottom) **Co-BEBN_{0.05}**.

3.4. Experimental Methods

3.4.1. *Single-Crystal X-Ray Diffraction*

Single-crystal X-ray diffraction data were collected using a Bruker D8 Venture at 100(2) K with Mo $K\alpha$ radiation. Data were collected and integrated using APEX 3 programs, reduced using Bruker SAINT program, and corrected for absorption using the SADABS multi-scan program. The structure was solved using SHELXT and refined with SHELXL-2015.

3.4.2. *FIRMS*

FIRMS spectra were collected at the NHMFL (Tallahassee, Florida, USA) using a Bruker Vertex 80v Fourier-transform infrared (FT-IR) spectrometer coupled with a 17.5 T vertical-bore superconducting magnet. The experimental setup is equipped with a mercury lamp and a composite silicon bolometer (Infrared Laboratories), as an incoherent (sub)-THz radiation source and detector, respectively. The THz radiation is free-space propagating inside the optical beamline, connecting the output of the spectrometer and the top of the sample probe. The radiation is then passed through the brass light pipe over a distance of 2.5 m from room temperature to the field center. The probe and beamline are evacuated to eliminate strong parasitic absorptions of the air. The studied samples are the mulls of *n*-eicosane, powder (~2 mg) of **Co-BEBN**, and 2 droplets of 1,2-dichlorobenzene. Both the sample and the bolometer were cooled by low-pressure helium gas to 5.5 K. The spectrum of the THz radiation transmitted through the samples was measured in the spectroscopic between 10 and 720 cm^{-1} (0.3–21.6 THz) with a resolution of 0.3 cm^{-1} (9 GHz), the acquisition time of 3 min and 10 kHz scanner speed.

3.4.3. *HFEPR*

HFEPR spectra were obtained at the NHMFL using the home-built spectrometer based on a 17-T superconducting magnet described previously,¹⁴⁰ and differs from that description only by the use of a low-frequency (8-20 GHz) microwave source complemented by a cascade of amplifiers and multipliers (Virginia Diodes, Charlottesville, VA, USA) to produce higher frequency harmonics.

3.4.4. *INS*

For variable-temperature INS at VISION, the sample (0.5 g) was sealed in an aluminum container and placed inside the neutron beam at Vibrational Spectrometer (VISION) at Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL). INS spectra of Co-TODA were measured at 5.0(5), 20.0(5), 40.0(5), 60.0(5), 80.0(5), 100.0(5), 120.0(5), 140.0(5) K. VISION offers two banks of detectors for both forward (low $|Q|$) and back (high $|Q|$) scattering of neutrons.¹⁴¹ The phonon population effect was corrected by normalizing the INS intensity at energy transfer ω with $\coth\left(\frac{\hbar\omega}{2k_B T}\right)$.¹⁴²

3.4.5. *Electronic Structure Calculations*

For the first CASSCF calculation, the basis sets for all atoms are atomic natural orbitals from the MOLCAS ANO-RCC library: ANO-RCC-VTZP for magnetic center ion Co^{II}; VTZ for close N and O atoms; VDZ for distant atoms. The calculations employed the second-order Douglas-Kroll-Hess Hamiltonian, where scalar relativistic contractions were considered in the basis set. The effect of the dynamical electronic correlation was applied using CASPT2 based on

the first CASSCF calculation. After that, the spin-orbit coupling (SOC) was handled separately in the restricted active space state interaction (RASSI-SO) procedure.^{146, 200} The active electrons in 5+5' active orbitals include all *d* electrons [CAS(7 in 5+5')] in the CASSCF calculations. To exclude all the doubts, we calculated all the roots in the active orbitals. The maximum number of the spin-free state were mixed, which was possible with our hardware (all from 10 quadruplets and 20 from 40 doublets). SINGLE_ANISO¹⁴³⁻¹⁴⁵ program was used to obtain zero-field splitting parameters *D*, *E* (cm⁻¹), *g* tensors, energy levels, magnetic axes based on the above CASPT2/RASSI-SO calculations.

To deeply analyze the magnetic anisotropy, ORCA 4.2 calculations¹¹⁷ were performed with complete active space self-consistent field calculations (CASSCF), followed by N-electron valence second-order perturbation theory (NEVPT2). The SOC operator used was the efficient implementation of the multicenter spin-orbit mean-field (SOMF) concept developed by Hess et al.¹⁴⁶ The spin-spin contributions (SSC) to the *D* values were also included, although they are very small for our complexes. The NEVPT2¹⁴⁷⁻¹⁵⁰ calculation with seven 3*d* electrons in five Co 3*d*-based orbitals [CAS(7, 5)]. In the calculations, the orbitals were determined for the average of 10 *S* = 3/2 and 40 *S* = 1/2 roots. All calculations were performed with triple- ζ with one polarization function def2-TZVP¹⁵¹⁻¹⁵³ basis set for all atoms.

3.4.6. DFT Calculations of INS Spectrum and Spin Densities

Spin-polarized density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP).¹⁵⁴ The calculation used Projector Augmented Wave (PAW) method^{122, 123} to describe the effects of core electrons, and Perdew-Burke-

Ernzerhof (PBE)¹²⁶ implementation of the Generalized Gradient Approximation (GGA) for the exchange-correlation functional. Energy cutoff was 600 eV for the plane-wave basis of the valence electrons. The lattice parameters and atomic coordinates from **Co-BEBN** CIF (Crystallographic Information Framework) file were used as the initial structure. Given the large unit cell containing 492 atoms, the electronic structure was calculated on Γ -point only. The total energy tolerance for electronic energy minimization was 10^{-6} eV. The maximum interatomic force after relaxation was below 0.001 eV/Å. The optB86b-vdW functional¹⁵⁵ for dispersion corrections was applied, and a Hubbard U term of 3.32 eV¹⁵⁶ was applied to account for the localized 3d orbitals of Co ion. The interatomic force constants were calculated on the unit cell by VASP, and the vibrational eigen-frequencies and modes were then calculated using Phonopy.¹⁵⁷ The OCLIMAX software¹⁵⁸ was used to convert the DFT-calculated phonon results to the simulated INS spectra.

3.4.7. Pulsed X-band EPR

Pulsed X-band EPR experiments were performed on a Bruker E680 spectrometer (Billerica, MA) operating at a microwave frequency of 9.5 GHz at the NHMFL. Echo detection and T_1 and T_2 relaxation times were collected using a dielectric ER4118X-MD-5 resonator equipped with an Oxford CF-935 helium flow cryostat. The temperature was controlled and monitored using an Oxford Instrument ITC503 temperature controller. The 4-mm outer-diameter EPR tubes were used to load samples. The experiments were conducted in the temperature range of 5(1)-30(1) K. Echo-detected field-swept spectra were obtained by measuring the Hahn echo intensity ($\pi/2-\tau-\pi-\tau$ -echo) as a function of the transverse field. The time delay (τ) between two

detection pulses was 200 ns. Echo detection was swept from 100 Gauss (G) to 10000 G magnetic field. T_1 was measured using an echo-detected inversion recovery pulse sequence ($\pi-\tau_1-\pi/2-\tau-\pi-\tau$ -echo). T_2 was measured using a standard two-pulse Hahn echo sequence ($\pi/2-\tau-\pi-\tau$ -echo). The lengths of the $\pi/2$ and π pulses were 16 and 32 ns for all experiments, respectively.

3.5. Conclusions

Comprehensive studies of the magnetic and phonon properties of **Co-BEBN** are reported here, showcasing a MOF containing isolated Co^{II} ions with unusually large magnetic anisotropy. The long distance (~ 20.9 Å) between Co^{II} ions is achieved through the use of bpeb ligands to form the MOF. Versatility and power of combined optical spectroscopies (FIRMS and HFEPR) to make a direct determination of the SH parameters are showcased in the current work, which is crucial in deconvoluting D' into D and E values. With a large E value, **Co-BEBN** exhibits a significant mixing of the spin states, allowing formally forbidden magnetic transitions to occur. The *ab initio* electronic structure calculations provide an insight into the origin of the anisotropy and the magneto-structural correlations to the spin-Hamiltonian (SH) parameters. INS and DFT calculations were crucial in understanding the phonon properties of **Co-BEBN**. In addition, pulse X-band EPR has provided a direct probe of the qubit properties through the determination of T_1 and T_2 and Rabi oscillations of **Co-BEBN**. The differences between the Zn^{II} -diluted **Co-BEBN**_{0.05} and non-diluted **Co-BEBN** suggest that the more isolated metal ions in the MOF contribute to a more effective qubit.

Chapter 4

Haldane Spin-1 Chain in a Planar Metal-Organic Framework

This chapter is based on a manuscript that has yet to be published.

List of authors and their contributions:

Pagnareach Tin, Michael J. Jenkins, Jie Xing, Nils Caci, Zheng Gai, Rongying Jin, Stefan Wessel, J. Krzystek, Cheng Li, Luke L. Daemen, Yongqiang Cheng, Zi-Ling Xue

P. Tin performed syntheses of **NiBO** and **NiBO-*d*₈** and grew single crystals of **NiBO-*d*₈**. He prepared all samples for the experiments indicated below. M.J. Jenkins performed the single-crystal X-ray diffraction experiment. MJJ and PT analyzed and interpreted the single-crystal data and solved the crystal structure. Z. Gai performed the magnetic susceptibility measurement at a low magnetic field (0.1 T). PT analyzed and interpreted the data. J. Xing performed the measurements of magnetic susceptibilities at high magnetic fields (>0.1 T) and specific heat capacity. JX, PT, and R. Jin analyzed and interpreted the data. RJ supervised the studies here. N. Caci and S. Wessel performed the quantum Monte-Carlo simulations for the magnetic susceptibility and the specific heat capacity data. NC, SW, and PT analyzed and interpreted the results. J. Krzystek performed the HFESR measurement. PT and JK analyzed the data and interpreted the results. C. Li performed PND experiments at POWGEN. CL and PT analyzed and interpreted the data. L.L. Daemen performed INS experiments at VISION. PT and LLD analyzed and interpreted the data. Y. Cheng performed the VASP calculations. PT and MJJ analyzed and interpreted the data. Z.-L. Xue initiated the project, supervised the research, including data analyses, and data interpretations.

4.1. Abstract

Haldane topological materials typically contain spin-1 chains embedded in extended three-dimensional (3-D) crystal structures. Here, we demonstrate that $[\text{Ni}(\mu\text{-}4,4'\text{-bipyridine})(\mu\text{-oxalate})]_n$ (**NiBO**) instead adopts a two-dimensional (2-D) metal-organic framework (MOF) structure of Ni^{II} spin-1 chains weakly linked by 4,4'-bipyridine. **NiBO** exhibits Haldane topological properties with a gap between the singlet ground state and the excited triplet state. The latter is split by weak axial and rhombic anisotropies. Several experimental probes, including single-crystal X-ray diffraction, variable-temperature powder neutron diffraction (VT-PND), inelastic neutron scattering (INS), DC susceptibility and specific heat measurements, high-field electron spin resonance, and unbiased quantum Monte Carlo simulations, provide a detailed, comprehensive characterization of **NiBO**. Phonon properties of **NiBO** have been probed by INS and density functional theory (DFT) calculations, indicating the absence of phonons near magnetic excitations in **NiBO**, reducing chance of spin-phonon coupling. The work here demonstrates that **NiBO** is indeed a rare 2-D MOF Haldane topological material with promising quantum applications.

4.2. Introduction

Introduction about Haldane spin-1 materials, including the energy levels (Figure 1.3) and the AKLT model representation of the Ni^{II} spin-1 Haldane chain (Figure 1.4), is given in Chapter 1, Subsection 1.1.3.

Properties of 1-D Haldane spin-1 materials have been probed experimentally using, e.g., Ni^{II} -based chains bridged by NO_2^- , N_3^- or $\text{C}_2\text{O}_4^{2-}$ (oxlate or ox^{2-}) ligands,⁴⁴ such as $[\text{Ni}(\text{en})_2(\mu\text{-}$

NO₂)](ClO₄) (NENP; en = ethylenediamine),⁶⁷⁻⁷² [Ni(1,3-propanediamine)₂(μ-NO₂)](ClO₄) (NINO),^{72, 73} [Ni(en)₂(μ-NO₂)](BF₄) (NENB),⁷⁴⁻⁷⁶ [Ni(dmpn)₂(μ-N₃)](ClO₄) (NDMAZ; dmpn = 1,3-diamino-2,2-dimethylpropane),²⁰¹ [Ni(3,2,3-tet)(μ-N₃)](ClO₄) [232-tet = bis(2-aminoethyl)-1,3-propanediamine],²⁰² [Ni(2,2'-bpy)(μ-ox)]_n (bpy = bipyridine),²⁰³ [Ni(benzimidazole)₂(μ-ox)]_n,²⁰⁴ and [NiI₂(3,5-lut)₄]_n (3,5-lut = 3,5-lutidine).²⁰⁵ In the 1-D chains with μ-NO₂⁻ or μ-N₃⁻ bridging ligands such as NENP or NENB, anions ClO₄⁻ or BF₄⁻ are needed to balance the charges, forming 3-D crystal structures. In [Ni(2,2'-bpy)(μ-ox)]_n²⁰³ and [Ni(benzimidazole)₂(μ-ox)]_n,²⁰⁴ the N-ligands, 2,2'-bpy or benzimidazole, are *cis*-coordinated to Ni^{II} ions, forming zig-zag structures.

Haldane spin-1 chains based on MOFs with oxalate-based ligands, [Ni(μ-bpa)(μ-ox)]_n [bpa = 1,2-bis(4-pyridyl)ethane],⁶⁴ [Ni(μ-bpe)(μ-ox)]_n [bpe = 1,2-di(4-pyridyl)ethylene],⁶⁴ [Ni(μ-en)(μ-ox)]_n,⁶⁵ and [Ni(μ-pip)(μ-ox)]_n (pip = piperazine),⁶⁶ have been reported to show the presence of a finite spin gap through DC magnetic susceptibility measurements. Unlike NENP and NDMAZ, the MOF-based compounds exhibit stacked 2-D planar structures with decoupled magnetic 1-D chains. The ox-bridged Haldane chains in the MOFs are linked by N-containing ligands. From DC magnetic susceptibility data, García-Couceiro and coworkers found that the spin gap = 7.32 and 10.29 cm⁻¹ for [Ni(μ-bpa)(μ-ox)]_n and [Ni(μ-bpe)(μ-ox)]_n, respectively.⁶⁴ Similarly, Keene and coworkers obtained spin gap = 11.5 cm⁻¹ for [Ni(μ-en)(μ-ox)]_n from DC susceptibility data.⁶⁵ The spin gaps are comparable to those of other spin-1 chain systems such as NENP and NENB.^{67, 74} The results show that 2-D MOFs containing inter-chain ligands that forms planar structures have the potential to exhibit Haldane spin-chain physics, as long as the inter-chain magnetic couplings is negligible. Moreover, 2-D MOFs can be exfoliated by

overcoming the relatively weak Van der Waals force between the layers. Exfoliation of the 2-D MOFs may yield 2-D nanosheets with interesting low-dimensional properties. Several exfoliation methods have been established to be effective in synthesizing the 2-D MOF nanosheets.⁷⁷⁻⁷⁹

Here, we report that $[\text{Ni}(\mu\text{-}4,4'\text{-bpy})(\mu\text{-ox})]_n$ (**NiBO**) is a Haldane spin-1 chain material. It has been comprehensively probed by a variety of techniques, including variable-temperature powder neutron diffraction (VT-PND), magnetization measurements (DC magnetic susceptibility at different fields), high-field ESR (HFESR), inelastic neutron scattering (INS), and specific heat measurements. In addition, we have performed quantum Monte Carlo (QMC) simulations of the spin-1 chains realized in **NiBO**, which show excellent agreement with the experimental DC magnetic susceptibility data. VT-PND data exhibit no long-range antiferromagnetic ordering down to 1.7 K, further supporting that **NiBO** is a quantum disordered spin-1 chain system. The spin gap extracted from the DC magnetic susceptibility measurements at 0.1 T agrees remarkably well with QMC simulations. The QMC results also identify magnetic parameters such as D , E , J , and g -factor (g) for **NiBO**, as detailed below. Additionally, both the magnetic susceptibility data and specific-heat data reveal a field-induced phase transition in **NiBO** for magnetic field beyond 9 T and temperatures below 5 K. HFESR was used to observe the effective anisotropy (D_{eff}) in ZFS through the transition within the triplet state. Furthermore, these magnetic measurements are well in accord with QMC simulations. X-ray single-crystal diffraction of deuterated $[\text{Ni}(\mu\text{-}4,4'\text{-bpy-}d_8)(\mu\text{-ox})]_n$ (**NiBO- d_8**) at 100 K revealed a non-planar structure of the 4,4'-bpy- d_8 ligand, which reduces magnetic inter-chain interactions. Inelastic neutron scattering (INS) studies provide the spin gaps between the singlet ground and the triplet excited state as well as the

phonon properties of **NiBO**, which are supported by density functional theory (DFT) calculations using Vienna Ab initio Simulation Package (VASP).²⁵

4.3. Results and Discussions

4.3.1. *Single-Crystal X-Ray Diffraction*

Single-crystal X-ray diffraction performed at 100(2) K provides an in-depth analysis of the structure of **NiBO-d₈** and compares it with that reported earlier at 295 K (Table C.1).²⁰⁶ Each Ni^{II} ion is coordinated with two oxalate ligands in a plane as intra-chain bridging ligands forming the spin-1 chains, while two 4,4'-bpy ligands coordinates in the *z*-direction as inter-chain bridging ligands, resulting in an overall 2-D framework. There are only one oxalate and one 4,4'-bpy ligand and one Ni^{II} ion in the asymmetric unit of the MOF. Figures 4.1 and C.5 illustrate the inter- and intra-chain directions of the 1-D spin chains in **NiBO** as well as a view down the *a*-axis. At 100 K, we have found that the two pyridine rings in the 4,4'-bpy ligands are not co-planar, likely due to the free rotational movement of the two rings along the C-C bond in thermal environment. The resulting effect could likely reduce magnetic interactions between neighboring spin chains due to limiting π -conjugations in the 4,4'-bpy ligand, a desirable property for the Haldane material. Although the co-planar structure of the two rings in the 4,4'-bpy ligand provides a larger π -conjugation, rotations of the two pyridine rings by the thermal energy may have led to the non-co-planar structure. Further discussions of the single-crystal structures are provided in Appendix C.

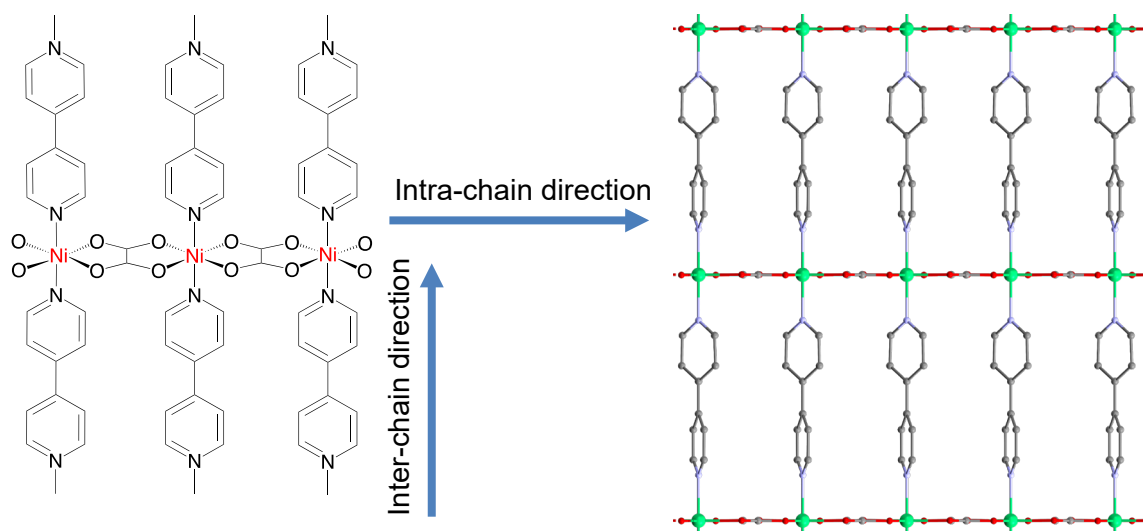


Figure 4.1. (Left) 2-D schematic of **NiBO-*d*₈** showing the bonding around three Ni^{II} ions within the chain. Blue arrows show intra- and inter-chain directions. (Right) Structure of **NiBO-*d*₈** along the crystallographic *a*-axis. Green: Ni; Red: O; Purple: N; Gray: C. Selected bond lengths (Å) and angles (°): Ni-O = 2.0488(10)-2.0533(9), Ni-N = 2.092(5). *cis*-ligand angles: O-Ni-O 82.53(4)-97.47(4), O-Ni-N 89.68(11)-90.32(11); *trans*-ligand angles: O-Ni-O 179.4(2)-179.5(2), N-Ni-N 180.0.

4.3.2. Variable-Temperature Powder Neutron Diffraction (VT-PND)

PND was conducted at 1.7, 10, 20, 100, and 200 K to study the magnetic properties of **NiBO** and any potential structural phase transition at zero-field. As shown in Figure 1.4-Top, in the Haldane phase, there is no magnetic ordering (or unit cell). Thus, only nuclear diffraction from the crystal unit cell is expected, whether the sample is in the paramagnetic and low-temperature Haldane phase. *In other words, no additional PND peaks are expected when the sample is cooled and became topological (i.e., Haldane).* In comparison, for antiferromagnetic NiO with long-range magnetic ordering (Figure 1.4-Bottom),⁵⁵ diffractions from both the magnetic unit cell and the crystal unit cell are observed.⁵⁵

No change was observed in the PND pattern between 1.7 and 200 K for a powder sample of **NiBO**. Figure 4.2-Top shows a comparison between the 1.7 and 100 K diffraction patterns, indicating *no* long-range antiferromagnetic correlations, as extra magnetic Bragg reflections were not observed at low temperature. The absence of such changes in **NiBO** indicates that the nature of its antiferromagnetic interaction is not of a long-range ordered state but is consistent with the Haldane phase in Figure 1.4. Furthermore, the Rietveld refinement of the PND pattern at 1.80 K reveals no long-range ordering or magnetic phase transition in **NiBO** at zero-field (Figure 4.2-Bottom), consistent with results obtained from both the magnetization and specific heat discussed below.

4.3.3. Magnetic Susceptibility (DC)

Temperature dependence of the DC magnetic susceptibility data on a powder sample of **NiBO** at 0.1 T applied external magnetic field is plotted in Figure 4.3. Upon lowering the

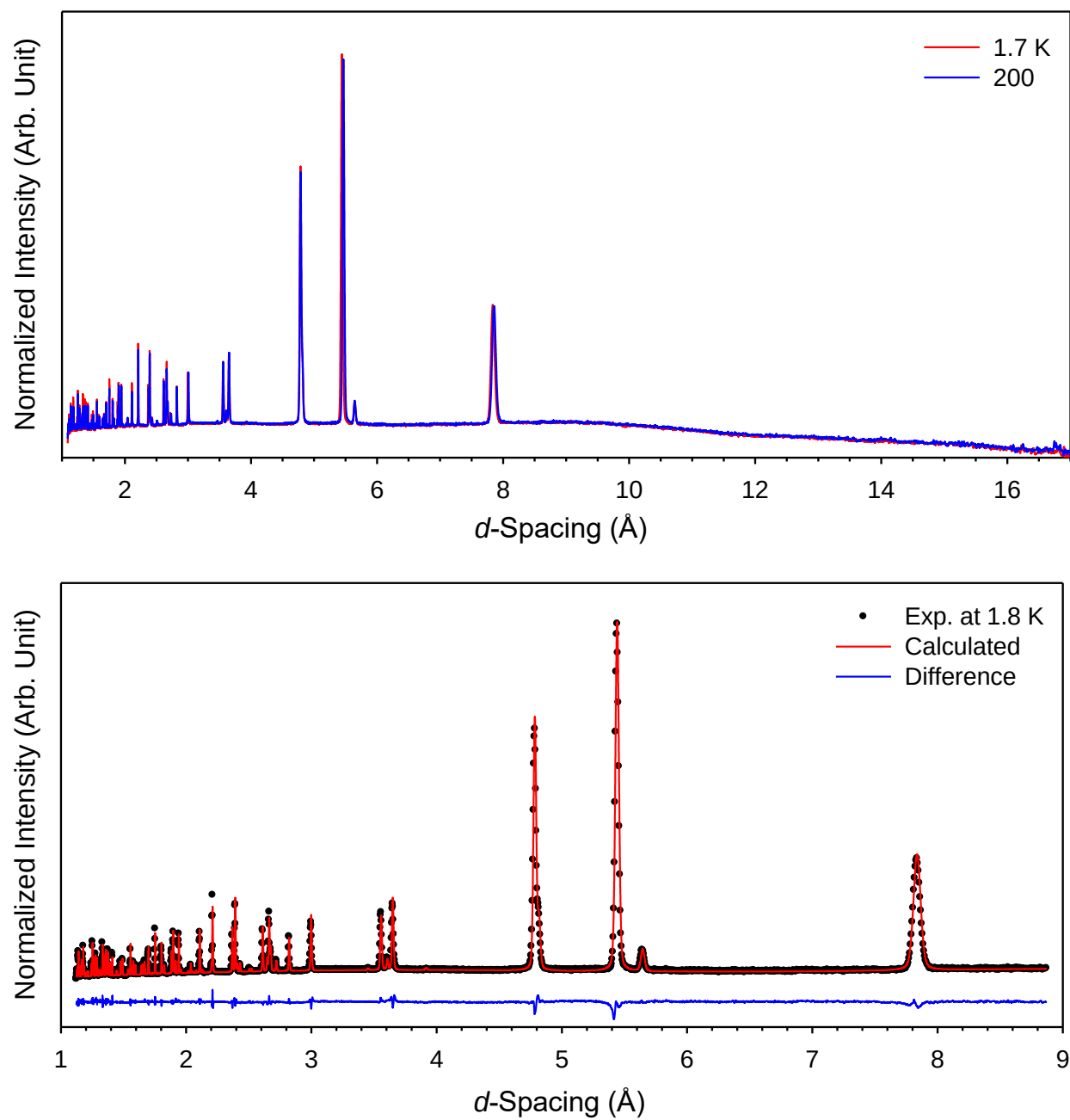


Figure 4.2. (Top) PND pattern of **NiBO** at 1.70 and 100 K. (Bottom) Rietveld refinement of the PND data at 1.8 K.

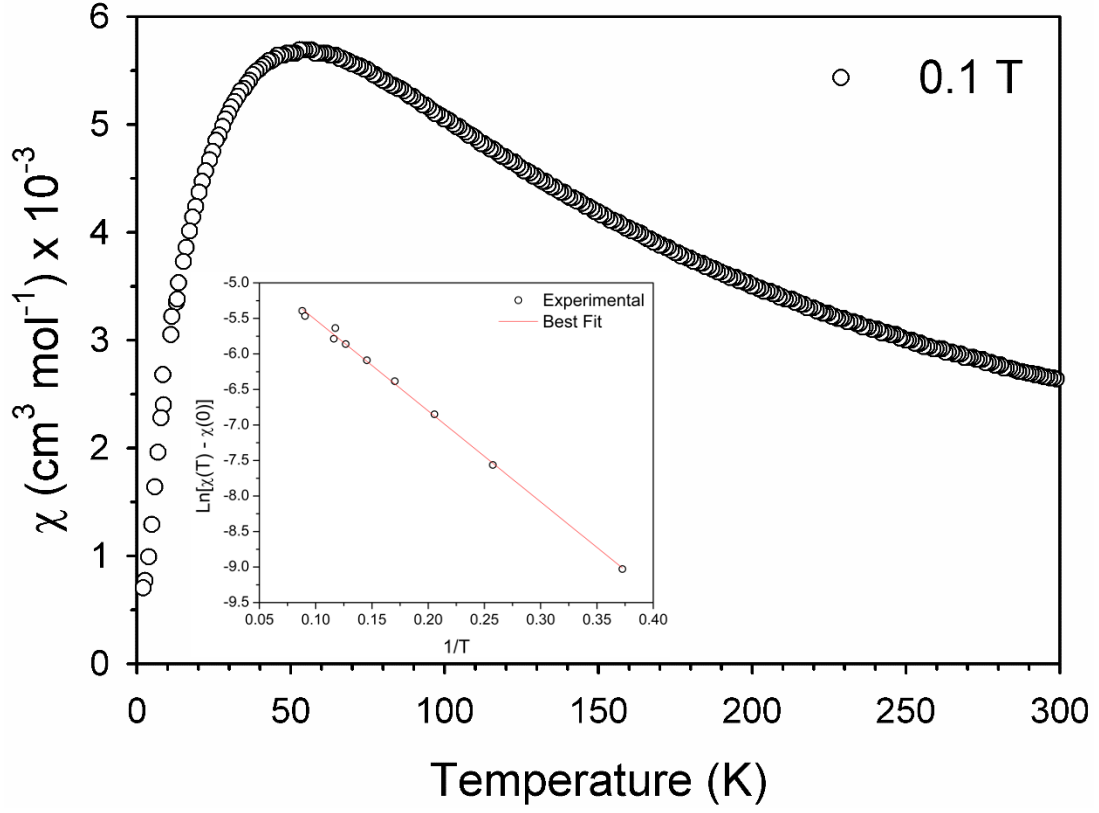


Figure 4.3. Temperature dependence of the DC magnetic susceptibility of **NiBO** at 0.1 T. Inset: magnetic susceptibility plot of $\ln[\chi(T) - \chi(0)]$ vs. $1/T$ for data below 11.5 K.

temperature from 300 K, the magnetic susceptibility (χ) first increases and exhibits a broad maximum around 52 K, below which it decreases down to near zero magnetic susceptibility at 2 K. In the 200-300 K range, the data can be well fitted to the Curie-Weiss law in *Eq. 4.1*.²⁰⁷

$$\chi = C/(T - \theta_{\text{CW}}) \quad (\text{Eq. 4.1})$$

with a Curie-Weiss temperature of $\theta_{\text{CW}} = -75.3(1)$ K, indicating antiferromagnetic interaction in **NiBO**. The Curie constant C can be used to extract the effective magnetic moment μ_{eff} in units of the Bohr magneton, μ_{B} , from *Eq. 4.2*:²⁰⁷

$$\mu_{\text{eff}} = \sqrt{8C} \mu_{\text{B}} \quad (\text{Eq. 4.2})$$

giving $\mu_{\text{eff}} = 2.7(1) \mu_{\text{B}}$, which is comparable to the Ni^{II} spin-only value of $2.8 \mu_{\text{B}}$.²⁰⁸ The suppression of the DC magnetic susceptibility data at low temperatures is indicative of a finite magnetic excitation gap in such spin-1 chain systems.^{64, 65} The spin gap was extracted by fitting DC magnetic susceptibility data in the low-temperature range ($T < 50$ K) to an activated behavior in *Eq. 4.3*,^{44, 64}

$$\chi(T) = \chi(0) + C \exp[-E_{\text{g}}/(k_{\text{B}}T)] \quad (\text{Eq. 4.3})$$

where E_{g} is the spin gap and $\chi(0)$ is an offset.

The inset of Figure 4.3 demonstrates an excellent fit of the experimental data to *Eq. 4.3*.

We obtain a value of $E_g = 7.5(5) \text{ cm}^{-1}$, which is in good agreement with the spin gap as extracted from QMC simulations, as discussed in the next section. In addition, the magnetization measurements show no increase in the magnetic susceptibility down to 2 K, suggesting that there is very little to no paramagnetic contamination of the Ni^{II} ions in **NiBO**.

To probe the stability of the gapped magnetic phase, we measured the DC magnetic susceptibility under various magnetic fields between 2 and 10 K (Figure 4.4). Note that at each temperature, χ initially decreases ($< 9 \text{ T}$) then increases ($> 9 \text{ T}$) with increasing magnetic field. In addition, at higher fields, the magnetic susceptibility starts to increase below 5 K, suggesting a possible magnetic phase transition. Figure C.8 shows the field dependence of the DC magnetization between 2 K and 300 K, revealing the nonlinear behavior below 5 K. The increase of magnetization signifies a possible field-induced phase transition. Background subtraction for the DC magnetic susceptibility data were performed through fittings of the data in the temperature range between 200 and 300 K using $\chi = C/(T - \theta_{\text{CW}}) + \chi_{\text{para}}$, where χ_{para} is the paramagnetic contribution in the background.

4.3.4. *Quantum Monte-Carlo Simulation (QMC)*

QMC simulations were performed in conjunction with the experimental DC magnetization measurements to identify the microscopic Haldane chain parameters for **NiBO**.

We considered an isolated spin-1 chain model, described by the Hamiltonian in Eq. 4.4:

$$H = J \sum_{i=1}^N \mathbf{S}_i \cdot \mathbf{S}_{i+1} + D \sum_{i=1}^N (S_i^z)^2 + E \sum_{i=1}^N [(S_i^x)^2 - (S_i^y)^2] \quad (\text{Eq. 4.4})$$

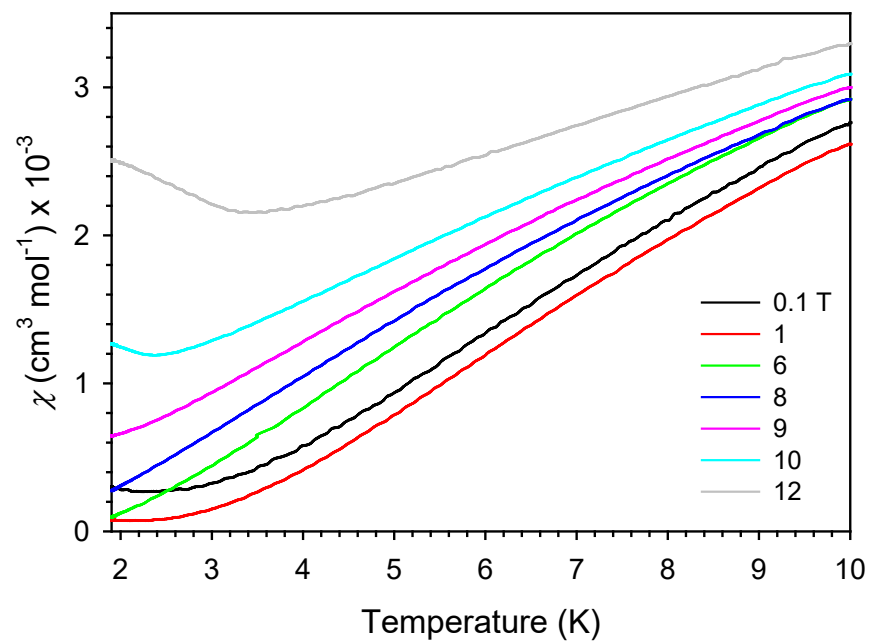


Figure 4.4. Temperature dependence of the DC magnetization of **NiBO** at various magnetic fields.

where J is the nearest-neighbor exchange coupling constant, D is the axial single-ion anisotropy for Ni^{II} , and E is the transverse (or rhombic) anisotropy.

To perform the QMC simulations, we used the stochastic series expansion (SSE) method,^{209, 210} and adjusted the above model parameters to obtain the best fit of the QMC magnetic susceptibility results to the experimental DC magnetic susceptibility data. The spin-1 chain was simulated with 512 sites and periodic boundary conditions to probe bulk properties. We note here the symmetry $E \rightarrow -E$. Therefore, we consider only $E > 0$ for the following. The Heisenberg coupling J , the g -factor, and the paramagnetic offset χ_{para} of the susceptibility can be obtained by comparing the susceptibility data to the QMC simulations of the isotropic chain (with $D = E = 0$) as seen in Figure C.11. Where $J = 29.44 \text{ cm}^{-1}$, $g = 1.87$ and $\chi_{\text{para}} = 10^{-5} \text{ cm}^3/\text{mol}$. The isotropic model agrees well with the experimental data at higher temperature but deviates at lower temperature. Therefore, the isotropic model does not reproduce **NiBO**'s low-energy spectrum. If the anisotropy $D < J$ is small and $|E| < D < J$, the full spectrum may be obtained using the following gaps^{211, 212} (where $\Delta_x < \Delta_y < \Delta_z$):

$$\begin{aligned}\Delta_x &= 0.41J - 0.57D - \kappa_0|E| \\ \Delta_y &= 0.41J - 0.57D + \kappa_0|E| \\ \Delta_z &= 0.41J + 1.41D\end{aligned}\tag{4.5}$$

To compare the QMC results to the experimental DC magnetic susceptibility data of the powder sample, we performed an orientational averaging, which yields the magnetic susceptibility in Eq. 4.5:

$$\chi = \frac{2}{3}\chi_{\perp} + \frac{1}{3}\chi_{\parallel} + \chi_{para} \quad (Eq. 4.5)$$

where $\chi_{\perp}$ ($\chi_{\parallel}$) denotes the QMC response perpendicular (parallel) to the direction of the anisotropy term and χ_{para} is a paramagnetic contribution.

The results obtained from QMC simulations are compared to the experimental results in Figure 4.5 where the D and E terms are included. We fixed J , $g_{\perp} = g_{\parallel}$, and χ_{para} to the values obtained from the isotropic model, where $g_{\parallel}$ ($g_{\perp}$) is the g factor for the magnetic fields applied parallel (perpendicular) to the direction of the anisotropy term [i.e., in a finite magnetic field with flux density B , the Zeeman terms $H_{\parallel} = g_{\parallel}\mu_B B \sum_i S_i^z$, and $H_{\perp} = g_{\perp}\mu_B B \sum_i S_i^x$ are added to the Hamiltonian (H), respectively]. The results show that with the inclusion of an additional D and E term, where $D = 4.99 \text{ cm}^{-1}$ and $|E| = 1.01 \text{ cm}^{-1}$, the simulation fits remarkably well to the experimental DC magnetic susceptibility data across the full temperature range of 1.841 to 300 K. The model parameters obtained from the simulations are listed in Table 4.1. Simulation results for different value of $|E|$ compared to the experimental data is in Figure C.12. From D , the axial anisotropy parameter of one Ni^{II} ion, the effective anisotropy parameter for the chain (i.e., the collective triplet) $D_{\text{eff}} = -1.98D = -9.88 \text{ cm}^{-1}$ is obtained.^{67, 213} It should be pointed out that $D_{\text{eff}} = -1.8D$ has also been used in the literature,^{67, 213} which would make D_{eff} here smaller.

The values of D and E are small enough for **NiBO** to reside within the Haldane phase rather than the large- D phase.^{214, 215} Based on the QMC simulations,²¹⁶ we obtain spin gaps of $\Delta_x = 7.16 \text{ cm}^{-1}$, $\Delta_y = 11.3 \text{ cm}^{-1}$, and $\Delta_z = 19.1 \text{ cm}^{-1}$. In addition, QMC results for the magnetization in finite fields are shown in Figures C.18 and C.19. Similar to the experimental magnetic susceptibility data obtained in finite magnetic fields shown above, the finite-field QMC data

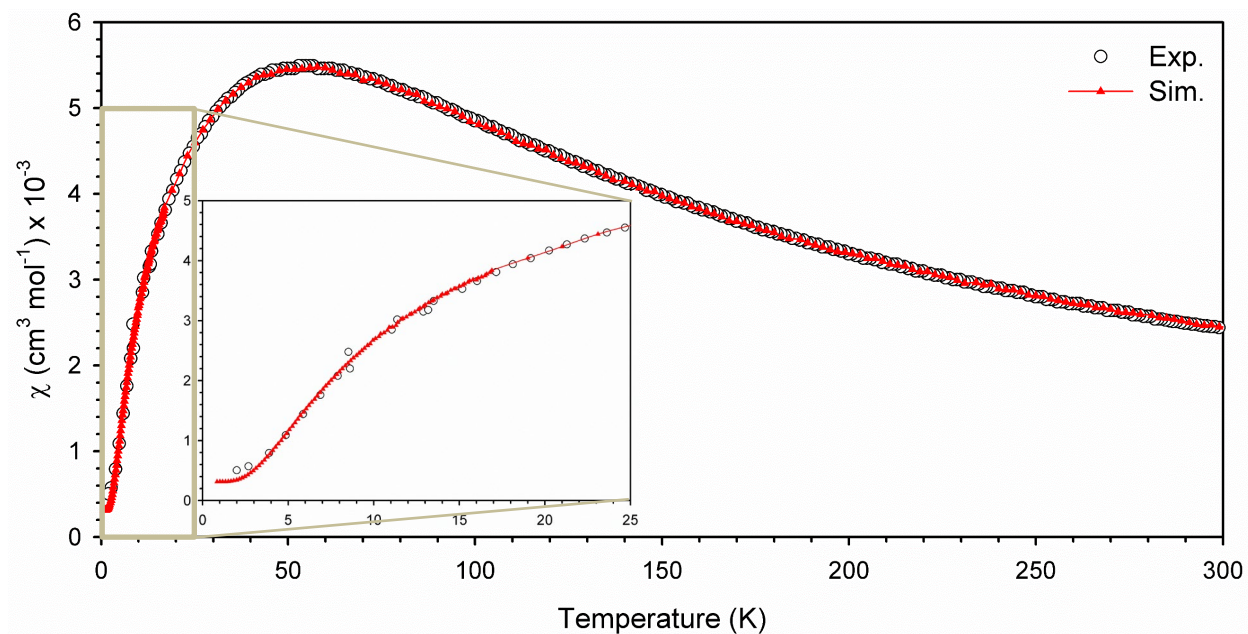


Figure 4.5. Quantum Monte Carlo results for the magnetic susceptibility as a function of temperature. The inset shows the magnetic susceptibility data in the low-temperature range. The QMC data fits well with the experimental data down to the low-temperature regime.

Table 4.1. Magnetic parameters obtained from the QMC simulations

Parameters	Energy (cm ⁻¹)
D	4.99
D_{eff}	−9.88
$ E $	1.01
$ E_{\text{eff}} $	2.07
J	29.44
Δ_x	7.16
Δ_y	11.3
Δ_z	19.1

demonstrate the stability of the Haldane phase for magnetic field strength up to the size of the zero-field spin gap. Additional QMC results and analysis can be found in Appendix C.

4.3.5. *Specific Heat*

Specific-heat measurements on **NiBO** were conducted to complement the magnetic susceptibility data. Figure C.20 shows the specific heat data between 1.8 K and 200 K at zero magnetic field and in a magnetic field of 12 T for a powder sample of **NiBO**. For the magnetic field beyond 9 T, a λ shape peak shows up below 5 K and shifts toward a higher temperature as the magnetic field increases, as shown in Figure 4.6. The peaks indicate a field-induced phase transition occurring in the above field and temperature range. A summary of the critical field and critical temperature of the transition line is shown in Figure C.21. The transition points observed in both the specific heat data and the magnetization data are consistent with each other, indicating that there is a single magnetic phase transition in **NiBO** at a magnetic field beyond 9 T and below 5 K. The change in the critical field and critical temperature of the transition is almost linear, which is similar to previous observations in NENP.²¹⁷

4.3.6. *INS at 0 T*

From the energy diagram of a Haldane spin-1 chain system and the Zeeman effect on the magnetic states in Figure 4.7, two transitions, **A** and **B** are expected at 0 T.

INS was conducted at VISION without a magnet to study the spin gaps in **NiBO-*d*₈**. The measurements were performed at 5, 7.5, 10, 15, and 20 K to determine the spin gaps between the singlet ground state and the triplet excited state. Two different spin gaps are observed at 5 K in

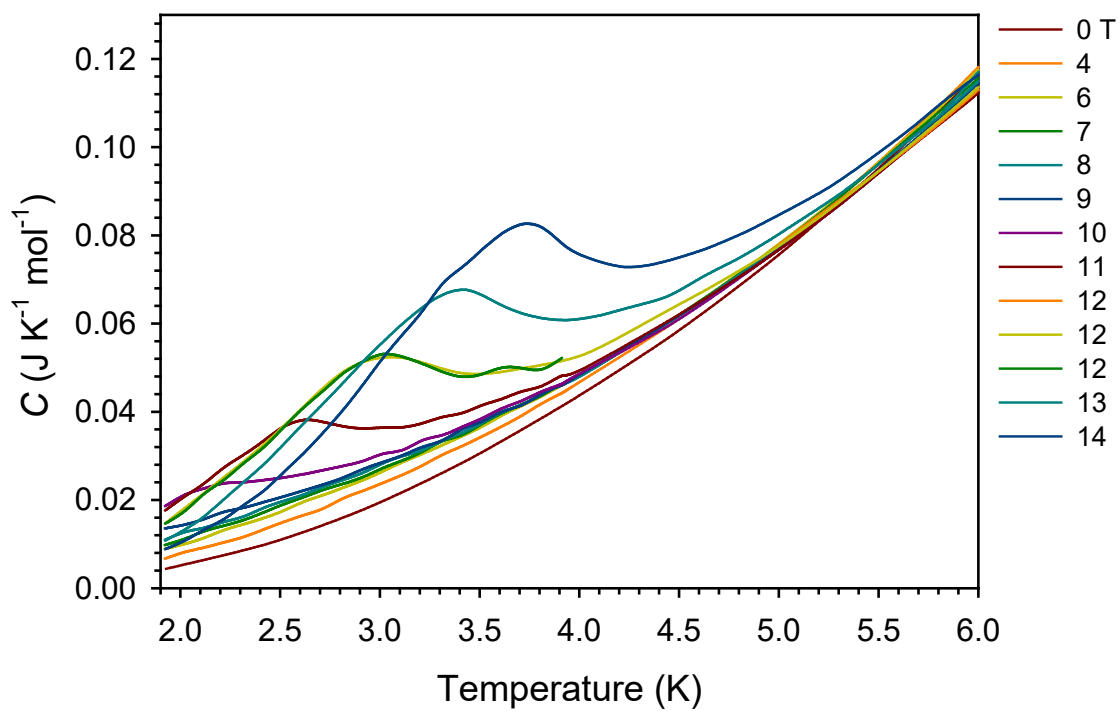


Figure 4.6. Magnetic field-dependent specific heats of **NiBO** from 1.92 to 6.00 K.

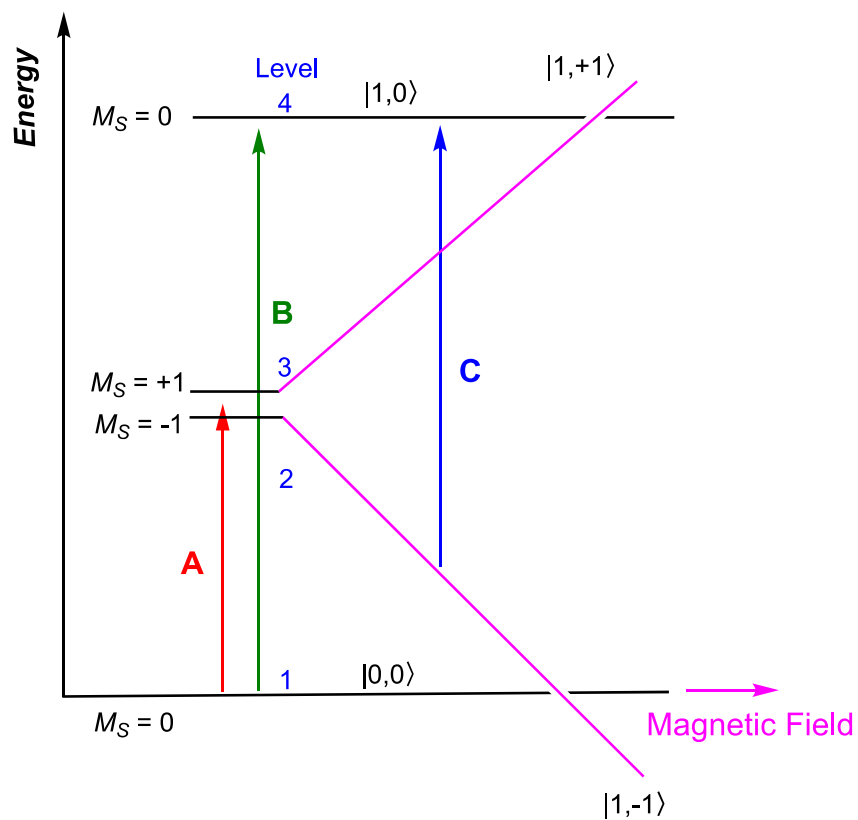


Figure 4.7. Expected transitions **A**, **B** at 0 T and **C** inside magnetic fields for a single-crystal of **NiBO**, with the magnetic field aligned in the z direction.

Figure 4.8. The intensities of the two peaks at ~ 10 and 19 cm^{-1} decreased with increasing temperature. The temperature-dependent of the peaks suggested magnetic origin and not phonon. The peak at $10.0(1) \text{ cm}^{-1}$ is determined to originate from the transition **A**, $|0,0\rangle \rightarrow |1, \pm 1\rangle$. The peak at $19.1(1) \text{ cm}^{-1}$ originates from the transition **B**, $|0,0\rangle \rightarrow |1, 0\rangle$. The value of the experimental $D_{\text{eff}}(\text{INS})$ and the single-ion anisotropy $D(\text{INS})$ can be determined using the magnetic coupling constant (J) from QMC (29.44 cm^{-1}) and peak **B** [$\Delta_z = 19.1(1) \text{ cm}^{-1}$] from INS in *Eqs.* 4.6 and 4.7:^{67, 74}

$$D(\text{INS}) = \frac{\Delta_z^{-0.41J}}{1.41} = 5.0(1) \text{ cm}^{-1} \quad (\text{Eq. 4.6})$$

$$D_{\text{eff}}(\text{INS}) = -1.98D(\text{INS}) = -9.9(1) \text{ cm}^{-1} \quad (\text{Eq. 4.7})$$

We are unable to observed the splitting of peak **A** (Δ_{xy}) due to the limited resolution of the instrument. With higher resolution, peak **A** should split into Δ_x and Δ_y indicating an existance of the transverse or rhombic anisotropy (E) in **NiBO-*d*8**. The results obtained from INS agree well with QMC and magnetic susceptibility results.

4.3.7. HFESR

HFESR measurements were performed at 4.5 K on a powder sample of **NiBO** to probe the electronic spin transition within the triplet excited state. The results show only a single low-intensity and broad resonance in Figure 4.9 at $\sim 6.8 \text{ T}$ and 511 GHz . The resonance moves to lower magnetic field upon decreasing the frequency, as shown in Figure 4.10. We interpret the observed resonance as originating from the transition $|1, -1\rangle \rightarrow |1, 0\rangle$. Extrapolation to 0 T

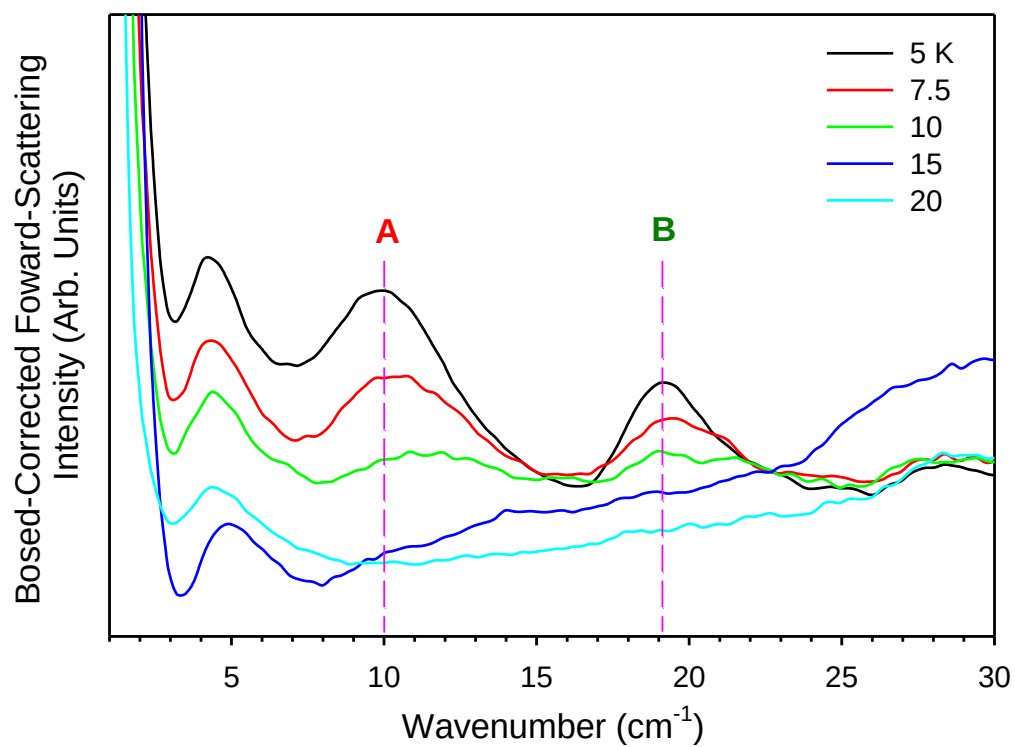


Figure 4.8. Temperature-dependent INS data for NiBO-d_8 . The pink dashed lines are at the peaks from excitations **A** and **B** in Figure 4.7 corresponding to the two spin gaps between levels 1 and 2/3 as well as between Levels 1 and 4.

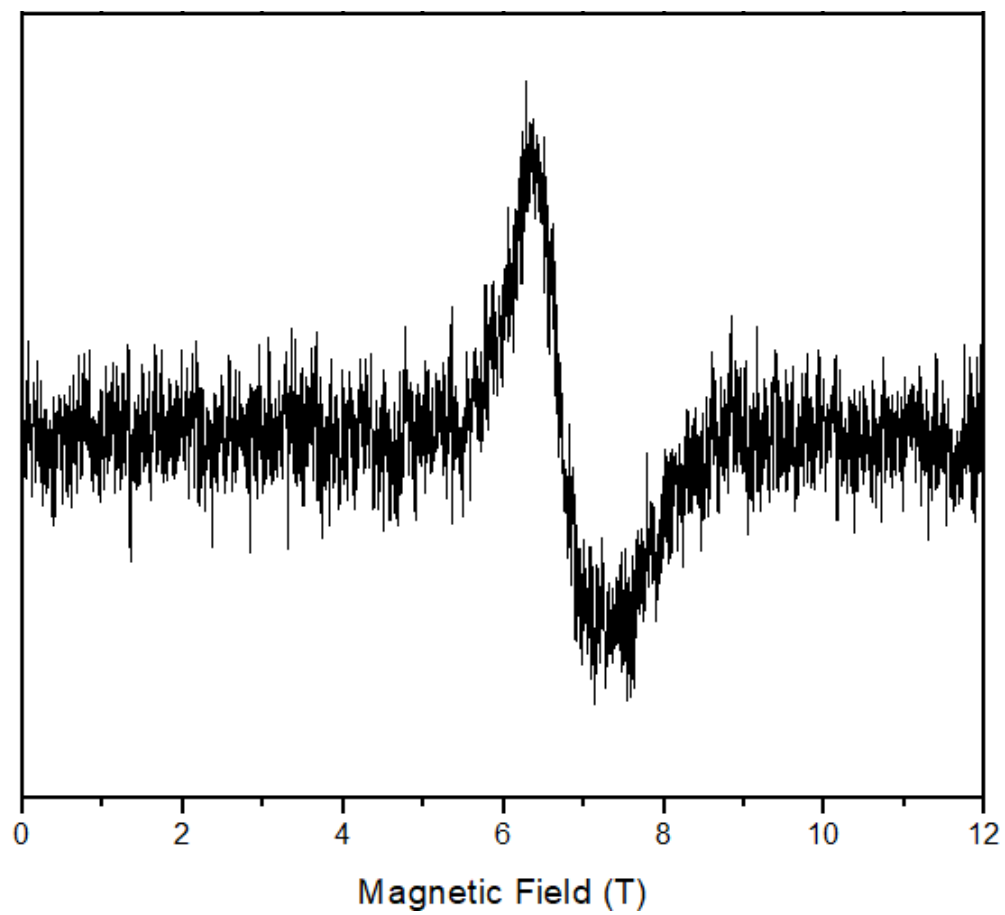


Figure 4.9. HFESR spectrum of **NiBO** at 4.5 K and 511 GHz.

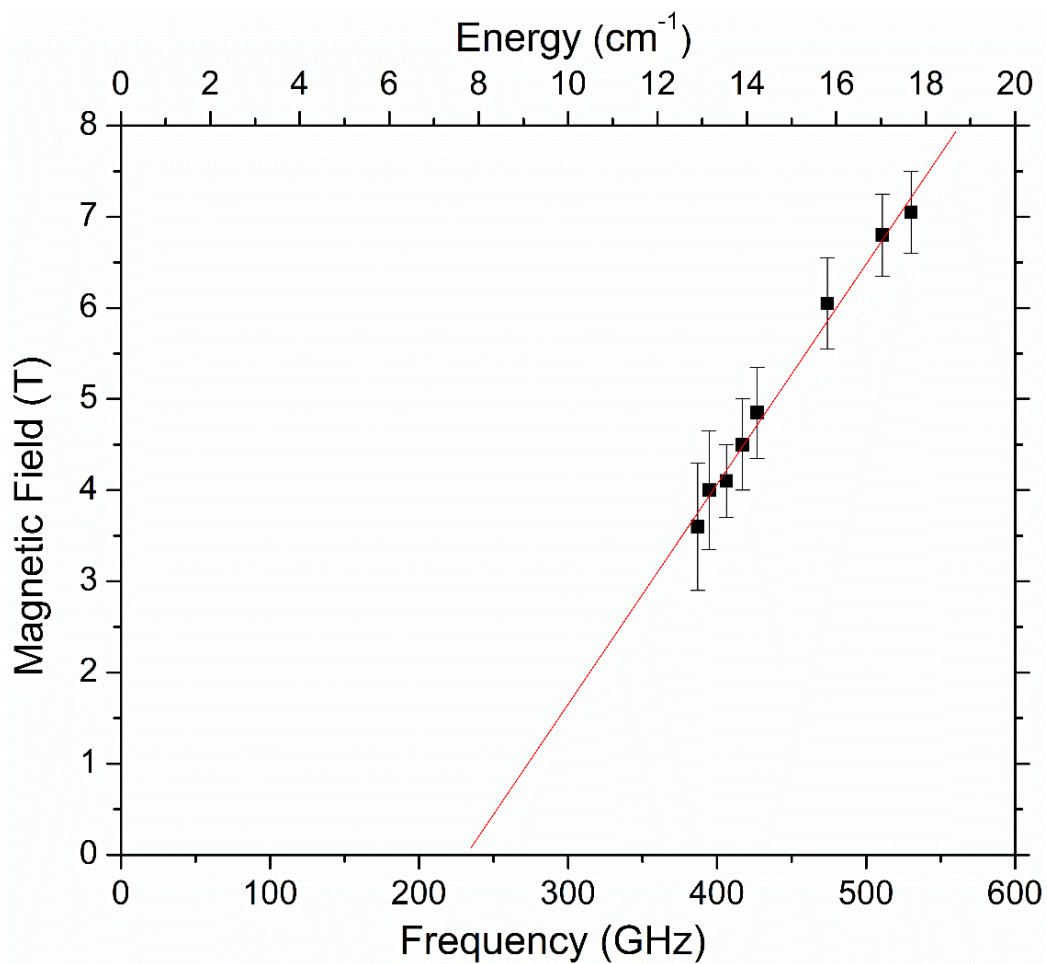


Figure 4.10. Frequency dependence of the resonance observed by HFESR. The red line is a linear fit to the data.

gives $D_{\text{eff}}(\text{HFESR}) = 7.8(2) \text{ cm}^{-1}$. However, this value underestimates the actual zero-field gap, as discussed in Appendix C. Instead, the results obtained based on the QMC simulations compare well with the experimental data and support the observed transition $|1, -1\rangle \rightarrow |1, 0\rangle$ in the powder-averaged spectrum of the HFESR, as shown in Figure C.17. Furthermore, the intensity of the resonance is weak, probably resulting from the thermal depopulation of the triplet state at 4.5 K. The even lower population of the $|1, +1\rangle$ state may furthermore explain the absence of the resonance transition $|1, +1\rangle \rightarrow |1, 0\rangle$ in the spectrum. The result is consistent with observations in the ESR spectra of $\text{PbNi}_2\text{V}_2\text{O}_8$.²¹⁸ No resonances are observed for the formally forbidden transitions from the singlet to the triplet state, based on the selection rules. The end-chain resonance is not discernable in the spectrum due to **NiBO** having little to no impurities in the MOF structure as well as negligible inter-chain coupling. According to Čižmár *et al.*, the intensity of the end-chain resonance can be attributed to the spin-1/2 fractional end-chain effect or the presence of the inter-chain coupling.⁷⁴ Impurities can cause fragmentation of the spin-1 chains leading to the presence of more end-chain spin-1/2. As determined in the magnetization measurements of **NiBO**, the magnetic susceptibility does not increase at low temperatures, which is the characteristic of a relatively pure system.

4.3.8. Phonon Spectrum from INS and Comparison with the DFT-Calculated INS Spectrum

The phonons described in these studies are of both inter- and intra-molecular vibrations. INS is based on the neutron kinetic energy transfer, which means the technique does not follow any selection rules, unlike optical spectroscopies such as HFESR. Therefore, INS can detect all the phonon excitations in the solid molecule.²¹⁹ Figure 4.11 shows the experimental INS

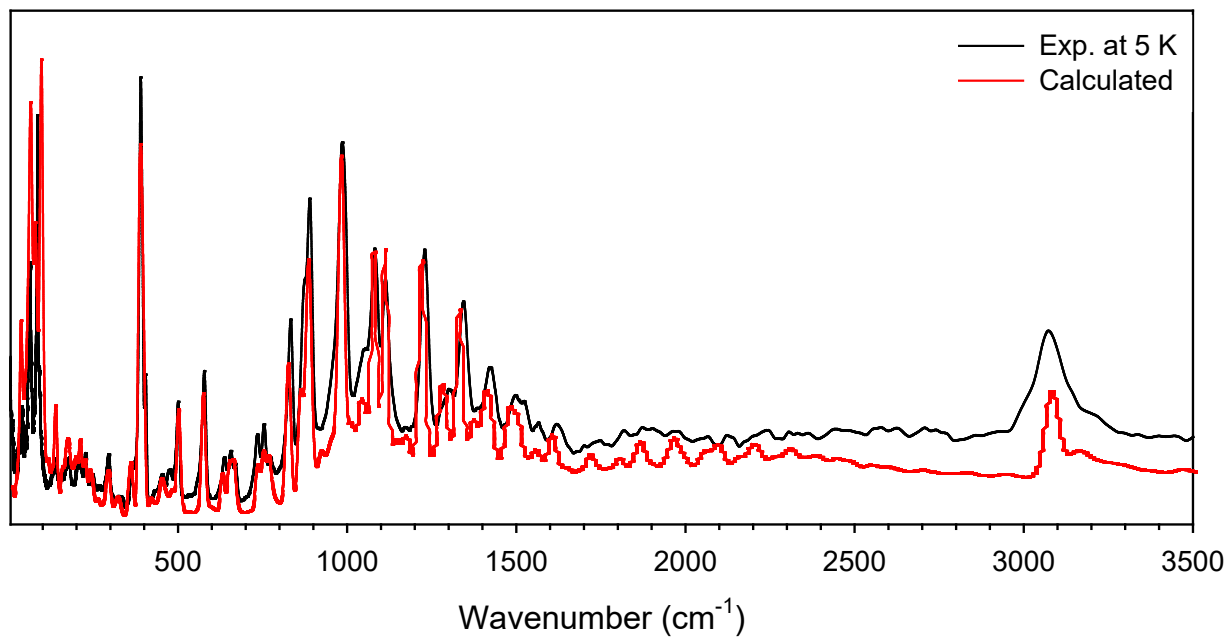


Figure 4.11. The calculated phonon spectrum compares to the experimental INS spectrum of **NiBO** at 5 K.

spectrum of **NiBO** at 5 K and the calculated phonon spectrum from DFT calculations. Most of the major phonon features are located below $1,700\text{ cm}^{-1}$, while one distinct major feature is at $3,100\text{ cm}^{-1}$. The calculated phonon spectrum fits well to the experimental phonon spectrum, especially at the higher energy region. Further discussion of the phonon features, phonon symmetries, and spin densities are provided in Appendix C.

4.4. Experimental Methods

4.4.1. *Single-Crystal X-Ray Diffraction (SCXRD)*

Single-crystal X-ray diffraction data were collected using a Bruker D8 Venture at 100 K with Mo $K\alpha$ radiation. Data were collected and integrated using APEX 3 programs, reduced using Bruker SAINT program, and corrected for absorption using the SADABS multi-scan program. The structure was solved using SHELXT and refined with SHELXL-2015. There was no distinction made for the D isotope in **NiBO-d₈**.²²⁰

4.4.2. *Magnetic Susceptibility (DC) and Specific Heat*

DC magnetic susceptibility measurements at 0.1 T were conducted at the Center for Nanophase Materials Sciences (CNMS) at Oak Ridge National Laboratory (ORNL) using the superconducting quantum interference device (SQUID) magnetometer by *Quantum Design*. A powder sample of **NiBO** with a total mass of 119.2 mg was used. Variable-temperature and variable-field DC magnetic susceptibility were measured using the Physical Property Measurement System (PPMS) Dynacool by *Quantum Design*. The magnetization measurement was measured using Vibrating Sample Magnetometer (VSM) option. The powder with a total

mass of 11.7 mg was used for the temperature-dependent magnetization under a magnetic field of 0.1 T from 2 K to 300 K. The magnetization was performed between 2 K and 300 K up to 14 T. Temperature-dependent of specific heat was measured by relaxation technique using the PPMS. A pressed pellet with a total mass of 6.5 mg was used for specific heat measurement between 2 K to 200 K from 0 T to 14 T.

4.4.3. HFESR

HFESR experiments were performed at the National High Magnetic Field Laboratory (NHMFL) using a homemade ESR spectrometer with a 17 T superconducting magnet and a powder sample of **NiBO** (0.116 g).¹⁴⁰ A low microwave source (8-20 GHz) was used in conjunction with an array of multipliers and amplifiers (Virginia Diodes, Charlottesville, VA, USA) to make higher frequency harmonics.

4.4.4. Powder Neutron Diffraction (PND)

Neutron diffraction data were collected at the POWGEN diffractometer at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL) between 1.8 K and 200 K using an Orange Cryostat. A powder sample of **NiBO** (~0.5 g) was loaded into a 6 mm-diameter, cylindrical vanadium sample can, and the data were collected for approximately 2 h in the high-resolution mode, using a center wavelength of 2.665 Å covering the d spacing from 1 Å to 15.0 Å. A background correction for the measured data was performed using an empty vanadium sample can measurement. The peak profile was described using a convolution of a Gaussian peak shape and a GSAS back-to-back exponential peak shape accounting for the

asymmetry. The peak profile was obtained by refining data from Si (SRM 640d, NIST). All refinement was carried out using the TOPAS 6 software of the academic version.²²¹

4.4.5. *INS*

VT INS data were collected by placing a powder sample of **NiBO** (~0.45 g) or **NiBO-*d*₈** (~1.0 g) into a vanadium can specifically made for the neutron instrument. The sample vanadium can was placed into the neutron beamline at the Vibrational Spectrometer (VISION) at SNS, ORNL. There are two detector banks for the forward (low $|Q|$) and the back (high $|Q|$) scattering of neutrons. The effect of phonon population was accounted for through normalization of the INS intensity at energy transfer ω with $\coth\left(\frac{\hbar\omega}{2k_B T}\right)$.¹⁴²

4.4.6. *DFT Calculations of Phonons and Spin Density*

Spin-polarized density functional theory (DFT) calculations of **NiBO** were performed at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL) using the Vienna Ab initio Simulation Package (VASP).¹⁵⁴ The calculation used Projector Augmented Wave (PAW) method^{122, 123} to describe the effects of core electrons, and Perdew-Burke-Ernzerhof (PBE)¹²⁶ implementation of the Generalized Gradient Approximation (GGA) for the exchange-correlation functional. The energy cutoff was 800 eV for the plane-wave basis of the valence electrons. The lattice parameters and atomic coordinates from the CIF file, generated by the single-crystal X-ray diffraction measurement of **NiBO-*d*₈** at 100 K, were used as the initial structure. The D atoms were replaced by H atoms in the calculations. The electronic structure was calculated on a $3 \times 3 \times 7$ Γ -centered mesh. The total energy tolerance for electronic energy

minimization was 10^{-8} eV, and for structure optimization, it was 10^{-7} eV. The maximum interatomic force after relaxation was below 0.001 eV/Å. The optB86b-vdW functional¹⁵⁵ for dispersion corrections was applied, and a Hubbard U term of 6.2 eV¹⁵⁶ was applied to account for the localized 3d orbitals of Ni. A $1 \times 1 \times 3$ supercell was created, for which the electronic structure was calculated on a $3 \times 3 \times 2$ Γ -centered mesh. The interatomic force constants were calculated on the supercell by VASP, and the vibrational eigenfrequencies and modes were then calculated using Phonopy.¹⁵⁷ The OCLIMAX software¹⁵⁸ was used to convert the DFT-calculated phonon results to the simulated INS spectra.

4.5. Conclusions

Many previous studies have focused on studying 1-D Haldane chains in 3-D structures, but rarely a 2-D material. Here, we have provided a thorough characterization of the magnetism in the 2-D MOF **NiBO**, which consists of stacked 2-D planes of parallel spin-1 chains, formed by Ni^{II} ions. From our combined analyses, using a wide range of experimental probes, including variable-temperature powder neutron diffraction (VT-PND), DC magnetic susceptibility, specific-heat and HFESR measurements, we identify **NiBO** as a clean realization of the Haldane spin-1 chain with weak interchain coupling, due to the stacked planar crystal structure and a twisting in the bipyridine ligands that stabilize the planar arrangement. This sets aside **NiBO** from various previously explored Haldane spin-1 chain compounds, which are mostly imbedded in a 3-D crystal structure. VT-PND confirms that **NiBO** does not exhibit long-range antiferromagnetic order, supporting that **NiBO** is a Haldane spin-1 chain material with short-range spin correlations and a disordered ground state. Furthermore, specific-heat and DC

magnetic susceptibility experiments indicate a phase transition induced by the magnetic fields beyond the gap-closing field of 9 T and at temperature below 5 K. We have conducted the first in-depth analysis of a 2-D MOF with decoupled spin-1 chain exhibiting Haldane physics, comparing remarkably well to a microscopic spin-1 chain model using unbiased QMC simulations. Parameters from QMC simulation of the microscopic spin model for **NiBO** are $J = 29.44 \text{ cm}^{-1}$, $D = 4.99 \text{ cm}^{-1}$, $D_{\text{eff}} = -9.88 \text{ cm}^{-1}$, $|E| = 1.01 \text{ cm}^{-1}$, $E_{\text{eff}} = 2.07 \text{ cm}^{-1}$, $\Delta_x = 7.16 \text{ cm}^{-1}$, $\Delta_y = 11.3 \text{ cm}^{-1}$, and $\Delta_z = 19.1 \text{ cm}^{-1}$. INS measurements provide the energy gaps between the singlet ground state and two levels of the excited triplet state in Figure 4.8 to be $10.0(1) \text{ cm}^{-1}$ and $19.1(1) \text{ cm}^{-1}$, respectively. In addition, INS studies give $D_{\text{eff}}(\text{INS}) = -9.9(1) \text{ cm}^{-1}$; $D(\text{INS}) = 5.0(1) \text{ cm}^{-1}$. HFESR probe the effective anisotropy of **NiBO** with a lower bound for $D_{\text{eff}}(\text{HFESR}) = 7.8(2) \text{ cm}^{-1}$. MOFs are unique among Haldane spin-1 chain materials by providing the possibility for exfoliation into 2-D nanosheets with unique magnetic properties. Our works open interesting new directions for future research on low-dimensional quantum magnetism in metal-organic frameworks.

Chapter 5

Advance Magnetic Resonance Studies of Tetraphenylporphyrinatoiron(III)

Halides

This chapter is based on the following paper:

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Author contributions:

P. Tin and M. Ozerov performed the FIRMS experiments. They analyzed and interpreted the FIRMS data. J. Krzystek, A.N. Ponomarev, S.A. Zvyagin, and J. Wosnitza performed the HFEPR experiments, analyzed, and interpreted the data. J. Telser conducted ligand-field analyses of the complexes and origins of the ZFS. S.E. Stavretis synthesized the samples of **Fe(TPP)F**, **Fe(TPP)Br**, and **Fe(TPP)I** for experiments. C.-C. Chen, P. P.-Y. Chen prepared the sample of **Fe(TPP)Cl**. Z.-L. Xue initiated the project, analyzed, and interpreted the data. All authors contributed to the writing of the manuscript.

5.1. Abstract

High-field/-frequency EPR (HFEPR) studies of **Fe(TPP)X** (**X** = **F**, **Cl**, **Br**; **I**, TPP²⁻ = *meso*-tetraphenylporphyrinate) and far-IR magno-spectroscopic (FIRMS) studies of **Fe(TPP)Br** and **Fe(TPP)I** have been conducted to probe magnetic intra- and inter-Kramers doublet transitions in these $S = 5/2$ metalloporphyrin complexes, yielding zero-field splitting (ZFS) and g parameters for the complexes: **Fe(TPP)F**, $D = +4.67(1) \text{ cm}^{-1}$, $E = 0.00(1) \text{ cm}^{-1}$, $g_{\perp} = 1.97(1)$, $g_{\parallel} = 2.000(5)$ by HFEPR; **Fe(TPP)Cl**, $D = +6.458(2) \text{ cm}^{-1}$, $E = +0.015(5) \text{ cm}^{-1}$, $E/D = 0.002$, $g_{\perp} =$

2.004(3), $g_{\parallel} = 2.02(1)$ by HFEPR; **Fe(TPP)Br**, $D = +9.03(5) \text{ cm}^{-1}$, $E = +0.047(5) \text{ cm}^{-1}$, $E/D = 0.005$, $g_{\text{iso}} = 1.99(1)$ by HFEPR and $D = 9.05 \text{ cm}^{-1}$, $g_{\text{iso}} = 2.0$ by FIRMS; **Fe(TPP)I**, $D = +13.84 \text{ cm}^{-1}$, $E = +0.07 \text{ cm}^{-1}$, $E/D = 0.005$, $g_{\text{iso}} = 2.0$ by HFEPR and $D = 13.95 \text{ cm}^{-1}$, $g_{\text{iso}} = 2.0$ by FIRMS (the sign of E was in each case arbitrarily assigned as that of D). These results demonstrate the complementary nature of field- and frequency-domain magnetic resonance experiments in extracting with high accuracy and precision spin-Hamiltonian parameters of metal complexes with $S > 1/2$. The spin-Hamiltonian parameters obtained from these experiments have been compared with those obtained from other physical methods such as magnetic susceptibility, magnetic Mössbauer spectroscopy, inelastic neutron scattering (INS), and variable-temperature and -field magnetic circular dichroism (VT-VH MCD) experiments. INS, Mössbauer and MCD give good agreement with the results of HFEPR/FIRMS; the others not as much. The electronic structure of **Fe(TPP)X** ($X = \text{F, Cl, Br, I}$) was studied earlier by multi-reference *ab initio* methods to explore the origin of the large and positive D -values, reproducing the trends of D from the experiments. In the current work, a simpler model based on ligand field theory (LFT) is used to explain qualitatively the trend of increasing ZFS from $X = \text{F}$ to Cl to Br and to I as the axial ligand. Tetragonally elongated high-spin d^5 systems such as **Fe(TPP)X** exhibit $D > 0$, but X plays a key role. Spin delocalization onto X means that there is a spin-orbit coupling (SOC) contribution to D from $X^{\bullet}$, as opposed to none from closed-shell X^{-} . Over the range $X = \text{F, Cl, Br, I}$, $X^{\bullet}$ character increases as does the intrinsic SOC of $X^{\bullet}$ so that D increases correspondingly over this range. To offer a brief historical background: Of the current series, **Fe(TPP)Cl** has been by far the most investigated of the four compounds presented here by both magnetic resonance and non-resonance methods. **Fe(TPP)Br** has been the next-often

researched member of the group, while **Fe(TPP)F** and **Fe(TPP)I** have been only covered by some of us in previous work.²⁸

5.2. Introduction

Iron porphyrin complexes, especially those penta-coordinated, have been actively studied through the years,^{81, 163, 222-227} the interest being driven to a large degree by a desire to understand how heme proteins function.²²²⁻²²⁶ In hemoglobin and myoglobin, penta-coordinated iron porphyrin(s) (hemin) use an open axial position to bind to O₂, thus transporting or storing oxygen in vertebrates. The porphyrins in metalloproteins typically have low symmetry due to their biosynthetically derived substituents, complicating their studies.²²⁸ In contrast, synthetic porphyrins such as tetraphenylporphyrin are strictly four-fold symmetric and their iron complexes have been widely used as symmetrically substituted analogs and model compounds for myoglobin and hemoglobin.²²²⁻²²⁶ These include five-coordinate tetraphenylporphyrinatoiron complexes such as **Fe^{III}(TPP)X** (X = F, Cl, Br, I; TPP²⁻ = *meso*-tetraphenylporphyrinate; Figure 5.1).^{28, 114, 163, 229-245}

Since the four equatorial nitrogen atoms in TPP²⁻ and the axial halide together exert a weak ligand field on the iron ion (i.e., the square pyramidal geometry being an extreme case of a tetragonally distorted octahedron), a key electronic feature of **Fe^{III}(TPP)X** compounds is that they are high-spin: the five 3*d* electrons are all unpaired, yielding an *S* = 5/2 spin state. Their magnetic properties have been a subject of many studies.^{28, 114, 163, 229-240, 242, 244} For example, the penta-coordinated hemes are also high-spin, and the unique binding between hemoglobin and O₂ (with two unpaired electrons itself) is believed to be driven in part by the magnetic interactions

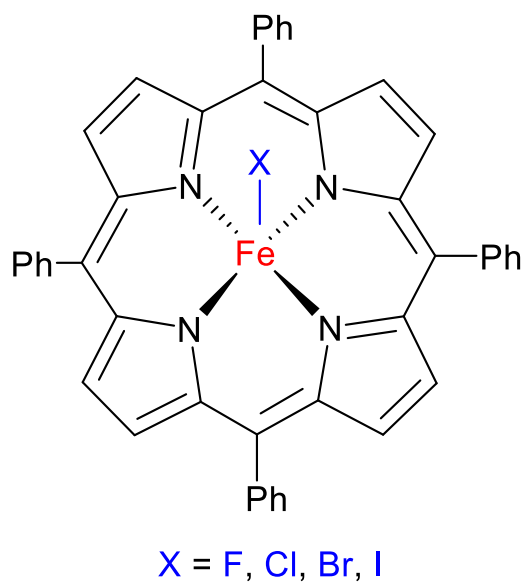


Figure 5.1. Structures of Fe(TPP)X .

between the two.²⁴⁶ As with any high-spin ($S \geq 1$) system in sufficiently low symmetry, the Fe^{III} ion in complexes such as $\text{Fe}^{\text{III}}(\text{TPP})\text{X}$ undergoes the zero-field splitting (ZFS), where the interaction of the excited electronic states with the ground state mediated by the second-order spin-orbit coupling (SOC) leads to a splitting of otherwise degenerate m_S states (Figure 5.2).⁶ (To a usually lesser degree, a direct interaction between the unpaired spins themselves, spin-spin coupling (SSC), also contributes to the ZFS.)

The ZFS provides a valuable window into the electronic structure of high-spin states, notably of transition-metal ions, but another of its aspects is as important, or perhaps even more important: the phenomenon of single-molecule magnetism. It is the ZFS that is responsible for the single-molecular magnet (SMM) behavior^{247, 248} of such archetypal clusters as Mn_{12} ^{4, 249-253} and Fe_8 .²⁵⁴⁻²⁵⁶ The magnetic properties of the clusters are a result of single-ion ZFS of Mn^{III} and Mn^{IV} ions in the former^{249, 257} and Fe^{III} in the latter.²⁵⁸ More recently, SMM properties were found in mononuclear complexes of, among others, $3d$ metal complexes,^{1, 100, 110, 247, 259-280} including iron,^{110, 260-269} that are often called single-ion magnets (SIMs). Of specific relevance, square pyramidal Fe^{III} complexes with intermediate spin ($S = 3/2$; as opposed to high-spin, $S = 5/2$) ground states have recently been shown to exhibit SIM properties.²⁸¹

Whichever of the above is the dominating motivation for studying iron porphyrins, accurately and precisely determining their ZFS is thus of utmost importance. A general review has been published on the subject of how best to determine ZFS in metal complexes in general.¹² The series of $\text{Fe}(\text{TPP})\text{X}$ complexes presented in this work, however, offers a specific case which (1) allows one to compare diverse experimental techniques, including relatively new and advanced magnetic resonance methods such as HFEPR and FIRMS, in terms of accuracy

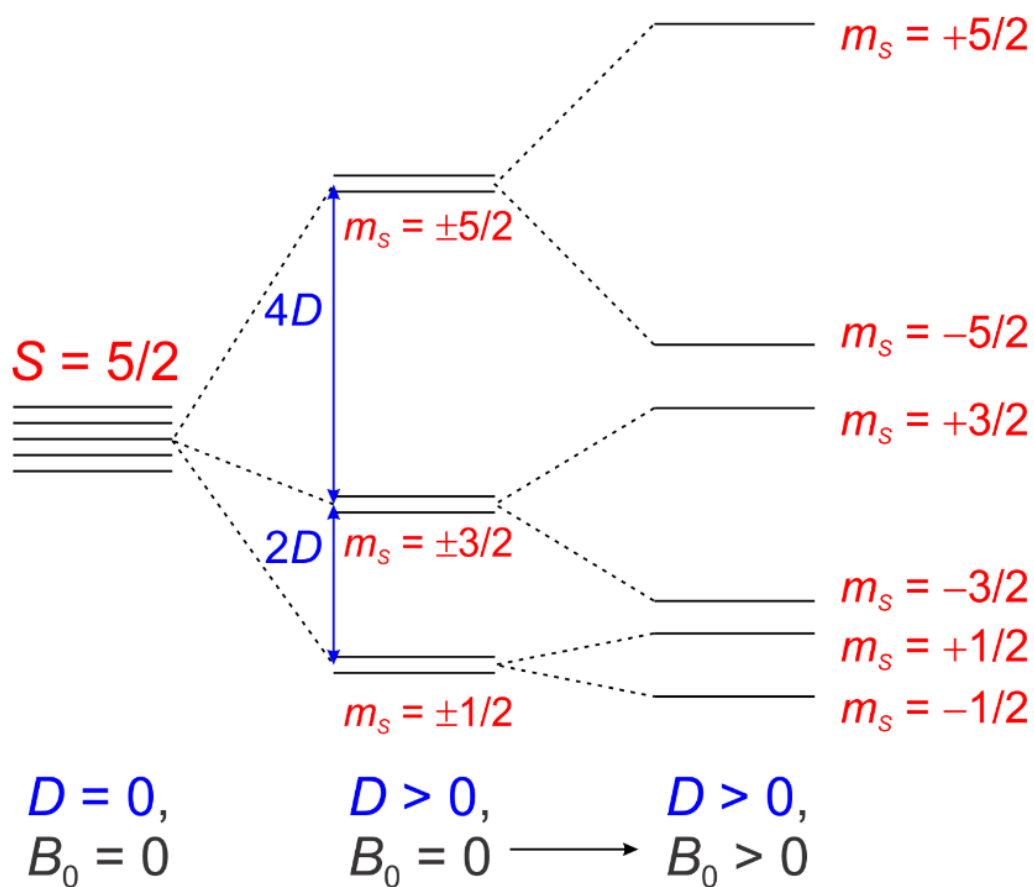


Figure 5.2. The effect of spin-Hamiltonian on an $S = 5/2$ wavefunction. In high symmetry (higher than two-fold), as provided by the porphyrin ligand, $E = 0$. An applied external magnetic field B_0 leads to additional splittings of the M_S levels due to the Zeeman effect.

and precision of measurement and (2) from a scientific viewpoint, allows one to methodically track the influence of the axial halide ligand on the resulting ZFS of the given complex. To offer a brief historical background: Of the current series, **Fe(TPP)Cl** has been by far the most investigated of the four compounds presented here by both magnetic resonance and non-resonance methods (Table 5.1 and references therein). **Fe(TPP)Br** has been the next-often researched member of the group, while **Fe(TPP)F** and **Fe(TPP)I** have been only covered recently.²⁸ This past research will be discussed in more detail in the Discussion section below.

5.3. Results

5.3.1. HFEPR

Fe(TPP)F produced a rich set of HFEPR spectra at low temperatures, and any frequency in the ~100–430 GHz range (Figure 5.3-Top left; see also Figure D.1, Appendix D; a multifrequency collection of experimental spectra is shown in Figure D.2). The spectra could be adequately simulated using spin-Hamiltonian parameters as in Figure 5.3 caption and assuming a powder distribution of crystallites in the sample. The parameters, particularly the *g*-values, however, tended to be slightly frequency-dependent, as is usually the case in multi-frequency experiments. In order to obtain a frequency-independent set of parameters, a 2-D energy (or frequency) vs. magnetic field map of turning points was constructed, and the parameters fitted by a least-square method to the complete data set according to the tunable-frequency methodology (Figure 5.4-Top left).²⁸² The resulting spin-Hamiltonian parameters are found in Table 5.1. Most importantly, for **Fe(TPP)F**, the *D* value is +4.67(1) cm⁻¹, while there is no detectable rhombicity of the ZFS tensor (*E* = 0); thus the complex symmetry remains perfectly fourfold.

Table 5.1. Spin-Hamiltonian parameters of **Fe^{III}(TPP)X** determined by different methods

Axial ligand	Method	D (cm ⁻¹)	E (cm ⁻¹)	$g_{\perp}$	$g_{\parallel}$	Ref.
X = F	HFEPR	+4.67(1)	0.00(1)	1.97(1)	2.000(5)	This work
	INS	+4.49(9)	0			28
X = Cl	HFEPR	+6.458(2)	+0.015(5) $E/D = 0.002$	2.004(3)	2.02(1)	This work
	INS	+6.33(8)	0			114
	FD-FT THz-EPR	6.465	0.02 $E/D = 0.003$	2.0	1.95	242
	Far-IR	6.5				163
	VTVH MCD	6.9				239
	Magnetic Mössbauer	7(1)				234
	X-band EPR	3.2				232
	NMR	11.3				230
	Magnetic susceptibility	6.0(1)-11.9				229, 233, 236, 237
X = Br	HFEPR	+9.01(5)	+0.047(5) $E/D = 0.005$	1.99(1)	1.99(1)	This work
	FIRMS	+9.05		2.0	2.0	This work
	INS	+8.8(2)	0.1(2)			28
	Far-IR	9.15				163
	Magnetic susceptibility	4.9-12.5(5)				229, 235, 238
X = I	HFEPR	+13.84 ^a	+0.07 $E/D = 0.005$	2.00	2.00	This work
	FIRMS	+13.95		2.0	2.0	This work
	INS	+13.4(6)	0.3(6)			28
	Magnetic susceptibility	13.5(5)				238

^a The number of data points from the HFEPR spectra of **Fe(TPP)I** was not sufficient to do a proper least-square fit to yield an error estimate of the D and E values.

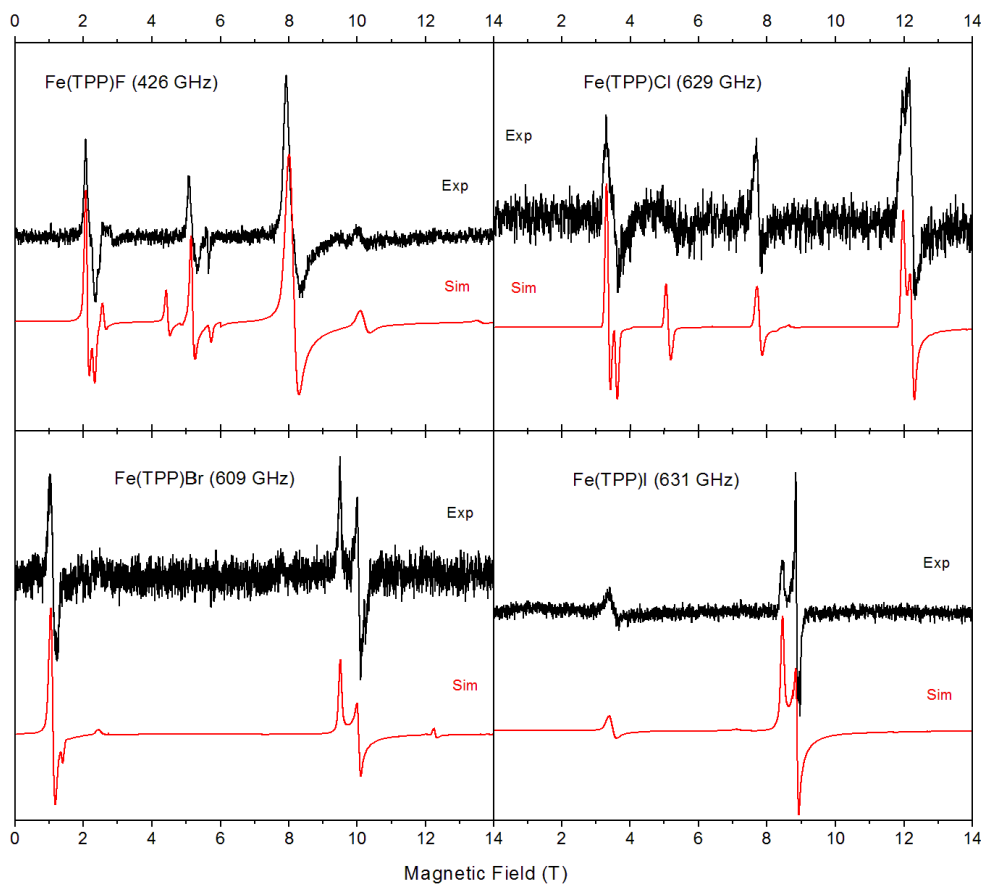


Figure 5.3. Experimental HFEPR spectra at 5-10 K of the **Fe(TPP)X** series of compounds (black traces) and their powder-pattern simulations (red traces). Particular frequencies and spin-Hamiltonian parameters used in the simulations are: **Fe(TPP)F**: frequency, 425.6 GHz, $D = +4.67 \text{ cm}^{-1}$, $E = 0$, $g_{\text{iso}} = 1.97$; **Fe(TPP)Cl**: frequency, 628.8 GHz, $D = +6.458 \text{ cm}^{-1}$, $E = +0.023 \text{ cm}^{-1}$, $\mathbf{g} = [2.01, 2.01, 2.00]$; **Fe(TPP)Br**: frequency, 609 GHz, $D = +9.01 \text{ cm}^{-1}$, $E = +0.05 \text{ cm}^{-1}$, $\mathbf{g} = [1.98, 1.99, 1.99]$; **Fe(TPP)I**: frequency, 631 GHz, $D = +13.83 \text{ cm}^{-1}$, $E = +0.07 \text{ cm}^{-1}$, $\mathbf{g} = [1.995, 1.995, 2.000]$ (the sign of E was in each case arbitrarily assigned as that of D). The splitting of the perpendicular intra-Kramers turning points [such as the one at 10 T in **Fe(TPP)Br**] is indicative of an exceedingly small ($E/D < 0.01$) yet measurable rhombicity of the ZFS tensor in each compound except **Fe(TPP)F**.

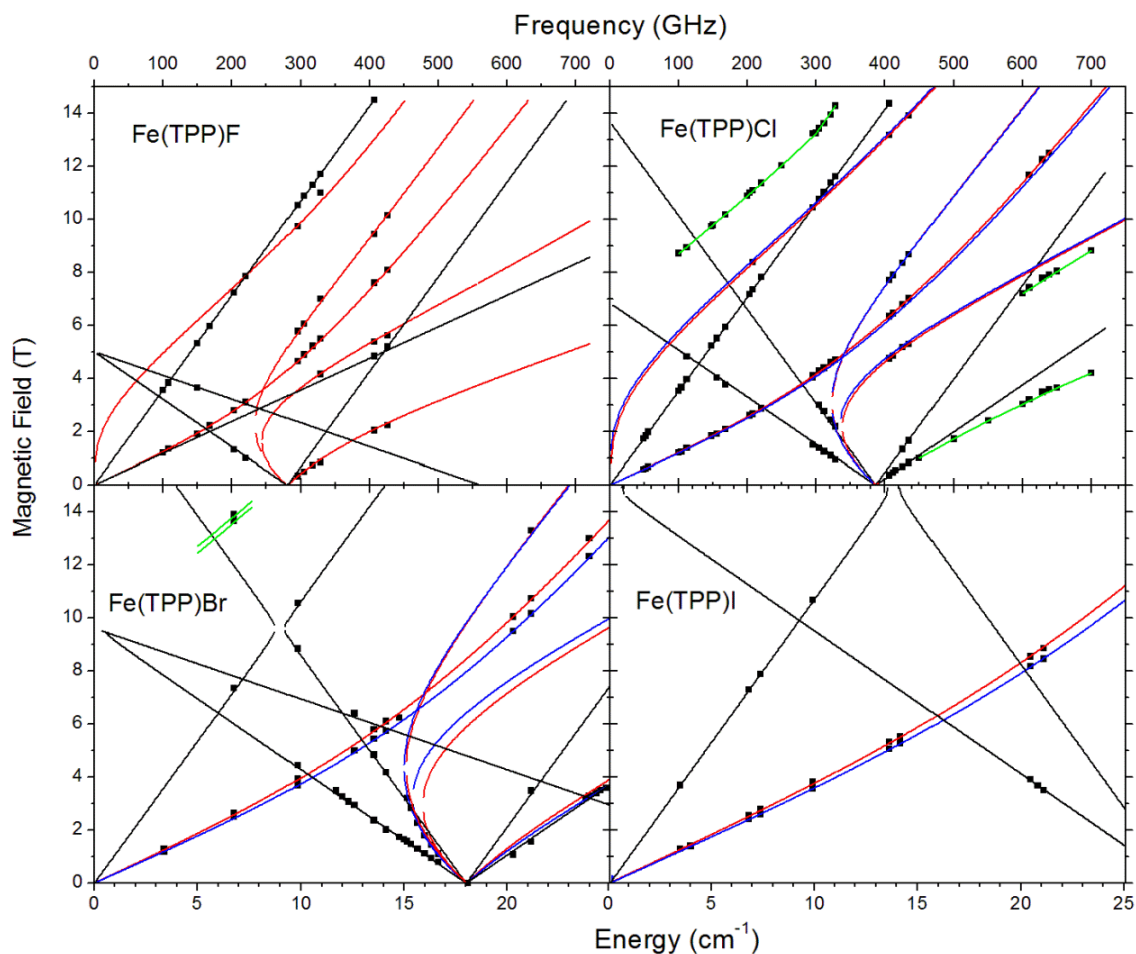


Figure 5.4. 2-D field vs. energy (frequency) HFEPR maps of the **Fe(TPP)X** series of compounds. Squares are experimental turning points in the EPR powder spectra including the zero-field resonance in **Fe(TPP)Br** detected by FIRMS at 18.1 cm^{-1} ; curves are simulations using spin-Hamiltonian parameters as in Table 5.1. Red curves: simulations with magnetic field parallel to the x -axis of the ZFS tensor; blue curves: $B_0 \parallel y$ axis, black curves: $B_0 \parallel z$ axis, green curves: off-axis turning points in **Fe(TPP)Cl** and **Fe(TPP)Br**. Only those simulated turning points were plotted that show experimental points on them; others were omitted for clarity. For **Fe(TPP)Cl**, the splitting of the perpendicular turning points is smaller than the symbol size. For that reason, only one set of perpendicular experimental data points is shown.

of the ZFS tensor ($E = 0$); thus the complex symmetry remains perfectly fourfold.

Fe(TPP)Cl produced an EPR response of very high quality at any temperature from 5 to 200 K and above, and in a wide frequency range of 50-630 GHz (Figure 5.3-Top right; see also Figure D.3 and D.4, Appendix D). The experimental spectra could be well simulated and thanks to a small linewidth of the turning points, a minute E value could be determined from the perpendicular resonance together with the D value of $+6.458(2) \text{ cm}^{-1}$, which translates into a rhombicity factor E/D of the ZFS tensor as small as 0.002-0.003. This is an indication that the fourfold symmetry provided by the ligand is not exactly kept by the molecule in the solid state, similarly to the other members of the series except Fe(TPP)F. The final frequency-independent spin-Hamiltonian parameters were obtained from a 2-D map similarly to **Fe(TPP)F** (Figure 5.4-Top right) and are to be found in Table 5.1.

The EPR response of the third complex of the series, **Fe(TPP)Br**, was almost as good as those of the two previously described analogs. Figure 5.3-Bottom left shows a typical spectrum accompanied by powder-pattern simulations using spin-Hamiltonian parameters as in the figure caption. Another spectrum, obtained at a lower frequency, is shown in Figure D.5 in Appendix D and additional multifrequency spectra in Figure D.6. The axial ZFS parameter D was established at $+9.01 \text{ cm}^{-1}$ and the very small rhombicity of the ZFS tensor ($E/D \sim 0.005$) shows in the visible splitting of the perpendicular turning point of the intra-Kramers transition at 10 T. The final frequency-independent spin-Hamiltonian parameters were obtained as before from a 2-D map of turning *points* shown in (Figure 5.4-Bottom left) and are to be found in Table 5.1.

Finally, the fourth complex, **Fe(TPP)I** also generated informative HFEPR spectra. Figure

5.3-Bottom right shows one of these spectra accompanied by powder-pattern simulations using spin-Hamiltonian parameters as in the figure caption. The axial ZFS parameters D was found to be $+13.84 \text{ cm}^{-1}$ and a minute rhombicity ($E/D \sim 0.005$) of the ZFS tensor shows in the visible splitting of the perpendicular turning point of the intra-Kramers transition at 9 T. Another spectrum, obtained at a lower frequency, is shown in Figure D.7 in Appendix D with a multi-frequency collection of experimental spectra shown in Figure D.8. The final frequency-independent spin-Hamiltonian parameters were obtained as before from a 2-D map of turning points shown in (Figure 5.4-Bottom right) and are to be found in Table 5.1. Note that although the highest HFEPR operating frequency (631 GHz , 21 cm^{-1}) was significantly lower than the $2|D|$ energy gap (27.9 cm^{-1} , see the FIRMS section below), an observation of the inter-Kramers turning points such as the one visible at 3.5 T in the corresponding spectrum made it possible to obtain the D value for **Fe(TPP)I** independent of FIRMS.

5.3.2. *FIRMS*

FIRMS has been used extensively to probe magnetic transitions in metal complexes with large zero-field splitting.^{11, 17, 27, 163, 164, 167, 278, 283-285} The great advantage of Fourier-transform spectroscopy is being able to cover the broad spectral range where transitions between zero-field energy levels might be observed. The application of the magnetic field gives the second variable for plotting the absorption spectrum in two dimensions, although significant costs are paid in terms of THz wave radiation power reaching the sample. Two spectra of the THz radiation transmitted through the sample were recorded for each magnetic field to estimate the signal-to-noise ratio. The magnetic resonance absorption spectrum is obtained as $A = 1 - T$, where T is the

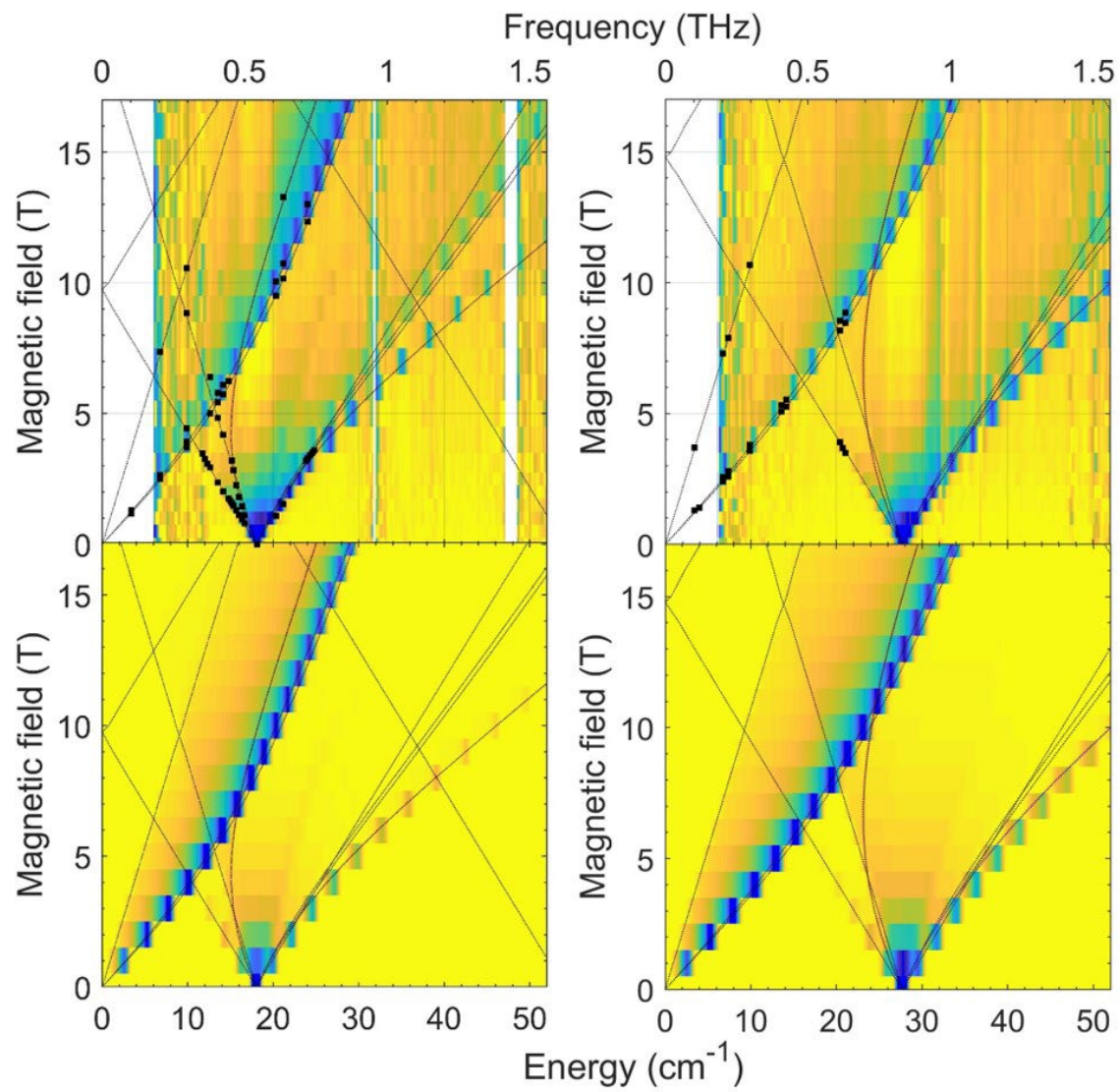
ratio between the THz transmission measured at each magnetic field and a reference spectrum. The latter is the average THz transmission for all magnetic fields. This approach allows one to distinguish field-dependent absorption among the field-independent spectral features, such as vibrational modes and instrumental function.

The experimental FIRMS spectra shown in Figure 5.5 in a form of 2-D maps (field vs. energy) were analyzed and simulated using an in-house written program based on the *EasySpin* toolbox.⁹⁴ This toolbox was originally developed for the analysis of magnetic resonance absorption in the field domain, but also provides a capability for calculations of the magnetic-dipole transition probability in the frequency domain. The effect of random orientation of the microcrystallites in the powder is taken into account and Lorentzian line broadening added to obtain the final simulated spectrum.

The lowest limit of the FIRMS spectral range is essential for spectroscopic studies of SMMs and is defined by the design of the particular experimental set-up. The intensity of the THz radiation emitted by a broadband thermal source is about 0.05% compared to mid-infrared range, which commercial FT-IR spectrometers are generally tailored to. The typical sensitivity of FIRMS measurements at NHMFL drops precipitously below 15 cm⁻¹ (Figure D.9 in Appendix D). This was one of the reasons why, of the four **Fe(TPP)X** complexes, only **Fe(TPP)I** and **Fe(TPP)Br** were addressed by the FIRMS technique, since the ZFS energies of **Fe(TPP)F** and **Fe(TPP)Cl** were fully determined by HFEPR. Nevertheless, a low-frequency resonance absorption at 10 cm⁻¹ (0.3 THz) can still be observed in both **Fe(TPP)Br** and **Fe(TPP)I**. This relatively strong (~30 %) absorption corresponds to the transition within the $M_S = \pm 1/2$ Kramers doublet and confirms the positive sign of D for both compounds. The quality of these spectra is

Figure 5.5. (Top left) 2-D map of FIRMS in **Fe(TPP)Br** at 4.6 K with HFEPR data points added as black squares. A zero-field transition is clearly visible at 18.1 cm^{-1} representing the transition between the $\pm 1/2$ and $\pm 3/2$ Kramers doublets. The intra-Kramers transition within the $\pm 1/2$ manifold is also visible at higher fields (4–17 T) in the low-energy region ($10\text{--}24 \text{ cm}^{-1}$). The lines are simulations of all possible turning points (including those of nominally forbidden transitions) in the powder spectrum using: $D = +9.05 \text{ cm}^{-1}$, $E = +0.05 \text{ cm}^{-1}$, $g_{\text{iso}} = 2.0$ (g_{iso} is the isotropic g factor). (Top right) 2-D map of magnetic resonance absorption in **Fe(TPP)I**. A zero-field transition is clearly visible at 27.9 cm^{-1} representing the transition between the $\pm 1/2$ and $\pm 3/2$ Kramers doublets. The intra-Kramers transition within the $\pm 1/2$ manifold is also visible at higher fields (4–17 T) in the low-energy region ($10\text{--}30 \text{ cm}^{-1}$). The lines are simulations of turning points in the powder spectrum using $D = +13.95 \text{ cm}^{-1}$, $E = +0.07 \text{ cm}^{-1}$, $g_{\text{iso}} = 2.0$.

(Bottom) Simulated maps for the respective compounds. The false-color simulation reproduces the allowed ($\Delta M_S = \pm 1$) transitions only, as different from the lines. That nominally forbidden resonances such as $|-1/2\rangle \rightarrow |+3/2\rangle$ appear in the experimental maps (the top two windows) is most likely due to the presence of a $B_1 \parallel B_0$ component in the THz radiation (B_1 is the magnetic, as opposed to electrical, field of the applied radiation) in addition to the standard $B_1 \perp B_0$ one.



essentially the same as those of the FD-FT THz-EPR (frequency-domain Fourier-transform terahertz-EPR) studies on **Fe(TPP)Cl** reported by the BESSY II facility in Berlin.²⁴² Despite the microcrystallites in the powder is taken into account and Lorentzian line broadening added to obtain the final simulated spectrum.

The lowest limit of the FIRMS spectral range is essential for spectroscopic studies of SMMs and is defined by the design of the particular experimental set-up. The intensity of the THz radiation emitted by a broadband thermal source is about 0.05% compared to mid-infrared range, which commercial FT-IR spectrometers are generally tailored to. The typical sensitivity of FIRMS measurements at NHMFL drops precipitously below 15 cm^{-1} (Figure D.9 in Appendix D). This was one of the reasons why, of the four **Fe(TPP)X** complexes, only **Fe(TPP)I** and **Fe(TPP)Br** were addressed by the FIRMS technique, since the ZFS energies of **Fe(TPP)F** and **Fe(TPP)Cl** were fully determined by HFEPR. Nevertheless, a low-frequency resonance absorption at 10 cm^{-1} (0.3 THz) can still be observed in both **Fe(TPP)Br** and **Fe(TPP)I**. This relatively strong ($\sim 30\%$) absorption corresponds to the transition within the $M_S = \pm 1/2$ Kramers doublet and confirms the positive sign of D for both compounds. The quality of these spectra is essentially the same as those of the FD-FT THz-EPR studies on **Fe(TPP)Cl** reported by the BESSY II facility in Berlin.²⁴² Despite the difference in terminology, their instrumental approach is basically the same as ours in terms of employing a Bruker FT-IR spectrometer. However, their spectrometer is coupled to an optical split-coil magnet, which yields sensitivity benefits due to the free-space propagation of the THz radiation and its direct incidence on the sample. A key difference of course is that BESSY II can also use coherent synchrotron radiation in the THz region as described elsewhere.²⁸⁶

5.4. Discussion

5.4.1. Spin-Hamiltonian and an Overview of the ZFS in *Fe(TPP)X*

ZFS is typically described by the spin-Hamiltonian in *Eq. 5.1*,^{6, 287} which is *Eq. 1.1* in Chapter 1 without the external magnetic field:

$$\hat{H} = D \left[\hat{S}_z^2 - \frac{1}{3}S(S+1) \right] + E(\hat{S}_x^2 - \hat{S}_y^2) \quad (\text{Eq. 5.1})$$

where D and E are the axial and rhombic ZFS parameters, respectively, and $\hat{S}_x$, $\hat{S}_y$, and $\hat{S}_z$ are the x , y and z components of the spin operator.

Although higher-order terms can be considered in a spin-Hamiltonian, e.g., fourth-order ZFS for $S \geq 2$ (such as the cubic ZFS terms denoted a or $B_4^{0,4}$),²⁸⁷ we have not done so here as the zero-field data fits were sufficiently successful using only those terms given in *Eq. 5.1*. Fourth-order ZFS has been determined by HFEPR on powder samples in other cases.²⁸⁸

For compounds with both molecular and crystallographic symmetries higher than 2-fold,⁶ the rhombic ZFS parameter E becomes zero and the spin-Hamiltonian in *Eq. 5.1* is simplified into *Eq. 5.2*, which now also includes the electronic Zeeman terms for an axial system. Analogous to the comment above for *Eq. 5.1*, higher-order Zeeman terms for $S \geq 3/2$ ²⁸⁹ are also possible, but were not considered as the parameters could be fitted to the field-dependent data sufficiently well without them.

$$\hat{H} = D \left[\hat{S}_z^2 - \frac{1}{3}S(S+1) \right] + \mu_B [g_{\parallel} B_z \hat{S}_z + g_{\perp} (B_x \hat{S}_x + B_y \hat{S}_y)] \quad (\text{Eq. 5.2})$$

where μ_B is electron Bohr magneton, $g_{\parallel}$ and $g_{\perp}$ are the parallel (along the z axis) and perpendicular (in the xy plane) components of the g factor, respectively, and B_x , B_y and B_z are the x , y and z components of the applied (external) magnetic field B .

The effect of the spin-Hamiltonian (Eq. 5.2) acting on the $S = 5/2$ wavefunction is depicted in Figure 5.2 for positive D , which happens to be the case of all known iron(III) porphyrins, including the **Fe(TPP)X** series investigated in the current work. It should be noted that because of the Kramers theorem, all the $\pm M_S$ levels are degenerate in the absence of magnetic field, and this makes the $\pm 1/2$ pair of spin sublevels amenable to EPR at any frequency, particularly at X-band, as the transition between these sublevels is fully allowed ($\Delta M_S = \pm 1$), and its energy scales with field. This is the reason why X-band EPR has been such a historically successful technique to investigate hemes and hemoglobin, although it alone does not offer information on the ZFS of these systems.

The most-researched complex of the **Fe(TPP)X** series has been **Fe(TPP)Cl**, its ZFS studied by a variety of experimental and theoretical methods, including magnetic susceptibility measurements,^{229, 233, 236, 237} THz-, FD-FT THz-EPR and HFEPR,²⁴² inelastic neutron scattering (INS),¹¹⁴ far-IR,¹⁶³ Mössbauer spectroscopy,²³⁴ magnetic circular dichroism (MCD),²³⁹ solution NMR,²³⁰ and X-band EPR.²³² It thus offers an excellent object for discussing the merits of particular techniques.

The most convenient (i.e., accessible) and least expensive method, DC magnetic susceptibility measurement as a function of temperature, is still the most widely used.²⁹⁰ This technique, however, suffers from a number of extrinsic, practical considerations that can

adversely affect the results: inaccuracy in sample mass (especially where sample quality is limited), insufficient diamagnetic corrections, ferromagnetic impurities (particularly for Fe-containing systems, where there can be Fe nanoparticle impurities) or other experimental problems such as a drift in the centering of the sample within the field. As an example of these difficulties in the present system, the reported D values for **Fe(TPP)Cl** from such measurements cover a very large range of energies: 6.0(1)–11.9 cm⁻¹.^{229, 233, 236, 237} While the lower end of these values is close to the true value as determined by direct methods like HFEPR or FIRMS, the upper end is about 100% off. The **Fe(TPP)Br** analog was also studied by magnetic susceptibility,^{229, 235, 238} with the resulting ZFS parameters widely varying on the energy scale from about 50% undervalued to 30% overvalued. Also note that in neither case was the magnetic susceptibility data analysis hampered by any degree of ZFS rhombicity, as is often the case in other spin systems. This indirect technique is thus generally not accurate and should be treated with utmost skepticism when evaluating ZFS.

Interestingly, the early far-IR studies of **Fe(TPP)Cl** and **Fe(TPP)Br** by Uenoyama in 1971,¹⁶³ which were performed using a home-made Michelson interferometer that Richards, Brackett, and coworkers had developed,^{81, 82, 227} offered accurate if not precise values for both compounds. A modern extension of this technique which different groups practicing it call FD-FT THz-EPR or FIRMS offers an improved accuracy and precision, particularly when complemented by HFEPR. It is particularly gratifying to see the almost perfect agreement between the ZFS parameters in **Fe(TPP)Cl** obtained by FD-FT THz-EPR at the BESSY II facility in Berlin²⁴² with those delivered by HFEPR at the NHMFL in Tallahassee (this work). Equally good agreement was achieved between HFEPR and FIRMS, both as performed within

this work on **Fe(TPP)Br** and **Fe(TPP)I**.

INS, A non-magnetic resonance method,^{25, 186, 291-293} has been practiced to measure ZFS in a variety of high-spin metal ions.^{13, 26-29, 91, 102, 114, 115, 185, 250, 251, 255, 294-304} It was employed previously by former group members on the same series of **Fe(TPP)X** compounds reported in this work.^{28, 114} Because the INS experiments for **Fe(TPP)X** were not conducted with an external magnet,^{28, 114} they did not deliver the *g*-values of the system under study. This, however, is not a problem for the **Fe(TPP)X** series in which the *g*-values of the Fe^{III} ion are consistently very close to 2.00. Otherwise, INS delivers very robust values of the ZFS parameters in agreement with magnetic resonance. There are two features of INS that make it advantageous to probe magnetic transitions in molecular compounds: (1) It offers a unique dependence of the magnetic transitions on the neutron scattering angles (or momentum transfer ***Q***), whether or not the INS experiments are conducted with an external magnet. This angular dependence was used to distinguish the magnetic transitions from those of phonons in the INS spectra of **Fe(TPP)X**.^{28, 114} Thus, although INS is typically used in zero-field, it can provide the discrimination between magnetic and vibrational (non-magnetic) signals. Since ***Q*** is a vector, 4-D INS (i.e., dimensions of *Q_x*, *Q_y*, *Q_z*, and *E* = energy of the neutrons scattered from the sample) has been used recently to probe magnetic exchange interactions, spin dynamics, and the entanglement between molecular qubits in metal complexes.^{253, 305-307} (2) INS experiments can also be conducted with external magnetic fields^{17, 27, 29} to probe both intra-Kramers ($M_S = -1/2 \rightarrow +1/2$)²⁹ and inter-Kramers doublet transitions in transition-metal and lanthanide SIMs.^{27, 29} For example, INS spectra of Co(acac-*d*₇)₂(D₂O)₂ (acac⁻ = acetylacetonate) at 0–10 T on the direct-geometry, time-of-flight Disk-Chopper Spectrometer (DCS)²⁵ revealed both $M_S = -1/2 \rightarrow +1/2$ and $M_S = \pm 1/2 \rightarrow \pm 3/2$

transitions,²⁹ offering comparisons with the results from other studies.^{11, 99} The intra-Kramers ($M_S = -1/2 \rightarrow +1/2$) transition at 0–10 T was simulated with D , E , and g values from an earlier work.⁹⁹ Another difference between the variable-temperature (VT) INS and HFEPR/FIRMS spectroscopies of **Fe(TPP)X** (**X** = **F**, **Cl**, **Br**, **I**) is that the INS spectra showed both the lower energy, $M_S = \pm 1/2 \rightarrow \pm 3/2$ absorptions (at $2D$ in the range of 9.5–27.4 cm⁻¹), and the higher energy, $M_S = \pm 3/2 \rightarrow \pm 5/2$ absorptions (at $4D$ in the range of ~18–55 cm⁻¹), at 10–100 K.^{28, 114} In addition, the transitions from the excited $M_S = \pm 3/2$ states to the ground $M_S = \pm 1/2$ states were also observed in the VT-INS spectra of all four **Fe(TPP)X** complexes.^{28, 114} For **Fe(TPP)F** and **Fe(TPP)Br** at 50 K when the highest energy ZFS states $M_S = \pm 5/2$ (Scheme 2) are sufficiently populated, the $M_S = \pm 5/2 \rightarrow \pm 3/2$ transitions (at $4D$) were also observed.^{28, 114} In such “emission” INS spectra, the neutrons scattered by the samples gain energy. For comparison, HFEPR and FIRMS spectra of the complexes in the current work were conducted at 2–10 and 4.6 K, respectively, when just the ground $M_S = \pm 1/2$ states were populated. Thus, these two spectroscopies essentially probed the $M_S = \pm 1/2 \rightarrow \pm 3/2$ absorptions (at $2D$).

A very small offset on the order of 2–4% in the D values obtained by INS, in comparison to those obtained from magnetic resonances, persists for all complexes reported in this work (Table 5.1), which we are not yet able to explain. As pointed out earlier, the D values from INS were from simulation of the spectra at zero magnetic field,^{28, 114} while those from magnetic resonances (HFEPR and FIRMS) are from simulations of the spectra collected in magnetic fields. In addition, the simulations of INS spectra involved the “emission” peaks as well as the higher energy, $M_S = \pm 3/2 \rightarrow \pm 5/2$ absorptions in **Fe(TPP)X** (**X** = **F**, **Br**, **I**).^{28, 114}

Of other experimental techniques, both Mössbauer and MCD spectroscopies deliver

dependable and accurate values of ZFS parameters, albeit without the precision of the magnetic resonance, and with Mössbauer requiring an external magnetic field and being essentially limited to Fe-containing systems.³⁰⁸ The indirect methods such as X-band EPR and solution NMR lead to very large errors and should generally be avoided for the purpose of evaluating ZFS.

5.4.2. *Understanding the ZFS in Fe(TPP)X*

The recent INS and *ab initio* studies by former group members^{28, 114} to calculate D and E values of all four complexes **Fe(TPP)X** were a comprehensive investigation of the iron porphyrin halides. The origin of the large and positive D values of the 6A_1 ground state in **Fe(TPP)X** was studied by the complete active space self-consistent field (CASSCF) and the N-electron valence perturbation theory (NEVPT2), reproducing the trends of D from INS.²⁸ The results showed a correlation between the increase of the D values and decrease of the π - and σ -antibonding energies (e_π^X and e_σ^X) of the Fe-X bonds from X = F to I.

We believe that a much simpler model based on ligand field theory (LFT) could also explain at least semi-quantitatively the trend of increasing ZFS along the series of axial ligands, from F to Cl to Br and to I. Of particular instruction might be a comparison with an analogous series of tetraphenylporphyrinate halide compounds with a different metal ion, Mn^{III} ($3d^4$), where the trend is exactly reversed.²⁶ This approach has already been used, by Gatteschi and Sorace for distorted octahedral complexes,³⁰⁹ specifically for both high-spin Fe^{III} and other high-spin ions, namely high-spin Mn^{III} ($3d^4$, $S = 2$),³¹⁰ perhaps most widely studied by HFEPR,^{12, 310, 311} as well as other techniques, including INS.^{28, 114} In the case of Mn^{III} , it is clear that, barring any complications from non-innocent (especially heavy atom) ligands,³¹² $D < 0$ corresponds to axial

(tetragonal) elongation, as is the case for $\text{Mn}(\text{TPP})\text{Cl}$,²⁶ and $D > 0$ to axial compression.³¹³ This situation for Mn^{III} is relatively simple because the ZFS is dominated by SOC involving excited states within the ground-state free-ion 5D ($L = 2, S = 2$) manifold. The D value depends on the ligand-field energy splitting as follows (Eq. 5.3)³¹⁴:

$$D = \lambda^2 \left(-\frac{4}{\Delta} + \frac{1}{\Delta - \delta_1} - \frac{4}{\delta_3} \right), \quad (\text{Eq. 5.3})$$

where Δ is the octahedral splitting, δ_1 is the tetragonal splitting, which is basically the energy difference between the d_{xy} and d_{xz}/d_{yz} orbitals (degenerate in C_{4v} symmetry), and δ_3 is the energy of the most relevant (among many) triplet excited state (derived from $^3T_{1g}({}^3\text{H})$, $t_2^4 e^0$).

In contrast, for Fe^{III} , there is no SOC within the ground state free-ion 6S manifold as $L = 0$. The ZFS results from mixing via SOC of primarily excited quartet states, of which there are many, even in high symmetry (i.e., O_h point-group): $^4T_{1g}({}^4G, {}^4F, {}^4P)$, $^4T_{2g}({}^4G, {}^4F, {}^4D)$, $^4E_g({}^4G, {}^4D)$, $^4A_{1g}({}^4G)$, and $^4A_{2g}({}^4F)$. Most of these, however, are at very high energy with respect to the $^6A_{1g}({}^6S)$ (in O_h) sextet ground state ($t_2^3 e^2$ in strong-field notation) and can be disregarded in a simple approach. This can be shown by an exact calculation using the matrix elements given by McClure³¹⁵ and the parameters used by Gatteschi and Sorace:³⁰⁹ Racah parameters $B = 536 \text{ cm}^{-1}$, $C = 3260 \text{ cm}^{-1}$, and $Dq = 1500 \text{ cm}^{-1}$ (roughly the average of the axial and equatorial octahedral splitting they used). This gives the $^4T_{1g}({}^4G)$ excited state ($t_2^4 e^1$) lying at $\sim 9400 \text{ cm}^{-1}$ above the $^6A_{1g}({}^6S)$ ground state and the $^4T_{2g}({}^4G)$ excited state (also $t_2^4 e^1$) lying at $\sim 13\,040 \text{ cm}^{-1}$. It should be noted that Paulat and Lehnert saw evidence in the MCD and UV-Vis-NIR spectra of **Fe(TPP)Cl**

for these transitions at 11 584 and 13 542 cm⁻¹, respectively.²⁴⁵ All the other spin quartet excited states lie greater than ~22 000 cm⁻¹ above the ground state. The many spin-doublet excited states are also at >20 000 cm⁻¹ above the ground state, and most are much higher in energy. There is one low-lying doublet excited state, ²T_{2g}(²I) (t₂⁵e⁰), but this requires a double-spin-flip to connect to the ground state, which is not allowed. The calculations by Gatteschi and Sorace showed that, similar to Mn^{III}, tetragonal elongation gave one sign of *D* and compression the other, but oppositely so [and more than an order of magnitude smaller, as |*D*| = 4.75(5) cm⁻¹ for Mn^{III}] in that elongation gave *D* ≈ +0.3 cm⁻¹ and compression gave *D* ≈ -0.3 cm⁻¹. In the case of **Fe(TPP)X**, however, due to the five-coordinate (square pyramidal) geometry, the situation is always one of tetragonal elongation, and indeed, the positive sign of *D* reported for these complexes (Table 5.1) is consistent with this simple model. The following LFT expression helps to demonstrate this behavior (Eq. 5.4)²⁸⁷:

$$D = \frac{1}{10} \zeta^2 \left(\frac{2}{E_z} - \frac{1}{E_x} - \frac{1}{E_y} \right) = \frac{1}{5} \zeta^2 \left(\frac{1}{E\left({}^4A_2\left({}^4T_{1g}\right)\right)} - \frac{1}{E\left({}^4E\left({}^4T_{1g}\right)\right)} \right), \quad (\text{Eq. 5.4})$$

where *E_i*, *i* = *x*, *y*, *z*, corresponds to the energies for excited states that involve pairing of the electron in the *d_{x²-y²}* (highest energy) orbital of the sextet ground state into the *d_{yz}*, *d_{xz}*, and *d_{xy}* orbitals, respectively. The second part of the equation is that given in the earlier *ab initio* studies by Stavretis et al.²⁸ and is suited to the axial symmetry found here, with the symmetry designations of the states derived from the ⁴T_{1g}(⁴G) excited state mentioned above. Due to π-bonding with the axial halide ligand, the ⁴E state [i.e., (*d_{xy}*)¹(*d_{yz}*)¹(*d_{xz}*)²(*d_{z²}*)¹ / (*d_{xy}*)¹(*d_{yz}*)²(*d_{xz}*)¹(*d_{z²}*)¹] is higher in energy than the ⁴A₂ state [i.e., (*d_{xy}*)²(*d_{yz}*)¹(*d_{xz}*)¹(*d_{z²}*)¹] so *D* is

positive.

These simple (i.e., d^n only, $n = 4, 5$) LFT models work well for complexes wherein all of the ligands are light atoms. The difficulty is when the ligand, in this case the axial halide ligand, has both some non-innocent character and a large intrinsic SOC. The first point means that the traditional oxidation state assignment/electronic configuration of a Group 17 ligand as closed shell X^- : [N.G.] ns^2np^6 (and likewise, a Group 16 ligand as E^{2-} : [N.G.] ns^2np^6 , etc.) is not a truly appropriate description, but the ligand may instead have atomic/radical character (i.e., $X^{\bullet 0}$: [N.G.] ns^2np^5 , and Group 16 as $E^{\bullet -}$: [N.G.] ns^2np^5 , etc.). The second point stems from the fact that the SOC constants of the Group 17 elements in their neutral atom state, i.e., [N.G.] np^5 electronic configuration ($^2P_{3/2}$), increases as follows (in cm^{-1}): F^0 , 269.3; Cl^0 , 588.2; Br^0 , 2328.8; I^0 , 5068.6.³¹⁶ For fluorine, non-innocence is decidedly not the case, neither for chlorine, but for bromine, and in particular iodine, the complexes can be described to some extent as “resonance forms” of $[Fe^{III}(TPP^{2-})X^-]$ and $[Fe^{II}(TPP^{2-})X^{\bullet 0}]$ ($X = Br, I$). This was the situation encountered by Mossin et al. for a *trans*-bisiiodide Mn^{III} cyclam (cyclam = 1,4,8,11-tetraazacyclotetradecane) complex,³¹² wherein $[Mn^{III}(\text{cyclam}^0)(I^-)_2]^+ \leftrightarrow [Mn^{III}(\text{cyclam}^0)(I^-)(I^{\bullet 0})]^+$ (i.e., $(5p^6)[(d_{xy})^1(d_{yz})^1(d_{xz})^1(d_{z^2})^1] \leftrightarrow (5p^5)[(d_{xy})^1(d_{yz})^1(d_{xz})^1(d_{z^2})^2] \leftrightarrow (5p^5)[(d_{xy})^1(d_{yz})^1(d_{xz})^2(d_{z^2})^1] \leftrightarrow (5p^5)[(d_{xy})^1(d_{yz})^2(d_{xz})^1(d_{z^2})^1]$) is minimally operative. This behavior is of course enhanced by the presence of *two* iodide ligands, which are involved in both σ -bonding (charge transfer into Mn d_{z^2} orbital) and π -bonding (charge transfer into Mn d_{xz} or d_{yz} orbitals). In a *tour-de-force* of ligand-field theory, Mossin et al. showed that the ZFS was positive due to this large SOC constant of iodine that makes a net *positive* contribution to D .³¹² Qualitatively, the same effect is seen in the $Mn(TPP)X$ series, wherein $Mn(TPP)Cl$ has ZFS that is typical for Mn^{III} in a

tetragonally elongated environment [$D = -2.26(3) \text{ cm}^{-1}$], while for $\text{Mn}(\text{TPP})\text{Br}$, the ZFS has changed substantially ($D = -1.09 \text{ cm}^{-1}$), and for $\text{Mn}(\text{TPP})\text{I}$, it has shifted to “the other side”: $D = +1.3 \text{ cm}^{-1}$. What about **Fe(TPP)X**? Fe^{III} would be expected to be a stronger Lewis acid than Mn^{III} and thus $[\text{Fe}^{\text{III}}(\text{TPP}^{2-})\text{X}^-] \leftrightarrow [\text{Fe}^{\text{II}}(\text{TPP}^{2-})\text{X}^{\bullet 0}]$ ($\text{X} = \text{Br}, \text{I}$) should be at least as relevant as in the cyclam complex. The question is, how does the right side “resonance form” contribute to D , positively or negatively? The method used by Mossin et al. is currently beyond our capabilities and is likely even more challenging for the Fe^{III} case as the operative electronic configurations have another electron: $(5p^6)[(d_{xy})^1(d_{yz})^1(d_{xz})^1(d_{z^2})^1(d_{x^2-y^2})^1] \leftrightarrow (5p^5)[(d_{xy})^1(d_{yz})^1(d_{xz})^1(d_{z^2})^2(d_{x^2-y^2})^1] \leftrightarrow (5p^5)[(d_{xy})^1(d_{yz})^2(d_{xz})^1(d_{z^2})^1(d_{x^2-y^2})^1] \leftrightarrow (5p^5)[(d_{xy})^1(d_{yz})^1(d_{xz})^2(d_{z^2})^1(d_{x^2-y^2})^1]$. All that we can propose here is that the net contribution of SOC from the axial halide ligand is positive in this high-spin d^5 case as well, so that the positive D value that obtains for the innocent electronic configuration, $(5p^6)[(d_{xy})^1(d_{yz})^1(d_{xz})^1(d_{z^2})^1(d_{x^2-y^2})^1]$, is overall added to by the contributions from the non-innocent ones. Thus, a positive D value always obtains for **Fe(TPP)X**, but increases smoothly in magnitude as one moves down the Group 17 elements; indeed, a plot of D values of **Fe(TPP)X** versus Z_{X} (atomic number of the halides X) is linear with $R^2 = 0.98$, as shown in Figure D.10 (Appendix D). Given that the behavior of the axial halide ligand is essentially the same in **Fe(TPP)X** as in $[\text{Mn}(\text{tetraaza-macrocycle})\text{X}]^{m+}$ ($m = 0, 1$) this analogous behavior is plausible.

5.5. Experimental

Fe(TPP)F,²⁴⁵ **Fe(TPP)Cl**,³¹⁷ **Fe(TPP)Br**,²²⁹ and **Fe(TPP)I**³¹⁷ were prepared by the literature methods. The syntheses of **Fe(TPP)F**,²⁴⁵ **Fe(TPP)Br**²²⁹ and **Fe(TPP)I**³¹⁷ were

described earlier.²⁸

5.5.1. HFEPR

HFEPR studies were performed at the National High Magnetic Field Laboratory (NHMFL, Tallahassee, FL, USA) and the Dresden High Magnetic Field Laboratory (HLD-EMFL, Dresden, Germany). The NHMFL EMR Facility operates a transmission spectrometer described elsewhere¹⁴⁰ modified by the use of Virginia Diodes Inc. (VDI, Charlottesville, VA, USA) sources, generating sub-THz wave radiation in a 50–640 GHz frequency range. The spectrometer is associated with a 15/17 T warm-bore superconducting magnet. HFEPR measurements at the HLD were performed at frequencies up to 750 GHz using a 16 T cold-bore magnet-based transmission-type multifrequency spectrometer (similar to that described earlier³¹⁸) equipped with VDI sub-THz sources. In both cases, pellets made of *n*-eicosane and the given compound as a powder in about ~30 mg quantity were used. Alternatively, the powder sample was immersed in an *n*-eicosane mull. The spectra were typically collected at 5–10 K in the NHMFL, and 2 K at HLD.

5.5.2. FIRMS

FIRMS spectra were collected at the NHMFL using a Bruker Vertex 80v FT-IR spectrometer coupled with a 17 T vertical-bore superconducting magnet in Voigt configuration. The experimental setup is equipped with a mercury lamp and a composite silicon bolometer (Infrared Laboratories), as an incoherent (sub)-THz radiation source and detector, respectively. Two gold-coated mirrors are used to guide the THz radiation from the spectrometer and to focus it onto the top of the probe. The mirrors are mounted inside the 7.6 cm (3 inch) diameter

beamline which is evacuated to 3 mbar to eliminate strong parasitic absorption of water vapor. The radiation is then passed through the brass lightpipe [OD 1.9 cm (0.75 inch)] over a distance of 2.5 m from the source at room temperature to the field center part of the probe at low temperature. An *n*-eicosane pellet containing the powdered compound of interest (~7 mg) was measured in the spectral region between 5 and 50 cm⁻¹ (0.15–1.5 THz) with a resolution of 0.3 cm⁻¹ (9 GHz). Both sample and bolometer were cooled by low-pressure helium gas to ~4.5 K.

5.6. Conclusions

The current HFEPR and FIRMS studies of the important series of axially halide-coordinated square pyramidal iron(III) porphyrins, **Fe(TPP)X** (**X** = **F**, **Cl**, **Br**, **I**), have probed intra- and inter-Kramers doublet magnetic transitions in these $S = 5/2$ complexes, yielding the spin-Hamiltonian parameters: ZFS (D and E) and g values. These parameters have been compared with those from earlier spectroscopic and magnetization studies and show the high level of accuracy and precision available from the combination of field-domain (i.e., HFEPR) and frequency-domain (i.e., FIRMS) magnetic resonance techniques. Other spectroscopic techniques, such as applied field Mössbauer and VTVH-MCD can yield reliable spin-Hamiltonian parameters and other useful information as well, such as ⁵⁷Fe hyperfine coupling constants via the former³⁰⁸ and electronic transition information via the latter technique.²⁴⁵ In contrast, magnetic susceptibility, while easy and readily available, is less reliable for yielding high accuracy information on spin-Hamiltonian parameters. The D values (in cm⁻¹) in the **Fe(TPP)X** series increase smoothly as follows: +4.67(1) (**X** = **F**), +6.458(2) (**X** = **Cl**), +9.05 (**X** = **Br**), +13.95 (**X** = **I**). A qualitative model based on LFT explained this trend by attributing it to

the combination of increasing spin delocalization from Fe onto the **X** ligand coupled with the large increase in atomic SOC constant as the halogen atomic number increases over the range from F to I.

Chapter 6

Concluding Remarks

Studies presented in this dissertation showcase the power and versatility of optical and neutron spectroscopies in the direct determination of the magnetic anisotropy in SIM-MOF systems such as **Co-TODA** and **Co-BEBN** and in molecular magnets, **Fe(TPP)X**, that exhibit second-order SOC. In addition, the phonon properties were characterized using INS and DFT phonon calculations to comprehensively understand the spin and phonon effects in the systems. In **Co-BEBN**, spin-phonon coupling was observed, and the coupling constant was determined through a data-fitting model. Qubit properties were probed for **Co-TODA** and **Co-BEBN** using pulsed EPR to determine the effectiveness of the qubit candidates. The combined use of FIRMS and HFEPR provided a direct probe of the ZFS parameters that is more accurate than the conventional magnetic susceptibility measurements. Furthermore, electronic structure calculations of **Co-TODA** and **Co-BEBN** were also conducted to understand the origin of the anisotropy as well as to calculate the ZFS parameters for comparison with the experimental results. The combination of optical experiments and calculations provides accurate results for the anisotropy of the systems.

For future studies, the determination of the ZFS parameters can be expanded into other techniques that could provide more unique information. Techniques such as Raman-magneto spectroscopy (RaMS) give information on the magnetic transitions and phonons in addition to FIRMS.¹¹ Further studies into the spin-phonon coupling can be understood through *ab initio* calculations. For the qubit properties of **Co-TODA**, future studies into the Zn^{II}-dilution of the MOF at various concentrations such as **Co-TODA_{0.005}**, **Co-TODA_{0.01}**, and **Co-TODA_{0.05}** using pulsed EPR can be useful in observing the correlations between the spatial separation of the Co^{II} ions and the T_1/T_2 times. Similar studies can be conducted for **Co-BEBN**. In addition, the 2-D

MOFs can be exfoliated into 2-D nanosheets for low-dimensional magnetic properties studies of individual Co^{II} ions using microscopy techniques such as scanning tunneling microscopy coupled with inelastic electron tunneling spectroscopy (STM-IETS).¹²

This dissertation also provides a comprehensive understanding of the topological properties of the symmetry-protected Haldane 1-D spin-1 chains in the form of a 2-D MOF. The studies involved the use of magnetic susceptibility, INS, and HFESR to probe the spin gap as well as the anisotropy of **NiBO**. The PND experiments reveal the nature of the magnetic interactions in **NiBO** as well as supporting the Haldane antiferromagnetic structure in the MOF. In addition, QMC simulations were conducted to support the experimental findings as well as to determine magnetic parameters such as the magnetic coupling constant and g-factors. Studies into the 2-D MOF Haldane properties are limited and not as common as that of 1-D chains. Our work provides insight into new studies on low-dimensional quantum magnetism in MOFs. MOFs are unique among Haldane spin-1 chain materials by providing the possibility for exfoliation into 2-D nanosheets with unique magnetic properties.

Future studies into the Haldane properties of the 2-D MOFs can include single-crystal magnetic experiments using DC magnetic susceptibility, INS, and HFESR which would prove useful in providing a clearer picture of the magnetic properties in x , y , and z directions. The HFESR studies can be improved with a variable-temperature (VT) HFESR measurement. The Boltzmann distribution can provide insight into various observable magnetic transitions of the system at different temperatures. The studies of INS can be improved using a direct-geometry spectrometer such as Disk-Chopper Spectrometer (DCS) at the National Institute of Standards and Technology (NIST), providing data in the $\mathbf{Q}$ space. The unique information extracted from

the $\mathcal{Q}$ space could prove useful in further understanding the anisotropy of the chain system.

Lastly, as mentioned above, the 2-D MOFs can be exfoliated into 2-D nanosheets used to study the Haldane properties of the end-chain spins using microscopy methods such as the STM-IETS.¹²

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Appendices

Appendix A. Supporting Information for Chapter 2

A1. Synthesis of Co-TODA

Polycrystalline sample of **Co-TODA** was prepared as reported in the literature.⁸⁸ Single-crystal sample of **Co-TODA** that was used in the single-crystal X-ray diffraction experiment was prepared as followed: an aqueous solution of $\text{K}_3\text{Co}(\text{CN})_6$ was made by dissolving 0.0136 mg of $\text{K}_3\text{Co}(\text{CN})_6$ in 3 mL of deionized (DI) water. An aqueous solution of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and TODA was made by dissolving 0.0184 g of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and 0.0211 g of TODA in 3 mL of DI water. Using an H-shaped tube, the aqueous solution of $\text{K}_3\text{Co}(\text{CN})_6$ was added to one side of the H, while the aqueous solution of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and TODA was added to the other side of the H. DI water was added to the top of both aqueous solutions until solution level passed the bridge of the H. DI water was used as a buffer. After one-week, pink block crystals were formed. Crystals were collected to be washed with water and dried in the air overnight.

A2. Additional Results from the Electronic Structure Calculations Using CASPT2/RASSI-SO with MOLCAS 8.4

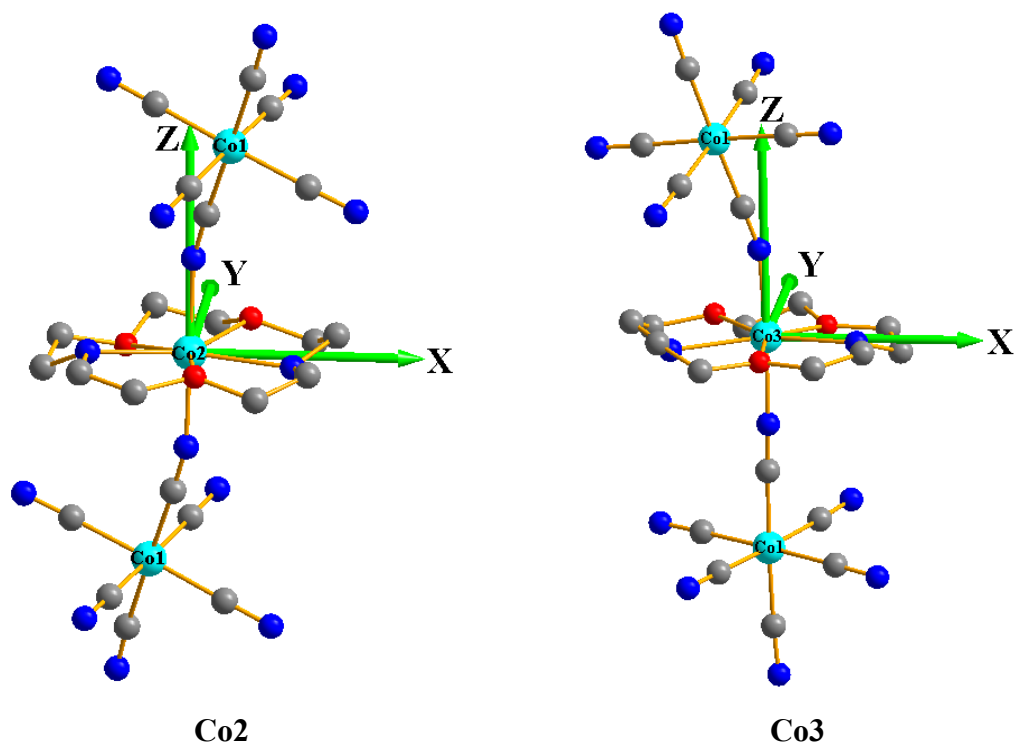


Figure A.1. Calculated molecular structures of individual Co^{II} fragments. H atoms are omitted for clarity.

Table A.1. Calculated spin-free energies (cm^{-1}) of the lowest ten terms ($S = 3/2$) of the Co^{II} ion of **Co2** and **Co3** using CASPT2/RASSI-SO with MOLCAS 8.4

Spin-free states	Co2, Energy (cm^{-1})	Co3, Energy (cm^{-1})
1	0.0	0.0
2	2022.5	2201.3
3	2532.0	2288.5
4	4378.8	3759.2
5	5731.6	5230.1
6	11519.7	13004.6
7	13780.2	13445.9
8	18943.6	19222.8
9	20359.8	20440.4
10	21083.3	21600.6

Table A.2. Calculated weights of the five most important spin-orbit-free states for the lowest two spin-orbit states of **Co2** and **Co3** using CASPT2/RASSI-SO with MOLCAS 8.4

	Spin-orbit states	Energy (cm ⁻¹)	Spin-free states, Spin, Weights				
Co2	1	0.0	1,1.5,0.9688	4,1.5,0.0115	2,1.5,0.0085	5,1.5,0.0049	3,1.5,0.0042
	2	62.3	1,1.5,0.9777	3,1.5,0.0072	2,1.5,0.0053	4,1.5,0.0051	5,1.5,0.0036
Co3	1	0.0	1,1.5,0.9665	4,1.5,0.0173	5,1.5,0.0062	2,1.5,0.0059	3,1.5,0.0019
	2	91.6	1,1.5,0.9842	5,1.5,0.0060	4,1.5,0.0050	2,1.5,0.0029	3,1.5,0.0008

Table A.3. Calculated ZFS parameters D , E (cm^{-1}) and $\mathbf{g}$ (g_x , g_y , g_z) tensors of **Co2** and **Co3** using CASPT2 and NEVPT2 with MOLCAS 8.4 and ORCA 4.2, respectively

Fragments	CASPT2					NEVPT2				
	D_{cal}	E_{cal}	g_x	g_y	g_z	D_{cal}	E_{cal}	g_x	g_y	g_z
Co2	30.5	-3.7	2.398	2.313	2.099	21.5	2.6	2.359	2.295	2.152
Co3	43.0	-9.2	2.503	2.295	2.004	34.7	5.4	2.412	2.289	2.034

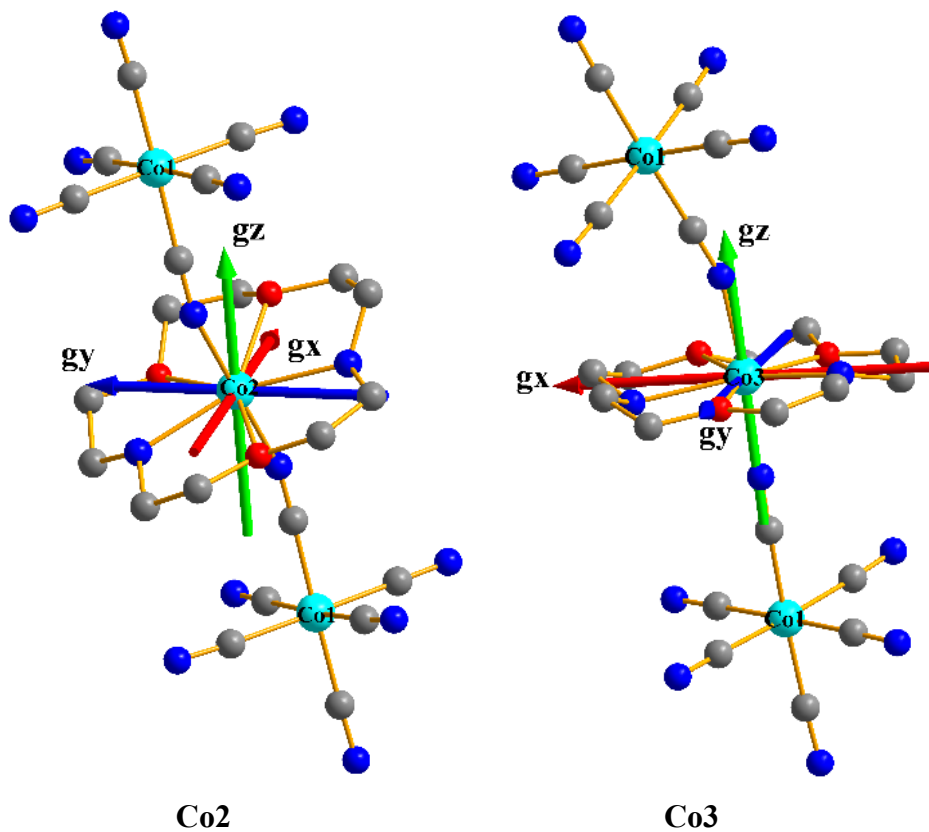


Figure A.2. Orientations of the local magnetic axes (red: g_x ; blue: g_y ; green: g_z) on Co^{II} ions of **Co2** and **Co3** in their ground spin-orbit states using CASPT2/RASSI-SO with MOLCAS 8.4.

Table A.4. Contributions of the excited states (with relative energy, cm^{-1}) to D values (cm^{-1}) for **Co2** and **Co3** using NEVPT2 with ORCA 4.2

Fragments	State No.	Multiplicity	Energy (cm^{-1})	Contribution (cm^{-1})
				D
Co2	3	4	3750.4	10.1
	4	4	4722.1	10.1
Co3	3	4	3454.5	18.4
	4	4	4571.4	13.1

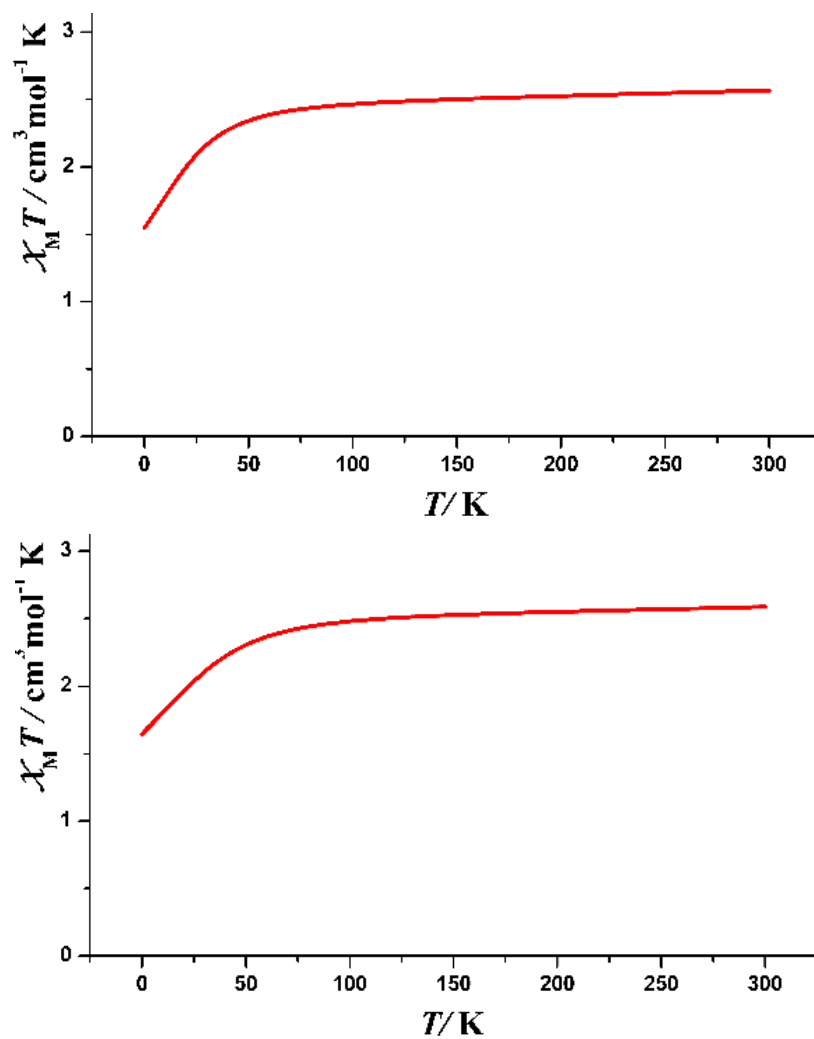


Figure A.3. Calculated (red solid line) data of magnetic susceptibilities. (Top) **Co2** and (Bottom) **Co3** using CASPT2/RASSI-SO with MOLCAS 8.4.

Table A.5. Relative energies (cm^{-1}) of ligand field one-electron states (in the basis of d -AOs) of **Co2** and **Co3** from AILFT analysis using NEVPT2 with ORCA 4.2

Fragments	No.	LF one-electron state	Energy (cm^{-1})
Co2	1	$-0.81 d_{yz} + 0.49 d_{xz} - 0.24 d_{xy}$	0.0
	2	$-0.84 d_{xz} - 0.45 d_{yz} - 0.20 d_{xy}$	138.1
	3	$0.77 d_{xy} + 0.50 d_{x^2-y^2} - 0.38 d_{yz}$	1782.9
	4	$-0.83 d_{x^2-y^2} + 0.55 d_{xy}$	3468.6
	5	$0.97 d_{z^2} + 0.20 d_{xz}$	8420.0
Co3	1	$0.95 d_{yz} - 0.30 d_{xz}$	0.0
	2	$0.95 d_{xz} + 0.31 d_{yz}$	49.3
	3	$0.77 d_{xy} + 0.63 d_{x^2-y^2}$	2559.6
	4	$0.77 d_{x^2-y^2} - 0.63 d_{xy}$	2770.1
	5	$0.99 d_{z^2} - 0.15 d_{x^2-y^2}$	8864.3

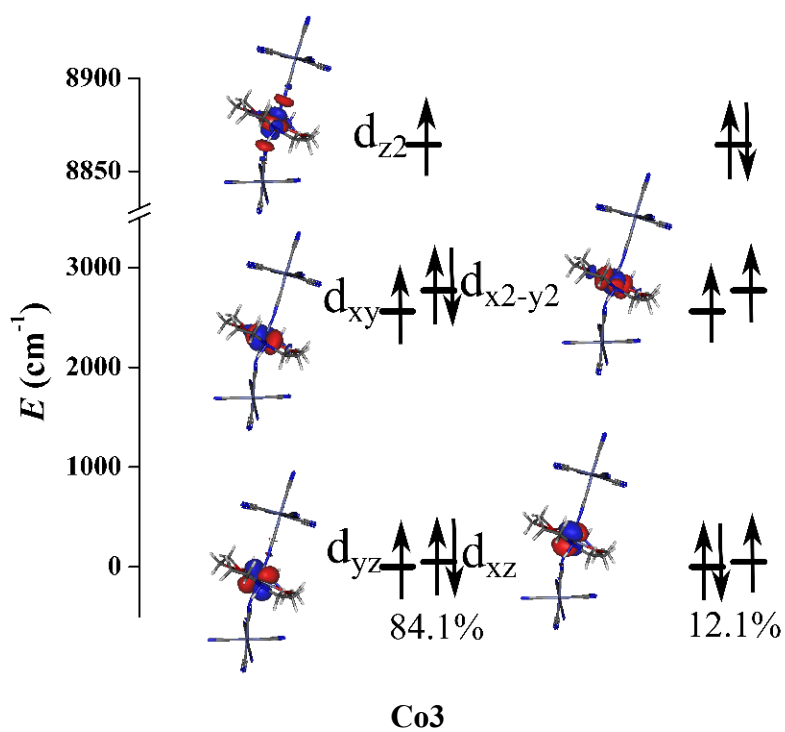
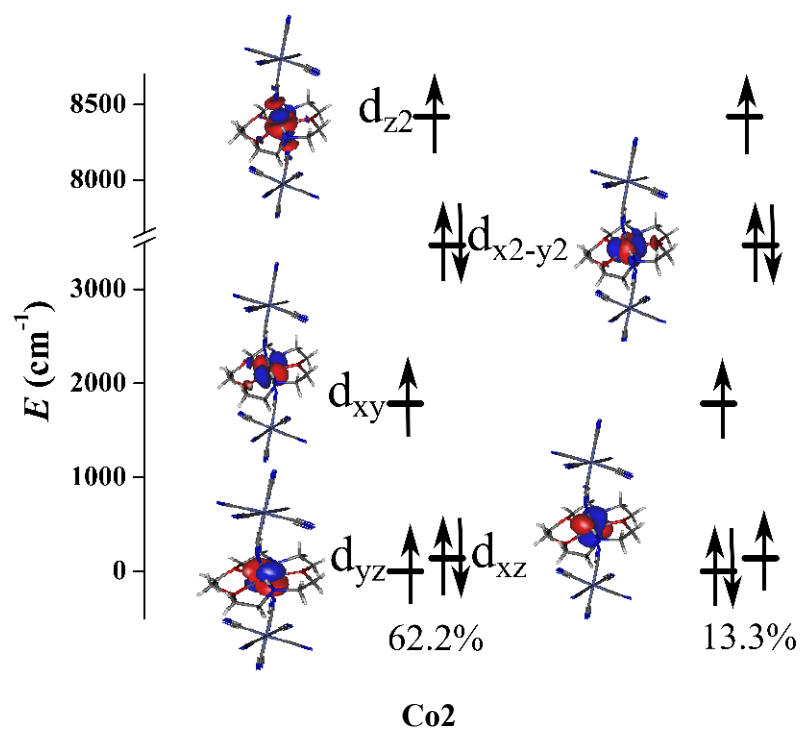


Figure A.4. Orbital energies computed for the ground state of **Co2** and **Co3** using NEVPT2 with ORCA 4.2. The percentage reveals the percentage of the corresponding configuration mixing.

d_{z^2}			
$d_{x^2-y^2}$			
d_{xy}			
d_{xz}			
d_{yz}			
3rd	40.5%	23.4%	21.1%

d_{z^2}			
$d_{x^2-y^2}$			
d_{xy}			
d_{xz}			
d_{yz}			
4th	48.8%	19.2%	12.8%

Co2

d_{z^2}			
$d_{x^2-y^2}$			
d_{xy}			
d_{xz}			
d_{yz}			
3rd	49.8%	25.9%	23.5%

d_{z^2}			
$d_{x^2-y^2}$			
d_{xy}			
d_{xz}			
d_{yz}			
4th	50.8%	25.2%	23.5%

Co3

Figure A.5. Multi-determinant wavefunction of the selected excited states having important contributions to D tensor for **Co2** and **Co3**. The computed CI coefficients that are larger than 10% are shown above.

A3. Crystal Structure of Co-TODA at 15(2) K and a Comparison of Selected Bond Lengths and Angles at 15(2) K and 123(2) K

Crystallographic data of **Co-TODA** using synchrotron X-ray diffraction were obtained at 15 K, confirming there is *no* phase change from 123(2) K to 15(2) K (Table A.6). ORTEP drawing of the crystal structure at 15(2) K is given in Figures 2.1-Right in the main text. Disorder in one TODA ligand is shown in Figure A.6. The disorder of the TODA at 15(2) K may stem from the rotation of the ligand. Additional plots of the structure at 15(2) K are given in Figures A.7-A.10.

The MOF crystallizes in the monoclinic space group $P2_1/c$ at 15(2) K, as at 123(2) K.⁸⁸ However, only 7 water molecules were observed at 15(2) K, while 9 water molecules were present at 123(2) K. The crystals were prepared over 3 years prior to the current 15(2) K structure determination. During that time, the crystals in air may have lost lattice waters in the MOF.

The structure of **Co-TODA** contains a core formed by one $[\text{Co}^{\text{III}}(\text{CN})_6]^{3-}$ and 1.5 $[\text{Co}(\text{TODA})]^{2+}$ unites along with lattice water molecules. The diamagnetic $[\text{Co}^{\text{III}}(\text{CN})_6]^{3-}$ center is bonded to the C atoms of six CN^- ligands and one and a half of the $[\text{Co}^{\text{II}}(\text{TODA})]^{2+}$ unit plus nine water molecules. Each Co^{III} unit connects to the Co^{II} unit through three CN^- bridges in the *fac*-position. Between each layer, there are hydrogen bondings that stack the layers in three dimensions along the *a* axis. The shortest Co^{II} to Co^{II} distance in a unit cell is 7.52 Å, while the longest Co^{II} to Co^{II} distance is 15.4 Å. The shortest interlayer distance between Co^{II} is 9.10 Å. The shortest Co^{II} to Co^{III} distance in a unit is 4.97 Å. The interlayer separation between the Co^{II} ions is 9.18 Å. The separation distance between the Co^{II} and Co^{II} ions are important for the

Table A.6. Comparison of crystallographic data for **Co-TODA** at 15(2) K and 123(2) K

	15(2) K	123(2) K⁸⁸
Empirical formula	C ₄₂ H ₈₀ Co ₅ N ₁₈ O ₁₆	C ₄₂ H ₁₀₂ Co ₅ N ₁₈ O ₂₇
Fw	1387.89	1586.06
Temp (K)	15(2)	123(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> , Å	9.1821(12)	9.0980(3)
<i>b</i> , Å	14.181(2)	15.3049(6)
<i>c</i> , Å	23.781(3)	25.3271(8)
α , °	90	90
β , °	92.110(4)	90.4180(10)
γ , °	90	90
<i>V</i> , Å ³	3094.4(7)	3526.6(2)
<i>Z</i>	2	2
<i>D</i> _{calc} , g/cm ³	1.490	1.494
Crystal size (mm ³)	0.04 × 0.04 × 0.06	0.220 × 0.350 × 0.530
θ range (°)	0.972–17.206	2.604–27.453
Reflections collected	9294	8027
Independent reflections	99274 [<i>R</i> (int) = 0.0886]	29795 [<i>R</i> (int) = 0.0335]
Completeness to θ	98.9%, 17.206°	99.8%, 27.453°
GOF on <i>F</i> ²	1.084	1.055

Table A.6. Continued		
Final R indices	$R1 = 0.0874$	$R1 = 0.0735$
$[I > 2\sigma(I)]^a$	$wR2 = 0.2595$	$wR2 = 0.2138$
R indices (all data)	$R1 = 0.0931$ $wR2 = 0.2659$	$R1 = 0.0852$ $wR2 = 0.2233$
Largest diff. peak and hole, e.Å ⁻³	1.693 and -1.171	1.720 and -1.370

$$^a R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; R_w = (\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2])^{1/2}$$

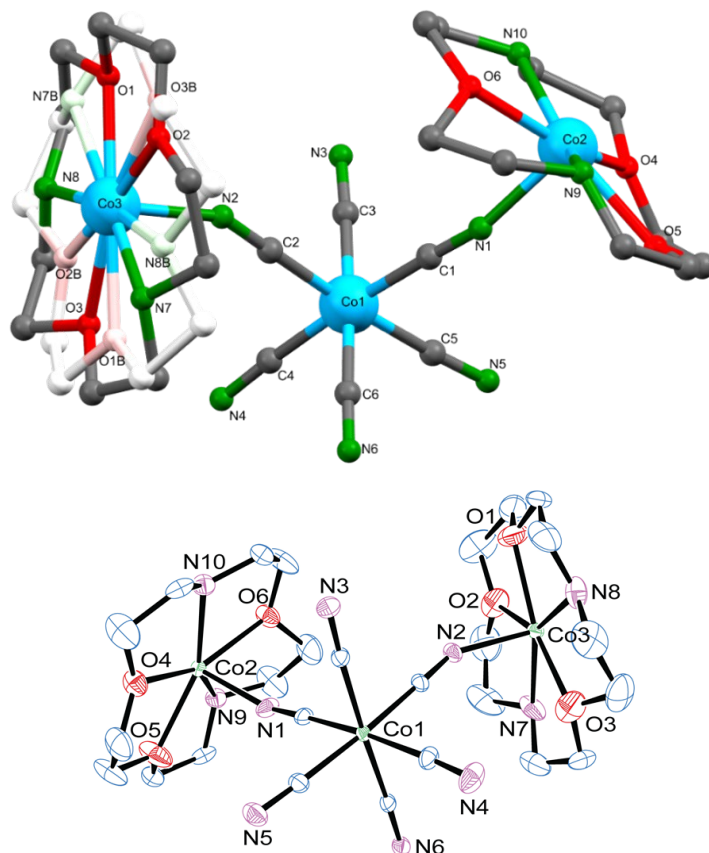


Figure A.6. Crystal structure of **Co-TODA** at 15(2) K. (Top) Disorder of one TODA ligand. The disordered position was contrasted in the fading of the TODA ligand in the background. The TODA ligands on both **Co2** and **Co3** are disordered. (Bottom) Selected bond lengths (Å) and bond angles (°): Co2-N1 2.052(4), Co2-N9 2.232(5), Co2-N10 2.216(5), Co2-O4 2.204(5), Co2-O5 2.228(5), Co2-O6 2.208(5), Co3-N2 2.063(4), Co3-N6 2.067(4), Co3-N7 2.215(5), Co3-N8 2.231(5), Co3-O1 2.212(5), Co3-O2 2.206(5), Co3-O3 2.221(5), O6-Co2-N10 72.8(3), N10-Co2-O4 74.7(3), O4-Co2-O5 73.2(3), O5-Co2-N9 70.5(3), N9-Co2-O6 71.3(3), N1-Co2-N9 101.6(3), N1-Co2-N10 92.5(3), N1-Co2-N9 78.4(3), N1-Co2-N10 87.53(3), O3-Co3-N7 73.4(3), N7-Co3-O2 75.2(3), O2-Co3-O1 70.0(3), O1-Co3-N8 71.7(3), N8-Co3-O3 70.5(3), N2-Co3-N7 91.4(2), N2-Co3-N8 93.9(2), N6-Co3-N7 84.4(2), N6-Co3-N8 86.6(2).

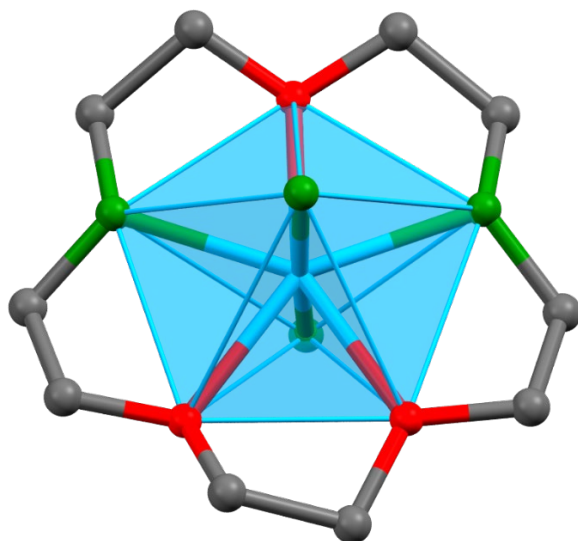


Figure A.7. Structure the **Co^{II}(TODA) (Co2)** moiety showing the pentagonal bipyramidal geometry. Red = O, green = N, Blue = Co^{II}. H atoms and the disordered atoms were omitted.

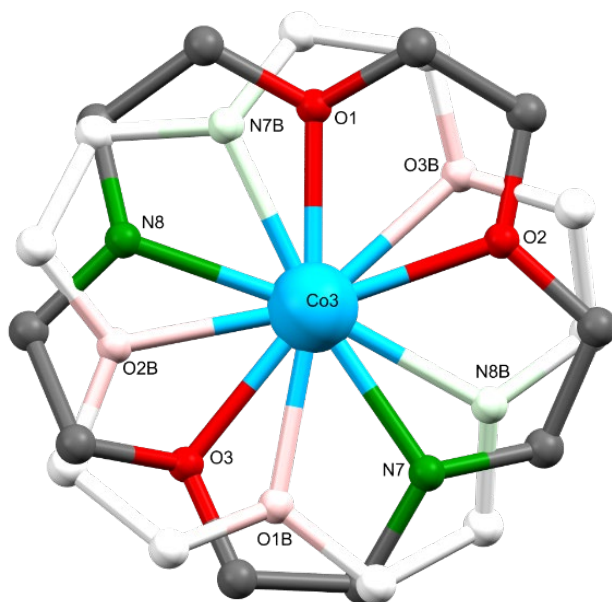


Figure A.8. Disordered $\text{Co}^{\text{II}}(\text{TODA})$ (Co3) moiety at 15(2) K. The disordered position was contrasted in the fading of the TODA ligand in the background. Two possible positions of the atoms of the TODA ligand were found in the crystal structure. H atoms were omitted for clarity.

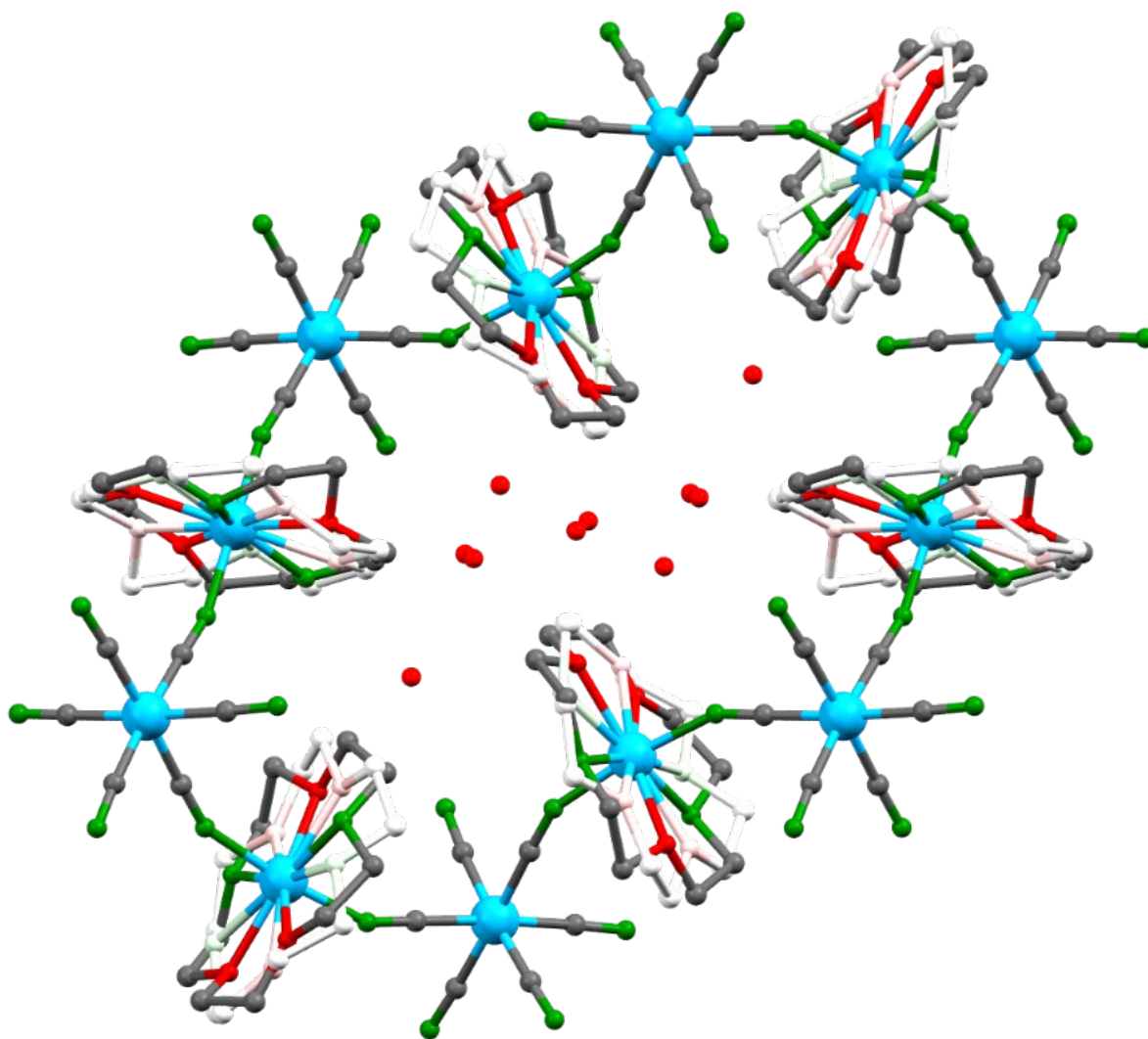


Figure A.9. Crystal structure of Co-TODA at 15(2) K showing the disorder and the lattice water molecules in the pore of the MOF. H atoms were omitted for clarity. Only one disordered TODA ligand is shown.

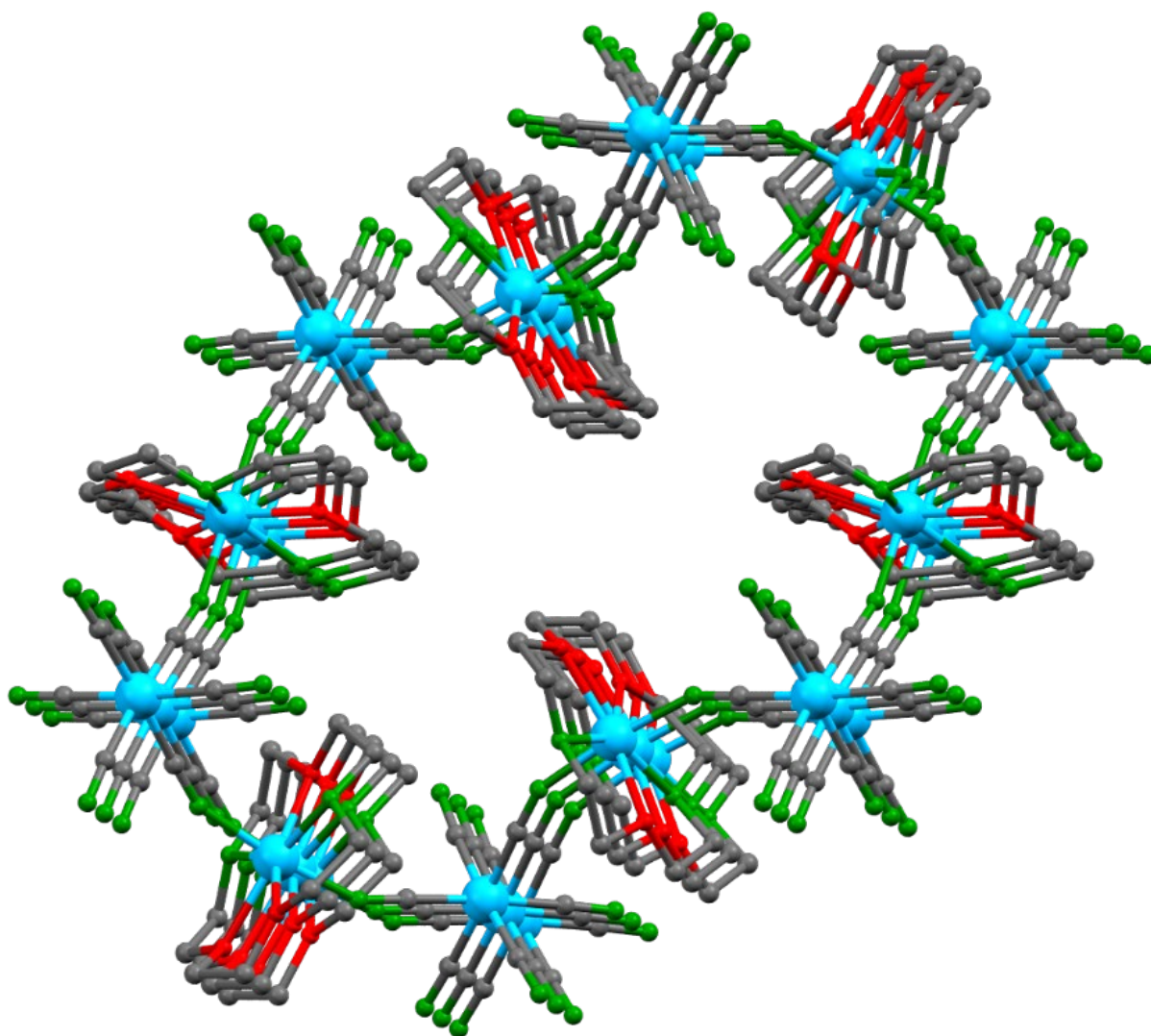


Figure A.10. Crystal structure of **Co-TODA** at 15(2) K showing multi-layer stacking of the MOF in the *a* axis. The disorders, lattice water molecules, and H atoms are omitted for clarity.

magnetic properties of **Co-TODA**. The larger the separation, the more isolated the individual Co^{II} ions are from each other, enhancing single-molecule magnet properties. The Co^{III} ions act as diamagnetic spacer between the paramagnetic Co^{II} ions, creating isolated $[\text{Co}^{\text{II}}(\text{TODA})]^{2+}$ units. All the TODA ligands are 2-fold disordered. There is a center of inversion on Co2, as shown in Figure 2.1-Left in the main text. The center of inversion at **Co2**, a Co^{II} ion, indicates that there are two different Co^{II} centers in the MOF.

Table A.6 gives a comparison of the crystallographic data at 15(2) K and 123(2) K. The unit cell shrinks at 15 K. The unit volume changes from 3526.6(2) Å³ to 3094.4(7) Å³, 12.3% reduction. Table A.7 shows a comparison of selected bond lengths and bond angles, showing no significant changes surrounding the Co^{II} centers at 15(2) K. Bond lengths at 15(2) K are slightly shorter than those at 123(2) K.

A4. Additional Results from Pulsed X-Band EPR Experiments

T_1 and T_2 times at four temperatures are listed in Table A.8. The pulsed X-band EPR experimental data (T_1 and T_2) for **Co-TODA** at 10(1) K, 20(1) K, and 30(1) K are given in Figure A.11, A.12, and A.13, respectively. The data at 5(1) K are in Chapter 2.

A5. Calculated Spin Densities in Co-TODA

The disorder in the original $P2_1/c$ (No. 14) crystal structure makes it impossible to conduct the VASP phonon and spin density calculations. Thus, the crystal symmetry was reduced to $P1$ (No. 1) to conduct the calculations. Co1-Co10 labels are shown in Figure A.16.

Table A.7. Comparison of selected bond lengths (Å) and bond angles (°) of **Co-TODA** at 15(2) K and 123(2) K. Atomic labeling in the two structures are different. The bond lengths and angles in the same rows are the same for comparison, although labeling may be different.

15 K		123 K	
Co2-N1	2.052(4)	Co2-N1	2.073(4)
Co2-N1	2.052(4)	Co2-N1	2.073(4)
Co2-N9	2.232(5)	Co2-N7	2.237(7)
Co2-N10	2.216(5)	Co2-N8	2.277(8)
Co2-O4	2.204(5)	Co2-O1	2.147(8)
Co2-O5	2.228(5)	Co2-O2	2.269(8)
Co2-O6	2.208(5)	Co2-O3	2.318(8)
Co3-N2	2.063(4)	Co3-N2	2.073(5)
Co3-N6	2.067(4)	Co3-N6	2.051(5)
Co3-N7	2.215(5)	Co3-N9	2.256(8)
Co3-N8	2.231(5)	Co3-N10	2.189(9)
Co3-O1	2.212(5)	Co3-O4	2.257(7)
Co3-O2	2.206(5)	Co3-O5	2.212(8)
Co3-O3	2.221(5)	Co3-O6	2.210(7)
O6-Co2-N10	72.8(3)	O1-Co2-N7	74.5(3)
N10-Co2-O4	74.7(3)	N7-Co2-O3	69.8(2)
O4-Co2-O5	73.2(3)	O3-Co2-O2	72.2(3)

Table A.7. Continued			
O5-Co2-N9	70.5(3)	O2-Co3-N8	71.7(3)
N9-Co2-O6	71.3(3)	N8-Co2-O1	74.9(3)
N1-Co2-N9	101.6(3)	N1-Co2-N7	93.1(2)
N1-Co2-N10	92.5(3)	N1-Co2-N8	86.8(3)
N1-Co2-N9	78.4(3)	N1-Co2-N7	93.1(2)
N1-Co2-N10	87.53(3)	N1-Co2-N8	86.8(3)
O3-Co3-N7	73.4(3)	O4-Co3-N9	70.7(3)
N7-Co3-O2	75.2(3)	N9-Co3-O6	73.5(3)
O2-Co3-O1	70.0(3)	O6-Co3-O5	70.6(3)
O1-Co3-N8	71.7(3)	O5-Co3-N10	73.1(3)
N8-Co3-O3	70.5(3)	N10-Co3-O4	72.8(3)
N2-Co3-N7	91.4(2)	N2-Co3-N9	89.4(3)
N2-Co3-N8	93.9(2)	N2-Co3-N10	92.0(4)
N6-Co3-N7	84.4(2)	N6-Co3-N9	87.1(3)
N6-Co3-N8	86.6(2)	N6-Co3-N10	90.5(4)

Table A.8. Values of T_1 and T_2 for the **Co-TODA** powder solid at 5(1), 10(1), 20(1) and 30(1) K

Temperature (K)	T_1 (μ s)	T_2 (μ s)
5(1)	235(4)	0.513(4)
10(1)	237(4)	0.498(4)
20(1)	209(4)	0.530(4)
30(1)	206(4)	0.550(4)

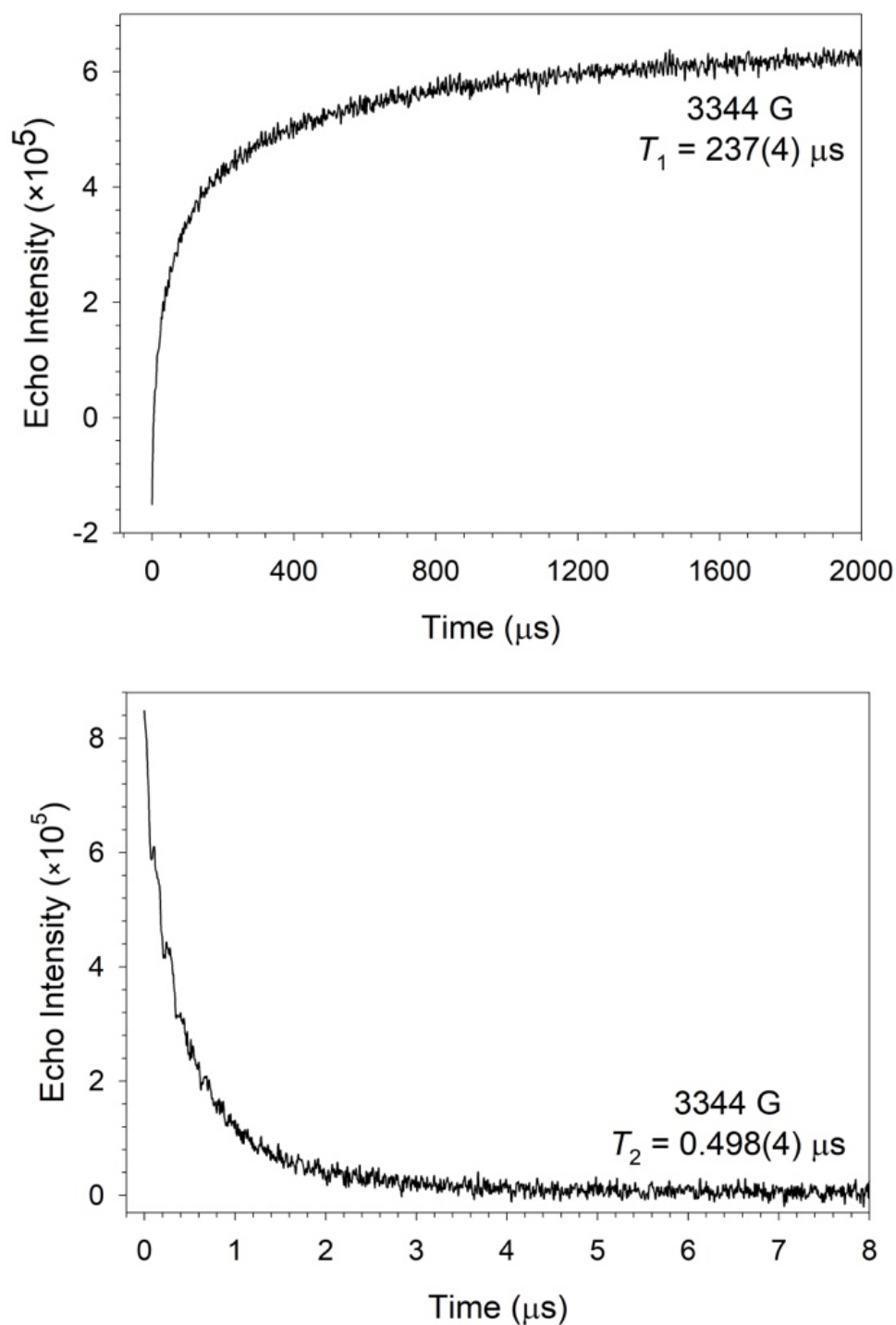


Figure A.11. Pulsed X-band EPR graphs at 10(1) K: (Top) Echo inversion recovery experiment; (Bottom) Hahn's echo decay experiment. External magnetic field = 3344(1) Gauss.

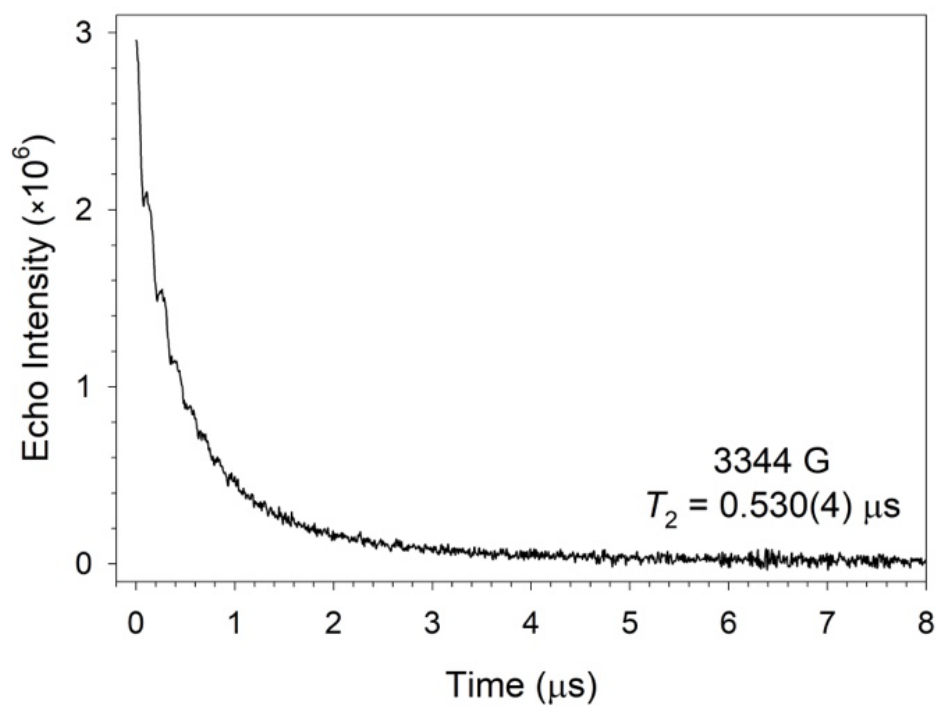
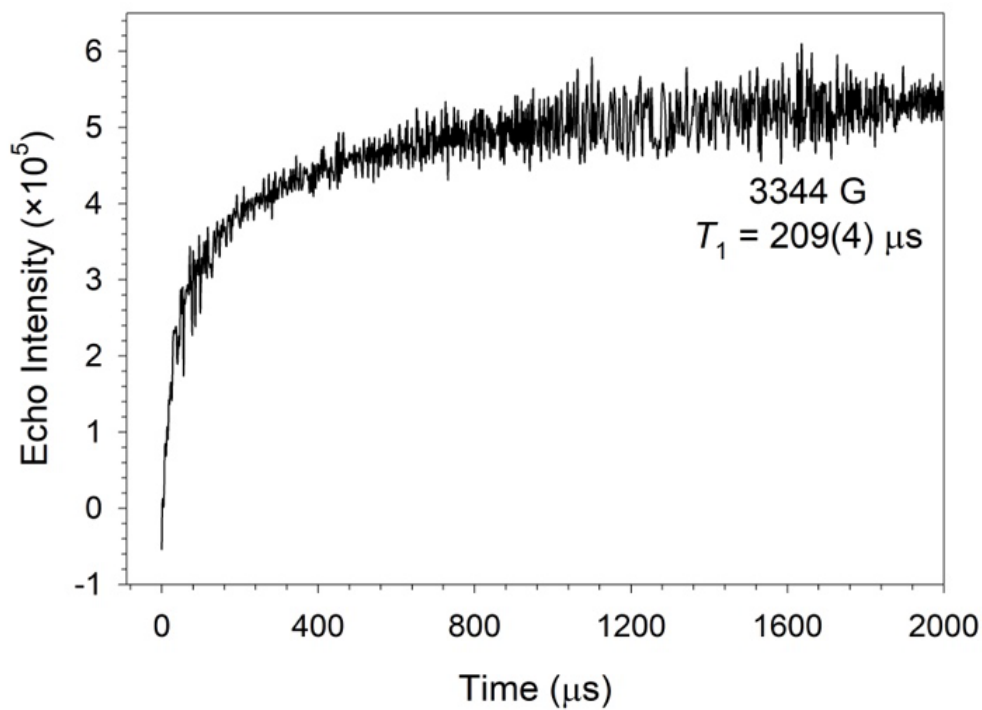


Figure A.12. Pulsed X-band EPR graphs at 20(1) K: (Top) Echo inversion recovery experiment; (Bottom) Hahn's echo decay experiment. External magnetic field = 3344(1) Gauss.

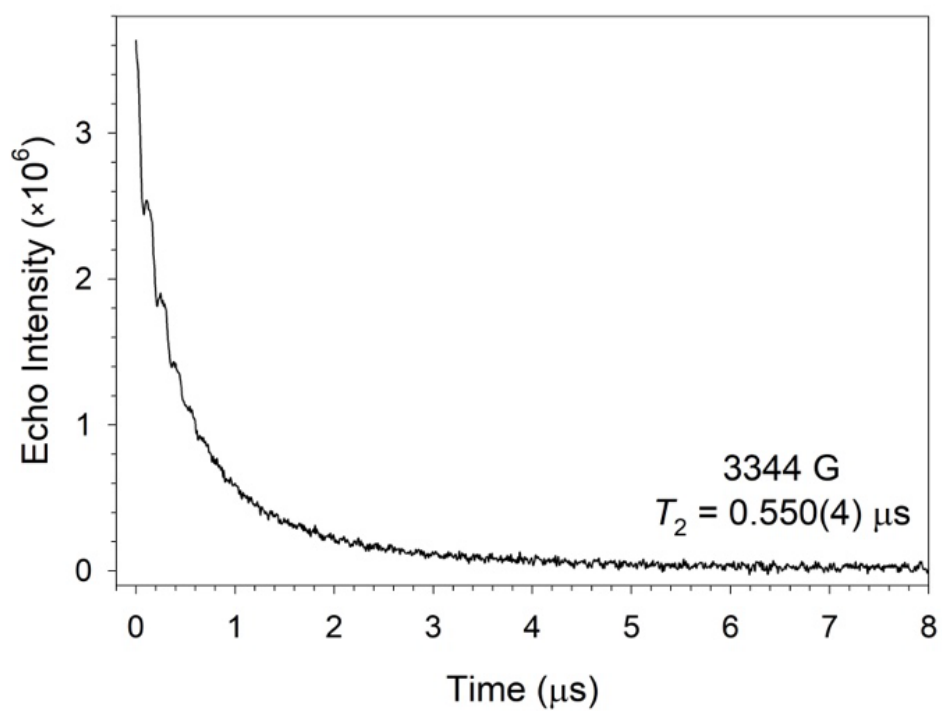
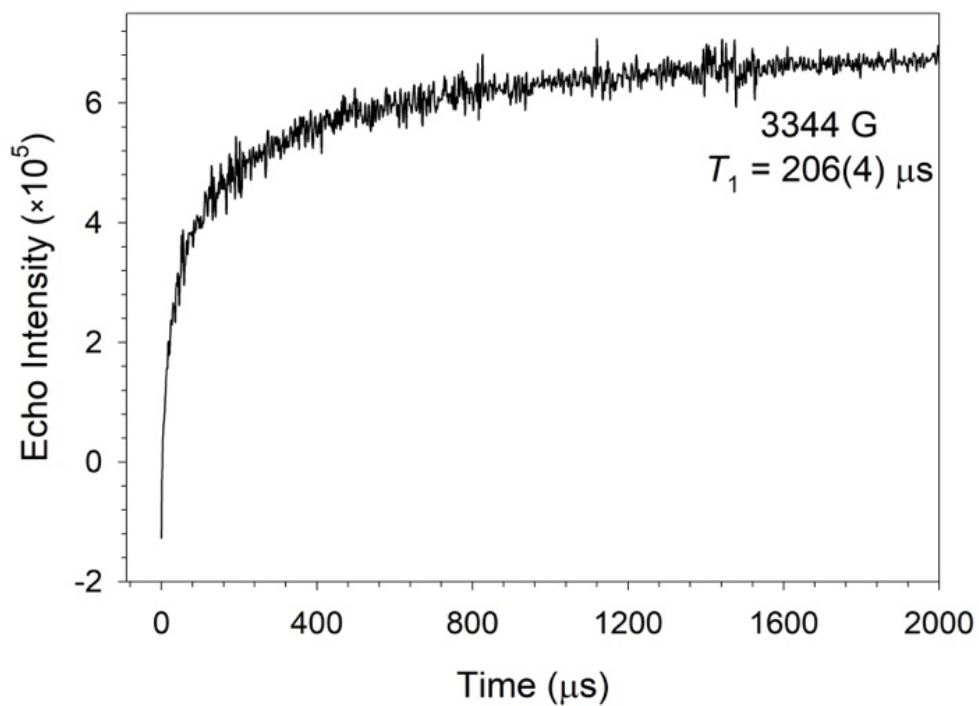


Figure A.13. Pulsed X-band EPR graphs at 30(1) K: (Top) Echo inversion recovery experiment; (Bottom) Hahn's echo decay experiment. External magnetic field = 3344(1) Gauss.

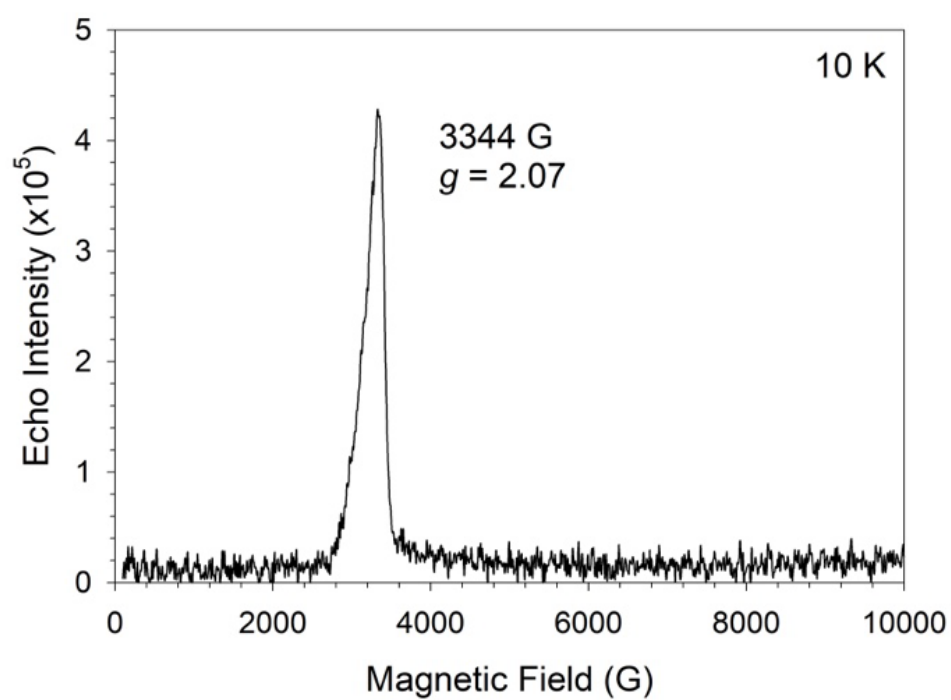
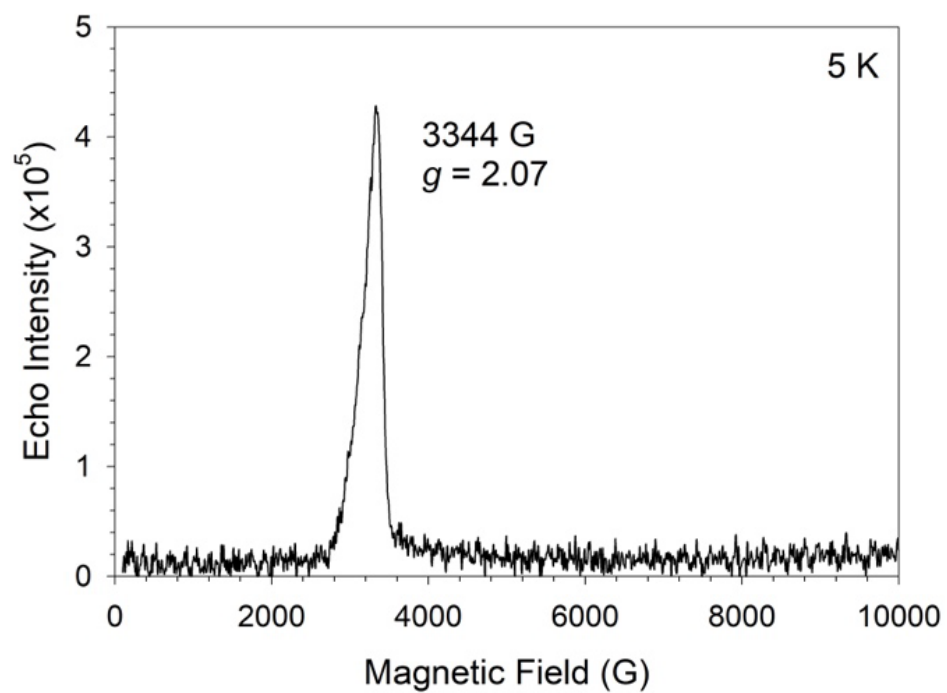


Figure A.14. Pulsed X-band EPR field swept echo graphs: (Top) 5(1) K; (Bottom) 10(1) K.

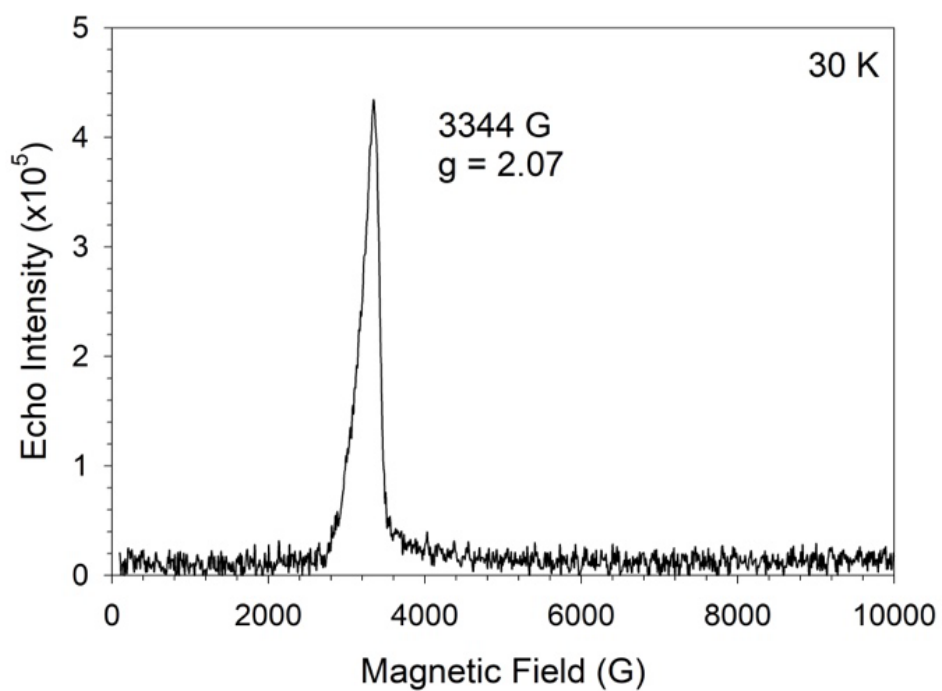
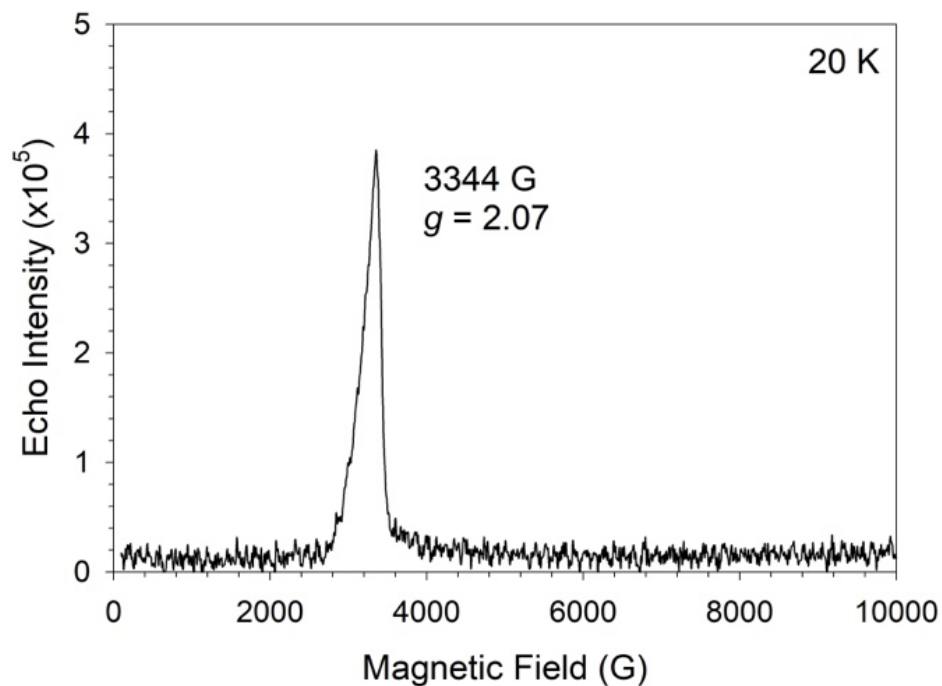


Figure A.15. Pulsed X-band EPR field swept echo graphs at 20(1) K and 30(1) K.

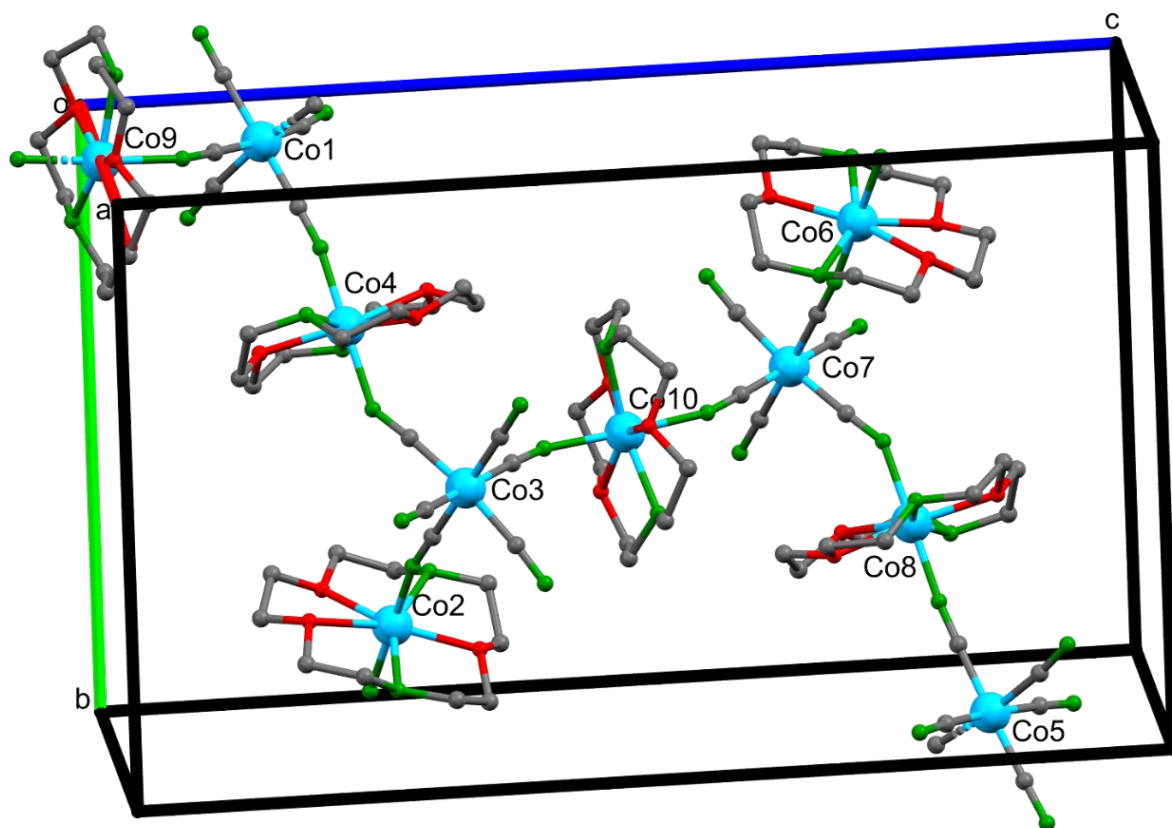


Figure A.16. *P1* structure used for VASP phonon and spin density calculations. A view down the *a* axis of the unit cell. Lattice water molecules, H atoms, and disordered components were omitted for clarity. Only Co1-Co10 are labeled. All atom labels are given in the *P1* CIF file.

Table A.9. Calculated spin densities of all atoms in the *P1* unit cell of **Co-TODA**

Atom	Spin Density	Atom	Spin Density
Co1	0.010293	H12	0.000962
Co2	2.690809	H13	-2.3×10^{-5}
Co3	0.01029	H14	0.001014
Co4	2.69109	H15	0.000685
Co5	0.010316	H16	-4.7×10^{-5}
Co6	2.692952	H17	0.001964
Co7	0.010307	H18	0.000315
Co8	2.692532	H19	0.000948
Co9	2.687921	H20	-8.6×10^{-5}
Co10	2.68799	H21	5.87×10^{-5}
O1	0.031695	H22	0.001536
O2	0.024277	H23	1.02×10^{-5}
O3	0.024686	H24	0.001009
O4	0.035667	H25	0.000657
O5	0.023172	H26	1.19×10^{-5}
O6	0.0215	H27	0.001407
O7	7.69×10^{-5}	H28	6.81×10^{-5}
O8	2.9×10^{-5}	H29	-0.00029
O9	6.62×10^{-5}	H30	0.00204
O10	0.000113	H31	0.0005

Table A.9. Continued			
O11	5.96×10^{-5}	H32	0.000549
O12	8.01×10^{-5}	H33	-4.5×10^{-5}
O13	7.46×10^{-5}	H34	-3.2×10^{-5}
O14	9.6×10^{-7}	H35	2.24×10^{-5}
O15	0.000169	H36	0.000784
O16	0.031651	H37	0.000454
O17	0.024294	H38	-4×10^{-5}
O18	0.024667	H39	0.001714
O19	0.035657	H40	0.000257
O20	0.023178	H41	9.09×10^{-6}
O21	0.021564	H42	2×10^{-8}
O22	7.55×10^{-5}	H43	4.13×10^{-6}
O23	2.86×10^{-5}	H44	9.8×10^{-7}
O24	6.7×10^{-5}	H45	-6.9×10^{-6}
O25	0.000116	H46	4.36×10^{-6}
O26	5.99×10^{-5}	H47	1.31×10^{-6}
O27	8.1×10^{-5}	H48	1.21×10^{-5}
O28	7.44×10^{-5}	H49	1.1×10^{-6}
O29	-1.8×10^{-7}	H50	4.2×10^{-7}
O30	0.000169	H51	5.5×10^{-7}

Table A.9. Continued			
O31	0.034733	H52	2.7×10^{-6}
O32	0.023538	H53	6.2×10^{-7}
O33	0.022636	H54	1.73×10^{-6}
O34	0.000101	H55	-5.8×10^{-7}
O35	3.22×10^{-5}	H56	-1.5×10^{-5}
O36	6.54×10^{-5}	H57	-2.4×10^{-6}
O37	9.81×10^{-5}	H58	5.7×10^{-6}
O38	8.22×10^{-5}	H59	-0.00022
O39	0.000209	H60	-8.7×10^{-5}
O40	7.74×10^{-5}	H61	2.28×10^{-5}
O41	4.88×10^{-6}	H62	0.001699
O42	0.000154	H63	3.38×10^{-5}
O43	0.034853	H64	0.000898
O44	0.02357	H65	0.000562
O45	0.022638	H66	2.23×10^{-5}
O46	0.000102	H67	0.001196
O47	3.18×10^{-5}	H68	0.000116
O48	6.43×10^{-5}	H69	0.001746
O49	9.33×10^{-5}	H70	0.00044
O50	8.4×10^{-5}	H71	0.000591

Table A.9. Continued			
O51	0.000211	H72	-3.8×10^{-5}
O52	7.73×10^{-5}	H73	3.49×10^{-5}
O53	7.55×10^{-6}	H74	0.000964
O54	0.00015	H75	-2.1×10^{-5}
N1	0.019245	H76	0.001013
N2	0.018035	H77	0.00069
N3	0.00027	H78	-4.7×10^{-5}
N4	-0.0001	H79	0.001965
N5	0.000218	H80	0.000321
N6	0.025113	H81	0.000948
N7	0.043315	H82	-8.1×10^{-5}
N8	0.043057	H83	5.72×10^{-5}
N9	0.04415	H84	0.001538
N10	0.047197	H85	1.02×10^{-5}
N11	0.019162	H86	0.001008
N12	0.018046	H87	0.000658
N13	0.000268	H88	1.18×10^{-5}
N14	-0.0001	H89	0.00141
N15	0.00022	H90	6.62×10^{-5}
N16	0.025103	H91	-0.00029
N17	0.043315	H92	0.002041

Table A.9. Continued			
N18	0.043082	H93	0.0005
N19	0.044105	H94	0.000551
N20	0.047137	H95	-4.5×10^{-5}
N21	0.020978	H96	-3.3×10^{-5}
N22	0.017931	H97	2.27×10^{-5}
N23	0.000308	H98	0.000786
N24	-0.00011	H99	0.000455
N25	0.000211	H100	-4×10^{-5}
N26	0.026817	H101	0.001714
N27	0.045433	H102	0.000259
N28	0.045294	H103	8.98×10^{-6}
N29	0.021095	H104	3×10^{-8}
N30	0.017958	H105	4.05×10^{-6}
N31	0.000304	H106	9.6×10^{-7}
N32	-0.00011	H107	-7.2×10^{-7}
N33	0.000218	H108	4.5×10^{-6}
N34	0.026747	H109	1.26×10^{-6}
N35	0.045528	H110	1.21×10^{-5}
N36	0.045434	H111	1.03×10^{-6}
C1	0.00053	H112	4×10^{-7}
C2	0.000297	H113	6.3×10^{-7}

Table A.9. Continued			
C3	0.001393	H114	2.82×10^{-6}
C4	0.000223	H115	6.7×10^{-7}
C5	-0.00062	H116	1.72×10^{-6}
C6	0.000571	H117	-7.6×10^{-7}
C7	0.000643	H118	-1.5×10^{-5}
C8	0.000505	H119	-2.4×10^{-6}
C9	0.000641	H120	5.75×10^{-6}
C10	-0.0005	H121	0.00059
C11	0.007198	H122	-3.6×10^{-5}
C12	0.006795	H123	3.33×10^{-5}
C13	0.000105	H124	0.001209
C14	0.0004	H125	0.001003
C15	-0.0002	H126	-7.9×10^{-5}
C16	0.002129	H127	7.19×10^{-5}
C17	0.000194	H128	0.001637
C18	0.000353	H129	1.08×10^{-5}
C19	0.001807	H130	0.000978
C20	-0.00029	H131	0.000652
C21	-0.00059	H132	4.29×10^{-6}
C22	0.000753	H133	0.001394
C23	0.001032	H134	4.05×10^{-5}

Table A.9. Continued			
C24	0.000303	H135	-0.0003
C25	0.000548	H136	0.001882
C26	-0.00072	H137	0.000449
C27	0.00054	H138	0.000553
C28	0.000292	H139	-3.7×10^{-5}
C29	0.001396	H140	3.44×10^{-5}
C30	0.000225	H141	-3.5×10^{-5}
C31	-0.00063	H142	0.000859
C32	0.000585	H143	0.000469
C33	0.000664	H144	-3.1×10^{-5}
C34	0.000497	H145	0.001813
C35	0.000631	H146	0.000323
C36	-0.00049	H147	8.82×10^{-6}
C37	0.007228	H148	-1.4×10^{-7}
C38	0.006754	H149	3.58×10^{-6}
C39	0.000108	H150	2.17×10^{-6}
C40	0.000399	H151	-8.1×10^{-7}
C41	-0.0002	H152	3.29×10^{-6}
C42	0.002165	H153	-3.1×10^{-7}
C43	0.000195	H154	5.49×10^{-6}
C44	0.00036	H155	5×10^{-7}

Table A.9. Continued			
C45	0.001803	H156	1.07×10^{-6}
C46	-0.00029	H157	3.03×10^{-6}
C47	-0.00059	H158	7.12×10^{-6}
C48	0.000752	H159	3.4×10^{-7}
C49	0.001033	H160	1.98×10^{-6}
C50	0.000301	H161	-1.5×10^{-5}
C51	0.000547	H162	1.85×10^{-6}
C52	-0.00072	H163	-2.4×10^{-6}
C53	0.004952	H164	2.97×10^{-6}
C54	0.006736	H165	0.001001
C55	8.3×10^{-5}	H166	-7.5×10^{-5}
C56	0.000392	H167	6.19×10^{-5}
C57	-0.00012	H168	0.001631
C58	0.000164	H169	1.09×10^{-5}
C59	7.62×10^{-5}	H170	0.00098
C60	0.000483	H171	0.000647
C61	0.001645	H172	5.2×10^{-6}
C62	-0.00029	H173	0.001386
C63	-0.0004	H174	4.47×10^{-5}
C64	0.000514	H175	-0.00031
C65	0.000536	H176	0.001878

Table A.9. Continued			
C66	0.000942	H177	0.000445
C67	0.001214	H178	0.000554
C68	-0.00088	H179	-3.7×10^{-5}
C69	0.004827	H180	4.03×10^{-5}
C70	0.006681	H181	-3.5×10^{-5}
C71	7.89×10^{-5}	H182	0.000854
C72	0.000397	H183	0.000464
C73	-0.00012	H184	-2.5×10^{-5}
C74	0.000251	H185	0.001806
C75	6.77×10^{-5}	H186	0.000328
C76	0.000501	H187	8.06×10^{-6}
C77	0.001659	H188	-1.2×10^{-7}
C78	-0.0003	H189	3.52×10^{-6}
C79	-0.00038	H190	2.16×10^{-6}
C80	0.000503	H191	-8×10^{-7}
C81	0.000505	H192	3.28×10^{-6}
C82	0.000963	H193	-3.5×10^{-7}
C83	0.001241	H194	5.14×10^{-6}
C84	-0.0009	H195	6.2×10^{-7}
H1	-0.00022	H196	1.23×10^{-6}
H2	-7.60×10^{-5}	H197	3.2×10^{-6}

Table A.9. Continued			
H3	2.30×10^{-5}	H198	6.3×10^{-6}
H4	0.001698	H199	2.8×10^{-7}
H5	0.0009	H200	2.16×10^{-6}
H6	0.000563	H201	-1.4×10^{-5}
H7	2.05×10^{-5}	H202	1.88×10^{-6}
H8	0.00011	H203	-2.6×10^{-6}
H9	0.001745	H204	2.98×10^{-6}
H10	0.000445	Total	17.616
H11	3.99×10^{-5}		

A6. Additional Calculated INS and Experimental INS Results

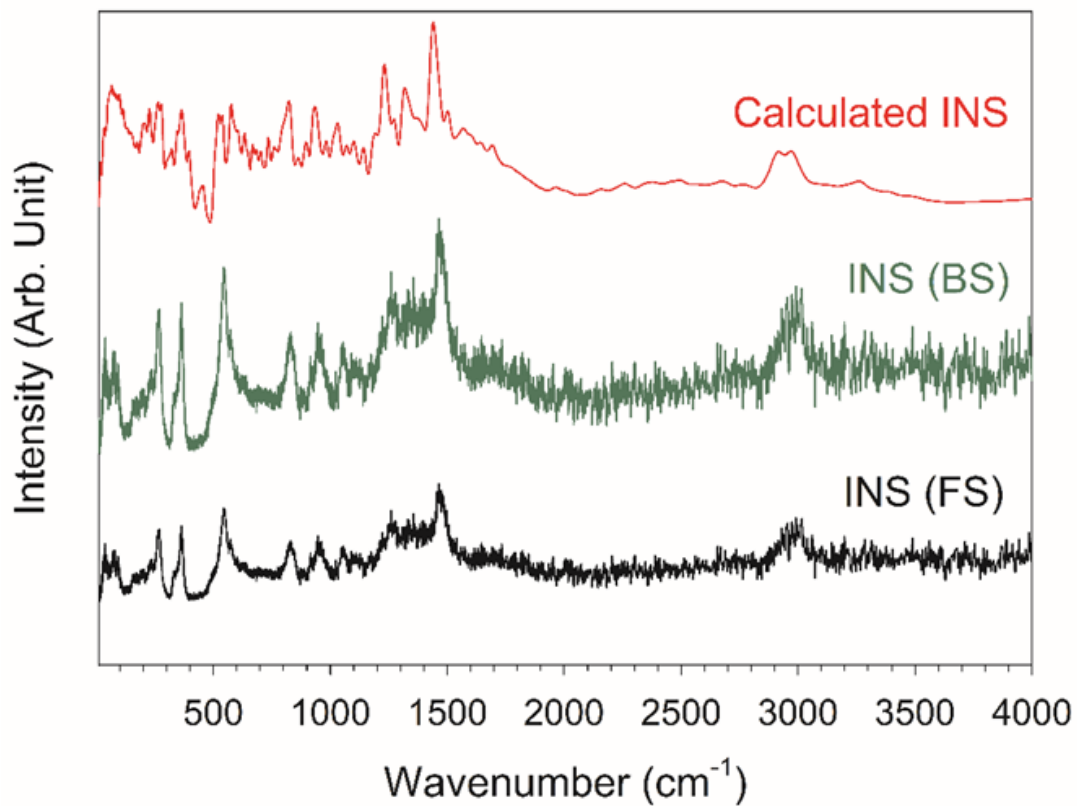


Figure A.17. Comparison range of 10-4000 cm⁻¹ between calculated INS spectrum (red) and experimental INS spectrum at 5.0(5) K [forward scattering (FS, black) and back scattering (BS, green)].

Appendix B. Supporting Information for Chapter 3

B1. Synthesis of $[Co(\mu\text{-bpeb})_2(NCS)_2]_n \bullet nG$ (Co-BEBN), Growth of Its Single Crystals, and Synthesis of Co-BEBN_{0.05}

The ligand 1,4-bis(pyridine-4-ylethynyl)benzene (bpeb) was prepared by a literature method.³¹⁹ The chemicals used in the synthesis of **Co-BEBN** and bpeb were purchased commercially and used without further purification. Cobalt(II) thiocyanate $[Co(SCN)_2]$, 98+%, Alfa Aesar; 4-Ethynylpyridine $[C_7H_5N]$, 95%, Enamine; Copper(I) bromide $[CuBr]$, 98%, Strem Chemicals, INC.; 1,4-Diiodobenzene $[C_6H_4I_2]$, 98%, Alfa Aesar; Zinc thiocyanate $[Zn(SCN)_2]$, 99.4%, Chemsavers; 1,2-Dichlorobenzene $[C_6H_4Cl_2]$, >99.0%, TCI; Methanol $[CH_3OH]$, 99.8%, Fisher Chemical].

Single-crystal samples of **Co-BEBN** were prepared by a three-layered method. A pink solution of 0.0019 g of cobalt(II) thiocyanate $[Co(SCN)_2]$, 0.010 mmol in 10 mL of MeOH was layered on top of a yellow solution of 0.0634 g of bpeb ligand $[C_{20}H_{12}N_2]$, 0.226 mmol in 8 mL of 1,2-dichlorobenzene and 2 mL of methanol. A buffer layer (middle layer) is a mixture of 5 mL of 1,2-dichlorobenzene and 5 mL of methanol. The three-layered mixture was placed in a glass vial. The reaction was left to grow single crystals at room temperature for up to 10 days. The longer the reaction is left to react, the larger the size of the single crystals. Orange block-shaped crystals were observed in the buffer layer in a couple of days. The orange crystals are sensitive to the environment. If the crystals are left out of the mother solution (a mixture of 1,2-dichlorobenzene and methanol) and let dry in air, the orange block-shaped crystals turn into gray polycrystalline (powder) sample. Determination of the yield was not possible due to the loss of

1,2-dichlorobenzene when crystals are outside of the mother solution. Single-crystal X-ray diffraction studies are given in Experimental Methods.

Polycrystalline samples of 95% Zn^{II} -containing **Co-BEBN**_{0.05} were prepared through a similar method. Instead of using 100% (0.010 mmol) of $\text{Co}(\text{SCN})_2$, a mixture of 95% (0.0017 g, 0.0095 mmol) of $\text{Zn}(\text{SCN})_2$ and 5% (0.00009 g, 0.0005 mmol) of $\text{Co}(\text{SCN})_2$ was used in the reaction.

B2. Additional Crystal Structural Data for $[\text{Co}(\mu\text{-bpeb})_2(\text{NCS})_2]_n \cdot n\text{G}$ (Co-BEBN)

Table B.1. Comparison of crystallographic data for **Co-BEBN** at 100(2) K between the reported¹⁷⁸ and current structure

	Current Studies	Reported¹⁷⁸
Empirical formula	$\text{C}_{66}\text{H}_{40}\text{Cl}_8\text{CoN}_6\text{S}_2$	$\text{C}_{84}\text{H}_{52}\text{Cl}_{14}\text{CoN}_6\text{S}_2$
Formula weight	1323.69	1764.66
Temperature (K)	100(2)	100(2)
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
a , Å	17.3276(4)	13.593(5)
b , Å	20.9222(5)	17.194(5)
c , Å	17.1575(4)	18.450(5)
α , °	90	99.319(5)
β , °	97.7120(10)	100.076(5)
γ , °	90	107.842(5)
V , Å ³	6163.9(3)	3933(2)
Z	4	2
D_{calc} , g/cm ³	1.426	1.490
Crystal size (mm ³)	N/A	$0.16 \times 0.18 \times 0.20$
θ range (°)	2.396–31.534	2.30–20.74
Reflections collected	10265	8262

Table B.1. Continued		
Independent reflections	33431 [$R(\text{int}) = 0.0221$]	59588 [$R(\text{int}) = 0.0728$]
Completeness to θ	99.9%, 31.502°	98.6%, 20.45°
GOF on F^2	1.021	2.434
Final R indices	$R1 = 0.0332$	$R1 = 0.2181$
$[I > 2\sigma(I)]^a$	$wR2 = 0.0825$	$wR2 = 0.5409$
R indices (all data)	$R1 = 0.0404$	$R1 = 0.2422$
	$wR2 = 0.0878$	$wR2 = 0.5584$
Largest diff. peak and hole, e.Å ⁻³	1.129 and -0.752	4.151 and -1.015

$$^a R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; R_w = (\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2])^{1/2}$$

Table B.2. Selected bond length and bond angles of Co^{II} ion local symmetry in **Co-BEBN**

Bond Lengths (Å)			
Current Studies		Reported¹⁷⁸	
Co1-N2	2.0877(11)	Co1-N1S	2.096(15)
Co1-N2	2.0877(11)	Co1-N1S	2.096(15)
Co1-N1	2.1554(10)	Co1-N4	2.237(11)
Co1-N1	2.1555(10)	Co1-N4	2.237(11)
Co1-N3	2.1751(14)	Co1-N1	2.248(9)
Co1-N4	2.1917(14)	Co1-N1	2.248(9)
Bond Angles (°)			
Current Studies		Reported¹⁷⁸	
N2-Co1-N2	179.16(6)	N1S-Co1-N1S	180.0
N2-Co1-N1	88.80(4)	N1S-Co1-N4	89.7(4)
N2-Co1-N1	91.21(4)	N1S-Co1-N4	90.3(4)
N2-Co1-N1	91.21(4)	N1S-Co1-N4	90.3(4)
N2-Co1-N1	88.79(4)	N1S-Co1-N4	89.7(4)
N1-Co1-N1	179.65(5)	N4-Co1-N4	180.0
N2-Co1-N3	90.42(3)	N1S-Co1-N1	92.8(4)
N2-Co1-N3	90.42(3)	N1S-Co1-N1	87.2(4)
N1-Co1-N3	89.82(3)	N4-Co1-N1	87.0(4)
N1-Co1-N3	89.82(3)	N4-Co1-N1	93.0(4)

Table B.2. Continued			
N2-Co1-N4	89.58(3)	N1S-Co1-N1	87.2(4)
N2-Co1-N4	89.58(3)	N1S-Co1-N1	92.8(4)
N1-Co1-N4	90.18(3)	N4-Co1-N1	93.0(4)
N1-Co1-N4	90.18(3)	N4-Co1-N1	87.0(4)
N3-Co1-N4	180.0	N1-Co1-N1	180.0

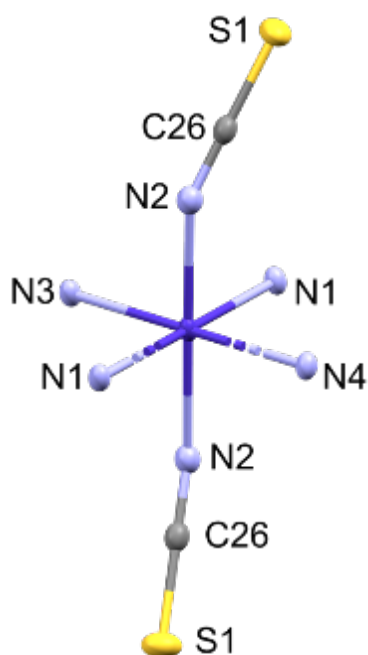


Figure B.1. Local symmetry of a Co^{II} ion in **Co-BEBN**. Atom N1, N3, and N4 are of the bpeb ligands in the x - y plane, while atom N2 are of the NCS ligands in the z -axis. Dark Purple: Co; Light purple: N; Yellow: S; Gray: C. Hydrogens are omitted for clarity.

B3. Magnetic Susceptibility (AC and DC) Data

Alternate current (AC) magnetic susceptibility measurements were conducted for **Co-BEBN** to probe the single-ion magnet (SIM) properties. It should be noted that, for **Co-BEBN-polymorph**, Vallejo, Pardo, Cano, and coworkers have reported DC and AC magnetic susceptibility studies, showing that **Co-BEBN-polymorph** has SIM behaviors.¹⁷⁸ Since **Co-BEBN** has a different structure and possibly different properties, its magnetic susceptibility properties have been investigated.

The measurements were performed at the temperature range between 2 and 10 K. Powder sample of **Co-BEBN** was used in the measurements by grinding the single crystals into fine powders. A couple drops of 1,2-dichlorobenzene were placed onto the powder sample to keep the sample from drying out in air. The “wet” powder samples were placed into a folded piece of weight paper with the help of some grease. The folded paper was placed into the middle of a plastic straw for mounting onto the instrument. The instrument used was the Superconducting Quantum Interference Device (SQUID) magnetometer by Quantum Design.

Temperature dependence of magnetization under 0.1 T were taken from 2 to 10 K. The in-phase magnetization of **Co-BEBN** shows a peak around 3.5 K at 119 Hz. The peak is moved to higher temperature (~5.5 K) as the frequency increases up to 1512 Hz. The frequency and temperature-dependent peak is the characteristic of a SIM at temperature below 10 K. Figure B.2-Top shows the in-phase magnetic susceptibility graph. Figure B.2-Bottom shows the out-of-phase magnetic susceptibility graph. The out-of-phase data shows a similar peak at temperature <2 K at 119 Hz. The peak moves to higher temperature as the frequency increases. The same SIM characteristic can be observed in the out-of-phase data. There are fluctuations in the data

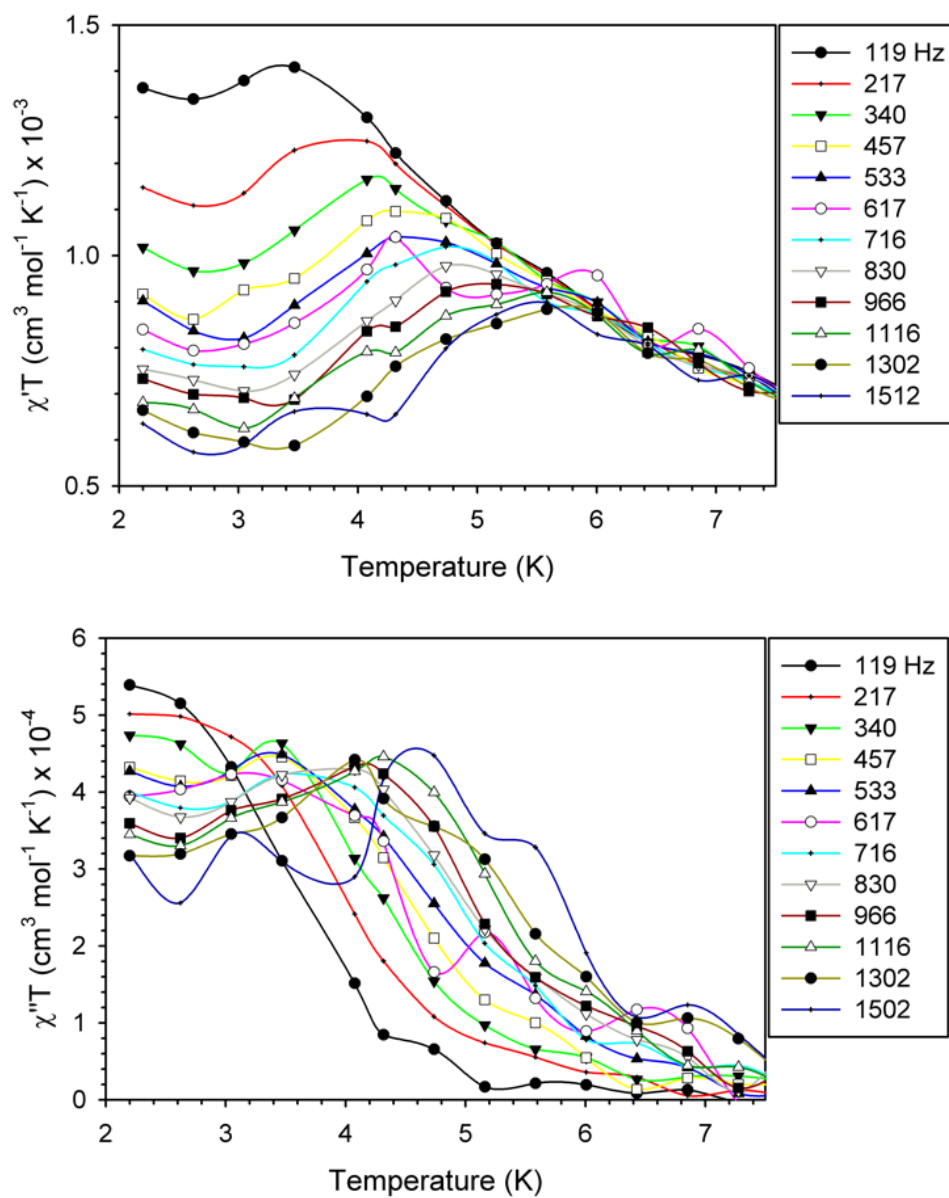


Figure B.2. (Top) Temperature-dependent AC magnetic susceptibility in-phase data of Co-BEBN. (Bottom) Temperature-dependent AC magnetic susceptibility out-of-phase data.

points across multiple frequencies for both the in-phase and the out-of-phase data. The reason for the fluctuation is due to temperature fluctuation that occurred in the instrument as well as a possible slight movement of the sample inside the sample mount. A background subtraction of the diamagnetic contribution from the weight paper, grease, and the solvent were corrected for the data.

Direct current (DC) magnetic susceptibility measurements were conducted for **Co-BEBN** to understand the magnetic interaction of the system. The data in Figure B.3 shows temperature-dependent data at 0.1 T from 1.8 to 200 K. The magnetic susceptibility increases as the temperature increases. The magnetic susceptibility value plateaued around 150 K at $2.65 \text{ cm}^3 \text{ mol}^{-1} \text{ K}^{-1}$. The value corresponds closely to the value of an $S = 3/2$ system. The fluctuation of the data points below 20 K is due to the temperature fluctuation originating from the instrument during measurements.

B4. Additional Inelastic Neutron Scattering (INS) Data and Phonon Calculations

The phonon calculation fits generally well to the experimental INS spectrum at 5 K in the full spectrum from 10 to 5000 cm^{-1} . However, there are some differences between the experimental and calculated phonon peaks. As shown in Figure B.4, the experimental phonon peak at $\sim 2400 \text{ cm}^{-1}$ is not observed in the calculated spectrum. The differences can be attributed to the single-crystal structure of **Co-BEBN** not being perfectly completed or that there are some contaminations in the solvent (1,2-dichlorobenzene) used in the INS experiments. The same peak is observed in the experimental solvent spectrum. Figure B.5 shows the comparison in the 0- 1500 cm^{-1} range.

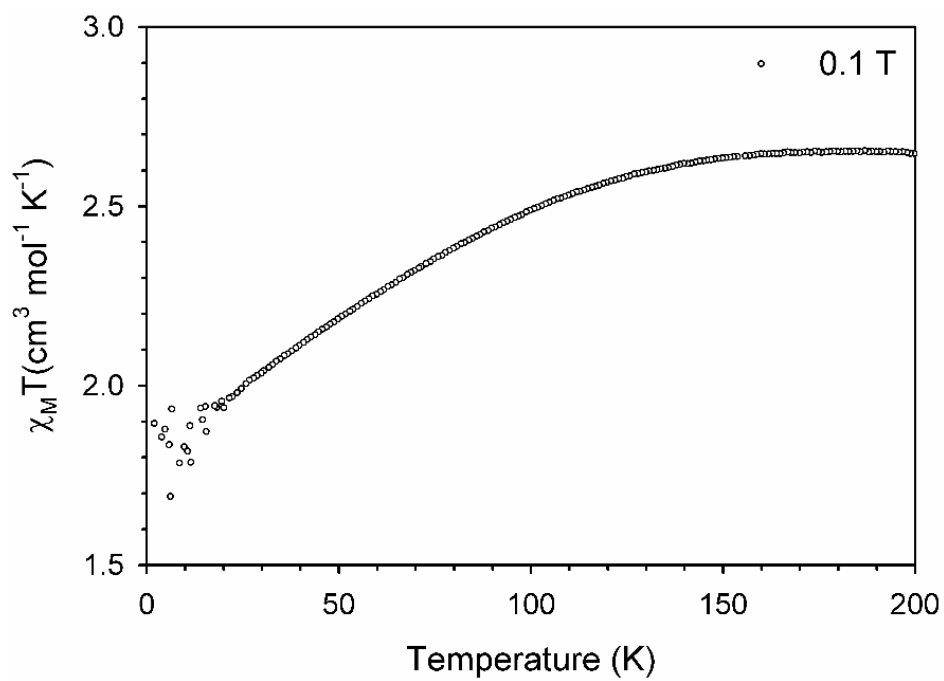


Figure B.3. Temperature-dependent DC magnetic susceptibility of **Co-BEBN**.

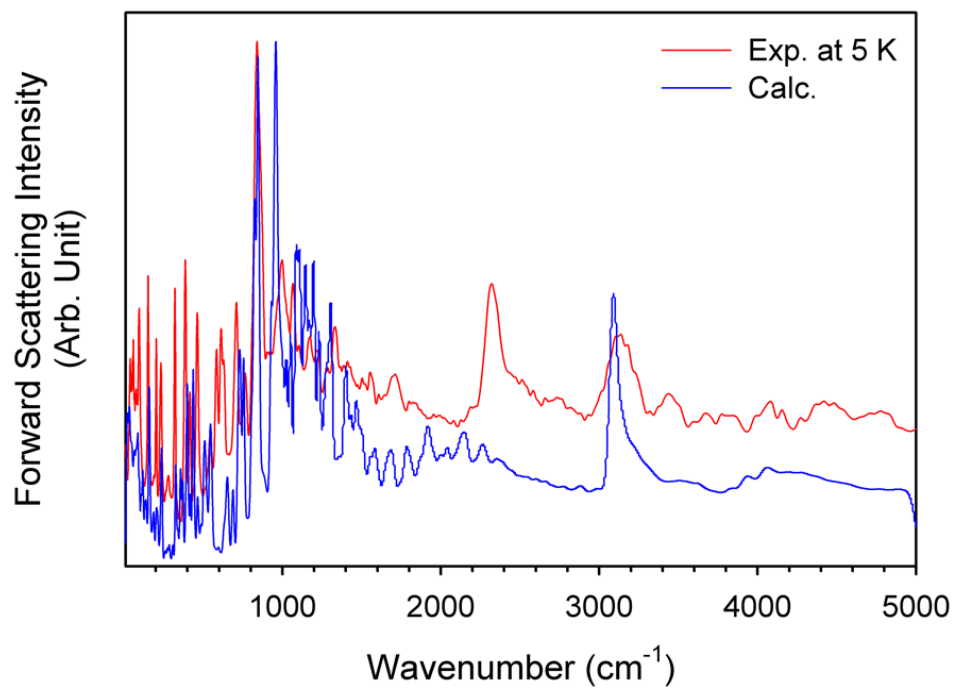


Figure B.4. Comparison between experimental INS spectrum at 5 K and calculated phonon spectrum from 10 to 5000 cm⁻¹.

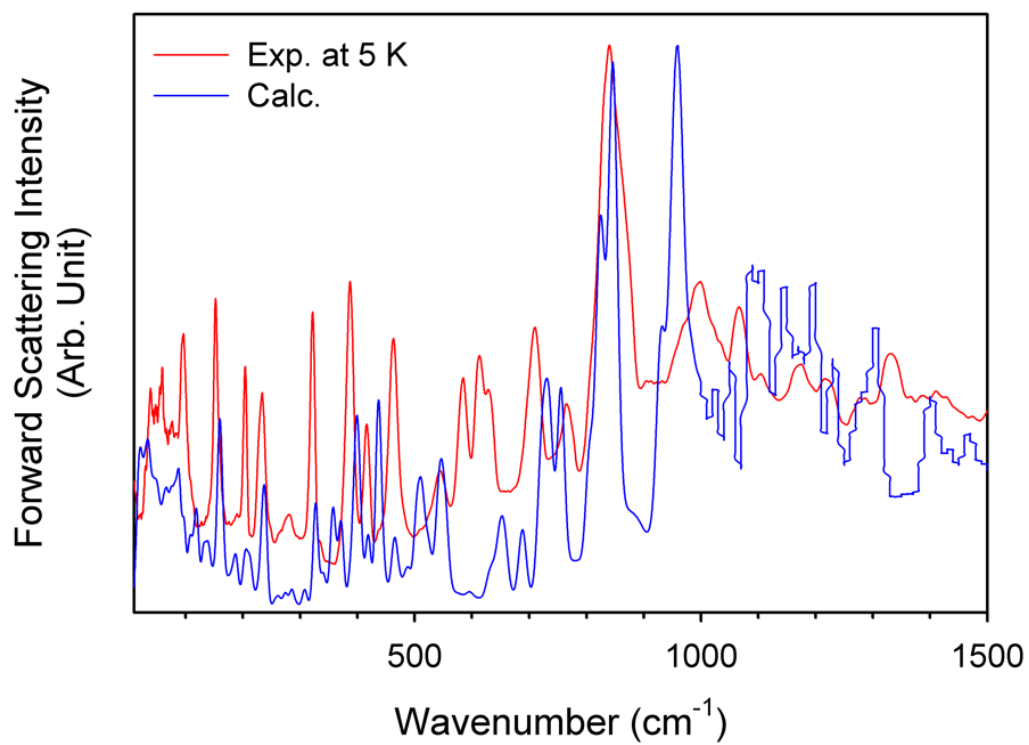


Figure B.5. Comparison between experimental INS spectrum at 5 K and calculated phonon spectrum from 10 to 1500 cm^{-1} .

B5. Additional Data from the Electronic Structure Calculations

For grid-like compound of **Co-BEBN**, we extracted one type of one-core unit. Complete active space second-order multiconfigurational perturbation theory (CASPT2) considering the effect of the dynamic electron correlation based on complete-active-space self-consistent field (CASSCF) method with MOLCAS 8.4 program package¹¹⁶ was performed on the basis of single-crystal X-ray determined geometries of **Co-BEBN**. See Figure B.6 for the calculated model structures.

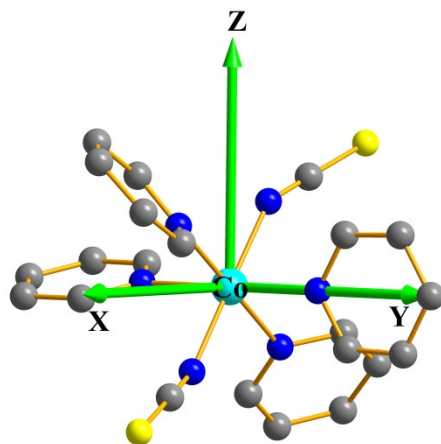


Figure B.6. Calculated model structure of individual Co^{II} fragment. H atoms are omitted for clarity.

Table B.3. Calculated spin-free energies (cm^{-1}) of the lowest ten terms ($S = 3/2$) of the Co^{II} ions of **Co-BEBN** using CASPT2/RASSI-SO with MOLCAS 8.4

Spin-free states	Energy (cm^{-1})
1	0.0
2	163.3
3	775.4
4	9507.5
5	9628.4
6	9955.7
7	20019.6
8	20794.6
9	21823.8
10	22587.1

Table B.4. Calculated weights of the five most important spin-orbit-free states for the lowest two spin-orbit states of **Co-BEBN** using CASPT2/RASSI-SO with MOLCAS 8.4

Spin-orbit states	Energy (cm ⁻¹)	Spin-free states, Spin, Weights				
1	0.0	1,1.5,0.5674	2,1.5,0.3492	3,1.5,0.0805	6,1.5,0.0007	22,0.5,0.0006
2	242.5	1,1.5,0.7380	2,1.5,0.2053	3,1.5,0.0534	4,1.5,0.0014	6,1.5,0.0005

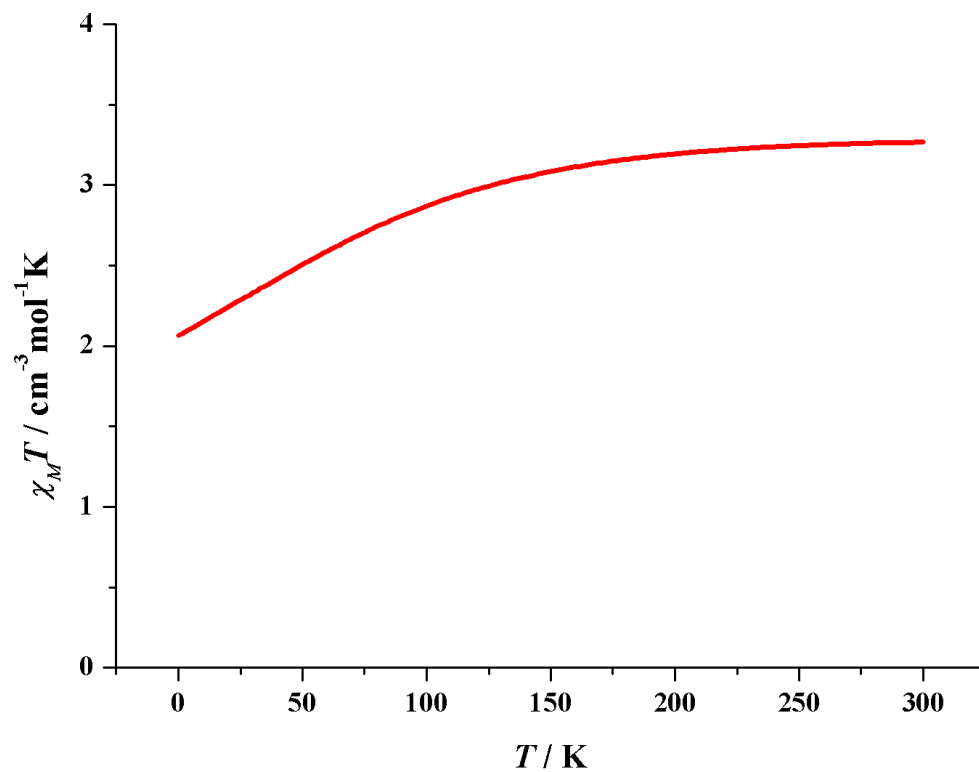


Figure B.7. Calculated (red solid line) data of magnetic susceptibilities of **Co-BEBN** using CASPT2/RASSI-SO with MOLCAS 8.4.

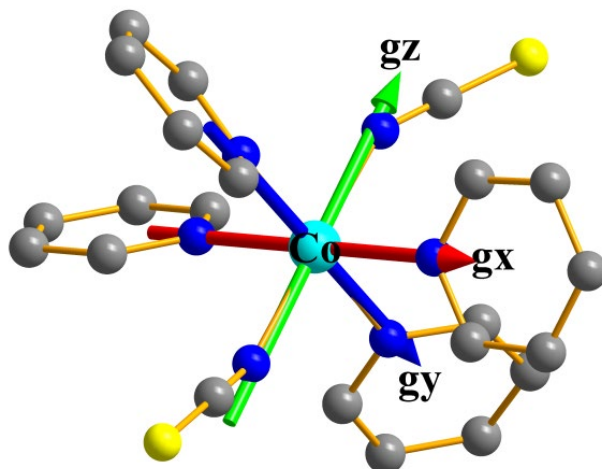


Figure B.8. Orientations of the local magnetic axes (red: g_x ; blue: g_y ; green: g_z) on Co^{II} ions of **Co-BEBN** in their ground spin-orbit states using CASPT2/RASSI-SO with MOLCAS 8.4.

Table B.5. Contributions of the excited states (with relative energy cm^{-1}) to D values (cm^{-1}) for **Co-BEBN** using NEVPT2 with ORCA 4.2

State No.	Multiplicity	Energy (cm^{-1})	Contribution (cm^{-1})
			D
1	4	133.6	60.4
2	4	609.5	30.2

Table B.6. Relative energies (cm^{-1}) of ligand field one-electron states (in the basis of d -AOs) of **Co-BEBN** from AILFT analysis using NEVPT2 with ORCA 4.2

No.	LF one-electron state	Energy (cm^{-1})
1	$-0.99 d_{yz}$	0.0
2	$-0.99 d_{xz}$	663.8
3	$0.99 d_{xy}$	868.8
4	$0.97 d_{z^2} + 0.23 d_{x^2-y^2}$	8391.3
5	$0.97 d_{x^2-y^2}$	9510.6

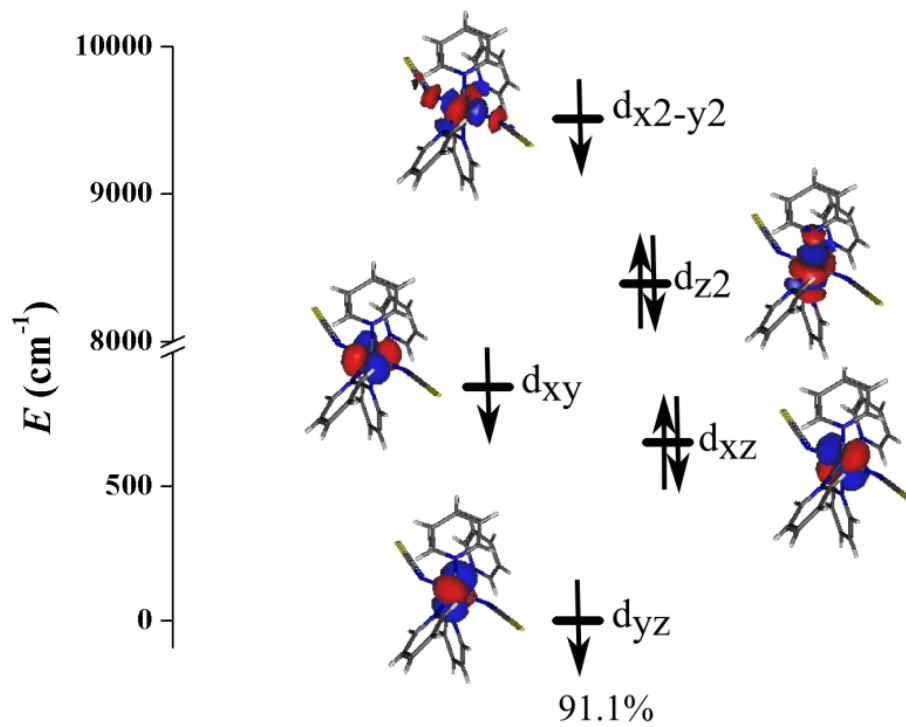


Figure B.9. Orbital energies computed for the ground states of Co-BEBN using NEVPT2 with ORCA 4.2. The percentages reveal the percents of the corresponding configuration mixings.

$d_{x^2-y^2}$	$\uparrow$	$d_{x^2-y^2}$	$\uparrow$
d_{z^2}	$\uparrow$	d_{z^2}	$\uparrow\downarrow$
d_{xy}	$\uparrow$	d_{xy}	$\uparrow$
d_{xz}	$\uparrow\downarrow$	d_{xz}	$\uparrow$
d_{yz}	$\uparrow\downarrow$	d_{yz}	$\uparrow\downarrow$
1st	88.8%	2nd	87.3%

Figure B.10. Multi-determinant wavefunction of the selected excited states having important contributions to D tensor for **Co-BEBN**. The computed CI coefficients that are larger than 10% are shown above.

B6. Phonon Symmetries

Table B.7. Calculated phonon symmetries and modes of Co-BEBN

Wavenumber (cm ⁻¹)	Symmetries of the modes	Wavenumber (cm ⁻¹)	Symmetries of the modes
16.183	B_g	846.233	A_g
19.086	A_g	846.933	B_u
20.036	B_u	847.386	B_g
22.333	A_u	849.038	A_u
22.345	B_g	849.101	A_g
23.341	B_u	850.947	A_u
23.437	A_g	851.255	A_g
24.144	A_u	851.289	B_u
26.207	A_g	851.667	B_g
26.680	B_g	857.090	B_g
26.980	B_g	857.253	A_g
27.665	A_u	860.528	A_u
28.230	B_u	860.548	A_g
29.200	A_g	927.933	B_g
29.746	B_u	928.256	A_g
30.819	B_g	929.009	B_u
31.610	B_u	929.221	A_u

Table B.7. Continued			
32.554	A_u	932.012	B_u
33.302	A_g	932.093	B_g
33.687	B_g	932.434	A_g
36.088	A_g	932.455	A_u
36.681	A_u	944.511	B_u
38.223	B_u	944.649	B_g
38.572	B_g	946.339	B_g
39.724	B_g	946.459	B_u
41.288	A_g	949.949	B_g
41.358	A_u	950.118	B_u
41.440	B_u	950.856	A_g
42.335	B_u	951.295	B_g
42.776	A_g	955.140	A_u
42.844	B_g	955.648	A_g
44.580	B_u	957.073	B_u
45.711	B_g	957.451	A_u
47.257	A_u	957.573	B_g
48.278	A_u	957.720	A_g
49.624	B_g	959.098	B_u
50.083	B_u	959.259	A_u
50.893	A_g	959.690	A_g

Table B.7. Continued			
51.205	A_u	959.870	A_u
52.256	B_g	963.303	A_g
53.715	A_u	963.500	A_u
54.092	A_g	964.056	B_g
55.066	B_u	964.539	A_g
56.102	A_g	966.758	A_u
57.203	B_g	966.772	B_u
58.403	A_u	967.974	B_g
58.573	B_u	968.149	B_u
60.834	B_g	968.587	A_g
60.851	A_g	969.017	A_u
61.849	A_g	982.460	B_g
61.963	A_u	982.470	B_u
63.484	B_g	982.742	A_g
64.109	B_g	982.753	A_u
64.115	A_u	988.358	A_g
65.098	B_u	988.574	A_u
66.699	A_g	991.004	A_g
67.112	A_u	991.043	A_u
68.602	B_u	996.709	A_g
69.506	B_g	997.305	A_u

Table B.7. Continued			
70.760	B_u	997.370	A_g
71.305	A_u	997.465	A_u
74.895	B_u	999.809	B_u
74.947	A_g	999.997	B_g
75.407	A_u	1001.017	A_u
75.435	B_g	1001.414	B_u
75.942	B_u	1006.341	B_u
77.593	A_u	1006.428	A_u
78.511	A_g	1008.540	B_g
80.674	A_g	1008.675	A_g
81.205	B_g	1010.902	A_g
82.813	A_g	1011.080	A_u
85.072	A_u	1011.082	B_g
85.693	B_u	1011.355	B_u
88.429	A_u	1023.978	B_u
88.991	B_g	1024.103	A_g
90.004	A_g	1024.112	B_g
90.187	B_u	1024.238	A_u
91.752	B_g	1026.513	B_u
93.946	B_u	1026.516	A_u
97.101	A_g	1026.908	A_g

Table B.7. Continued			
98.447	B_u	1027.029	B_g
98.802	A_u	1049.041	A_g
102.034	B_g	1049.334	A_u
104.263	B_u	1050.759	B_g
106.565	B_g	1051.015	B_u
106.997	B_u	1054.300	A_u
107.003	A_u	1054.415	A_g
108.466	A_g	1054.704	A_g
110.778	B_g	1054.767	A_u
112.580	A_u	1083.394	B_u
117.742	B_g	1083.758	B_g
122.226	B_u	1084.010	A_u
122.553	A_g	1084.155	B_u
124.518	B_g	1084.187	A_g
128.625	A_u	1084.316	B_g
132.244	A_g	1085.831	B_u
136.092	B_u	1085.838	B_g
138.973	B_g	1095.270	B_u
140.330	A_g	1095.303	B_g
140.801	A_u	1099.236	B_u
141.943	B_g	1099.412	A_u

Table B.7. Continued			
150.370	A_u	1103.594	A_g
151.258	A_g	1103.727	A_u
155.158	B_u	1104.152	B_u
156.770	B_g	1104.437	B_g
157.347	B_u	1106.749	A_u
158.324	A_u	1106.899	B_u
160.531	B_g	1106.988	A_g
161.081	A_g	1107.124	B_g
162.437	A_u	1109.470	A_g
163.426	A_g	1109.676	B_g
164.354	B_u	1110.910	B_u
166.374	B_g	1111.084	A_u
167.260	A_g	1113.324	B_u
167.507	B_u	1113.565	A_u
173.658	B_g	1113.983	B_g
177.703	B_u	1114.217	A_g
180.284	A_g	1121.486	B_g
180.599	B_g	1121.542	A_g
185.796	B_u	1127.571	A_g
185.906	B_g	1127.638	A_u
186.772	A_u	1139.019	B_g

Table B.7. Continued			
189.529	B_g	1139.059	A_g
189.742	B_u	1139.450	B_u
196.794	B_u	1139.495	A_u
197.061	A_g	1143.405	A_u
197.095	A_u	1143.478	B_u
197.144	B_g	1146.206	A_u
200.304	A_g	1146.260	A_g
204.314	A_u	1150.079	B_u
205.043	B_u	1150.196	A_u
207.601	B_g	1150.507	A_g
208.497	A_u	1150.573	B_g
209.086	A_g	1167.236	A_g
210.868	B_u	1167.262	A_u
212.064	B_g	1173.148	B_g
213.242	A_g	1173.638	A_g
214.453	B_g	1193.988	A_g
214.602	B_u	1193.993	A_u
223.751	A_u	1194.847	B_u
225.003	B_g	1195.500	B_g
228.597	B_u	1198.979	A_g
231.870	A_g	1199.120	A_u

Table B.7. Continued			
235.384	A_g	1201.572	A_u
235.863	B_g	1201.813	A_g
235.915	A_u	1231.141	B_u
235.946	B_u	1231.194	A_u
240.209	A_u	1231.200	B_g
240.322	B_u	1231.249	A_g
240.326	B_g	1232.594	B_g
240.533	A_g	1232.629	B_u
240.982	A_u	1232.649	A_g
256.953	B_g	1232.674	A_u
266.580	A_g	1261.495	B_u
273.054	A_u	1261.629	B_g
276.599	A_g	1261.717	A_g
286.045	B_u	1261.739	A_u
286.717	B_g	1268.501	B_u
288.712	B_u	1268.533	B_g
301.364	B_g	1272.566	B_g
307.920	B_u	1272.571	B_u
309.620	A_u	1278.077	B_u
326.281	B_u	1278.088	B_g
326.303	B_g	1284.720	A_g

Table B.7. Continued			
327.658	B_g	1284.813	B_g
327.671	A_g	1285.812	A_u
327.703	A_u	1285.817	B_u
327.725	B_u	1295.223	B_g
328.664	B_g	1295.224	B_u
328.671	A_g	1299.192	A_u
328.778	B_u	1299.402	B_u
328.897	A_u	1302.421	B_g
338.725	A_u	1302.683	A_g
339.025	A_g	1303.470	B_u
341.078	A_u	1303.479	A_u
341.529	B_u	1307.696	B_u
343.703	B_g	1307.744	B_g
357.101	A_g	1308.789	B_g
357.141	A_u	1308.814	A_g
360.110	B_u	1309.148	B_u
360.564	B_g	1309.194	B_g
361.825	B_u	1311.855	A_u
364.224	A_g	1311.883	B_u
366.217	A_u	1311.948	A_g
372.647	A_g	1311.980	B_g

Table B.7. Continued			
372.686	A_u	1314.744	A_u
387.303	B_u	1314.765	A_g
388.516	B_g	1315.259	B_g
394.938	A_u	1315.299	A_g
395.024	A_g	1315.393	B_u
399.636	A_g	1315.419	A_u
400.081	B_u	1336.385	A_u
400.434	A_u	1336.435	A_g
400.543	B_g	1390.623	B_u
405.935	A_u	1390.808	A_u
406.006	B_u	1395.707	B_u
418.578	B_u	1395.837	B_g
418.627	B_g	1395.967	A_u
418.780	A_g	1396.219	A_g
418.807	A_u	1400.718	B_u
420.205	B_g	1400.785	B_g
420.291	A_g	1401.710	B_g
420.343	B_u	1401.765	B_u
420.499	A_u	1403.865	B_g
435.643	B_g	1403.867	B_u
435.786	B_u	1409.963	A_g

Table B.7. Continued			
436.075	B_g	1410.075	B_g
436.488	A_g	1411.106	A_u
436.924	A_g	1411.198	B_u
436.997	A_u	1413.920	A_g
438.752	B_u	1413.949	A_u
439.729	B_g	1414.109	B_g
440.102	A_u	1414.213	B_u
440.674	B_u	1433.203	A_g
444.587	B_g	1433.385	B_u
444.970	A_g	1433.504	A_u
447.804	B_u	1433.854	B_u
447.832	B_g	1433.948	A_u
450.576	A_u	1434.067	B_g
450.778	A_g	1434.338	B_g
464.567	B_u	1434.687	A_g
464.579	A_u	1462.097	A_u
464.620	A_g	1462.933	B_u
464.751	B_g	1462.999	A_u
465.314	A_u	1463.030	A_g
465.417	B_u	1470.008	A_g
465.714	B_g	1471.251	B_g

Table B.7. Continued			
465.829	A_g	1475.054	A_u
467.597	A_u	1475.187	A_g
468.532	A_g	1490.009	A_u
471.651	B_u	1490.180	B_u
471.752	B_g	1497.682	A_g
476.994	B_u	1497.696	A_u
477.073	B_g	1502.990	B_g
483.504	A_u	1503.097	B_u
484.372	B_u	1503.580	A_g
490.445	B_g	1503.611	A_u
490.508	B_u	1506.829	A_g
502.587	B_u	1506.838	B_g
503.783	A_g	1511.001	B_g
503.826	B_g	1511.016	B_u
503.886	A_u	1515.373	B_u
504.577	A_u	1515.417	B_g
504.656	B_u	1516.421	B_g
511.313	B_g	1516.440	B_u
511.406	B_u	1553.025	B_u
511.569	A_g	1553.133	B_g
511.625	A_u	1553.133	A_u

Table B.7. Continued			
511.793	A_g	1553.146	A_g
513.390	B_g	1553.638	B_u
513.669	A_g	1553.667	A_g
515.698	B_u	1553.776	B_g
515.702	B_g	1553.850	A_u
515.798	A_u	1554.416	B_u
518.857	A_g	1554.704	A_u
521.884	B_g	1554.833	A_g
523.822	B_u	1554.945	B_g
523.986	B_g	1557.614	B_g
526.694	B_g	1557.616	A_u
526.836	A_g	1557.681	A_g
538.544	B_u	1557.784	B_u
538.709	B_g	1579.014	A_g
542.369	B_u	1579.177	B_g
542.498	B_g	1581.473	A_u
545.588	B_u	1581.577	B_u
546.435	B_g	1581.611	A_g
547.494	A_u	1582.072	A_u
547.752	B_u	1584.111	B_g
553.384	A_u	1584.226	A_g

Table B.7. Continued			
553.953	B_u	1584.438	A_u
555.946	A_g	1584.576	A_g
556.438	B_g	1592.657	A_g
629.454	A_u	1592.683	A_u
629.491	A_g	2078.398	B_u
631.179	A_u	2078.972	B_g
635.682	B_u	2080.396	A_g
639.429	A_g	2081.165	A_u
639.450	B_g	2203.198	B_g
641.053	B_u	2203.233	A_g
641.131	B_g	2208.958	B_u
648.997	A_u	2208.963	A_u
649.066	B_u	2226.240	A_g
649.073	A_g	2226.266	A_u
649.127	B_g	2240.566	A_g
649.913	A_u	2240.575	A_u
650.121	B_u	3050.618	A_g
650.174	A_g	3050.620	A_u
650.377	B_g	3050.621	B_u
657.215	B_g	3050.643	B_g
657.251	B_u	3071.150	B_u

Table B.7. Continued			
657.706	B_g	3071.172	A_u
658.126	A_g	3071.231	B_g
658.131	A_u	3071.279	A_g
658.133	B_u	3073.484	A_u
659.436	B_u	3073.516	A_g
659.525	B_g	3073.736	B_u
686.333	B_g	3073.755	B_g
686.376	A_g	3076.108	B_g
686.577	B_u	3076.109	B_u
686.629	A_u	3076.113	A_g
691.771	B_g	3076.120	A_u
691.792	B_u	3076.300	A_u
691.890	A_g	3076.324	B_u
691.923	A_u	3076.766	A_g
717.015	B_g	3076.783	B_g
717.755	B_u	3079.275	B_u
717.902	A_g	3079.307	A_u
718.604	B_g	3080.551	B_g
721.265	B_u	3080.574	A_g
721.825	B_g	3080.604	A_u
722.277	A_u	3080.609	B_u

Table B.7. Continued			
722.630	B_u	3080.776	B_g
722.797	B_g	3080.845	A_g
723.230	B_g	3082.740	B_u
723.247	B_u	3082.795	A_u
723.351	A_g	3082.885	B_g
723.714	A_u	3082.916	A_g
724.142	A_g	3083.238	B_g
724.313	B_u	3083.238	B_u
725.360	B_g	3084.208	B_g
726.935	A_g	3084.221	A_g
727.029	A_u	3084.336	B_u
727.533	A_g	3084.419	A_u
728.746	B_g	3084.658	A_g
729.347	A_u	3084.681	A_u
729.605	B_u	3084.758	B_g
729.850	A_g	3084.790	B_u
730.252	B_g	3084.794	A_u
734.310	A_g	3084.806	A_g
734.389	B_g	3086.374	B_u
737.885	B_u	3086.455	A_u
740.037	A_u	3086.497	A_g

Table B.7. Continued			
755.311	B_g	3086.540	B_g
755.527	A_g	3088.336	B_g
755.988	B_u	3088.342	B_u
756.134	A_u	3090.350	A_g
805.101	B_u	3090.366	A_u
805.238	B_g	3091.087	B_u
805.929	B_u	3091.177	A_u
806.202	B_g	3091.848	B_g
817.813	A_u	3092.007	A_g
817.977	A_g	3096.059	B_u
818.693	A_u	3096.133	A_u
818.799	A_g	3097.567	B_g
822.588	B_u	3097.604	A_g
822.955	B_g	3099.773	A_g
823.375	A_g	3099.860	B_g
824.345	B_g	3099.977	A_u
825.948	B_u	3100.054	B_u
826.257	B_g	3100.470	B_u
826.293	A_u	3100.515	A_u
827.273	A_g	3100.769	A_g
827.274	B_u	3100.793	B_g

Table B.7. Continued			
828.638	B_g	3101.925	B_g
828.831	A_u	3101.926	B_u
829.295	B_u	3102.546	A_g
836.362	A_u	3102.566	A_u
836.447	B_u	3103.935	B_u
837.560	A_u	3103.959	B_g
837.576	A_g	3104.148	A_u
841.311	A_g	3104.214	A_g
841.363	A_u	3141.604	A_u
842.351	A_u	3141.625	A_g
842.466	A_g	3141.730	B_g
844.814	B_u	3141.754	B_u
845.493	B_g		
845.544	A_u		

B7. Spin Densities

Spin densities of **Co-BEBN** were also calculated using VASP (Vienna Ab initio Simulation Package) with the Projector Augmented Wave (PAW)¹²²⁻¹²⁵ method and the local density approximation (GGA)¹²⁶ + U ($U = 4.4$ eV)^{127, 128} exchange correlation functional. The calculated spin density here does not include the densities that reside in the chemical bonds but rather just the densities in the individual atoms in a unit cell. The spin density results show that there are 4 different Co^{II} ions in a unit cell of the crystal structure. The calculations show that each Co^{II} ion contains 0.955 unpaired electron, suggesting that a majority of spin densities are on the ligands with π bonds. Table B.8 shows a range of spin densities for all the atoms in a unit cell of **Co-BEBN**. The single-crystal structure of **Co-BEBN** used in the calculations contains solvent molecules of the 1,2-dichlorobenzene that could potentially cause the calculations to treat the low-spin Co^{II} system as the lower energy system for **Co-BEBN**.

Table B.8. Ranges of the calculated spin densities of all the atoms in a unit cell of **Co-BEBN**

Atoms	Ranges of Spin Densities
Co ^{II}	-0.955
Cl from 1,2-dichlorobenzene	0
S from NCS	0.003
N from the bpeb ligand	-0.041, -0.039, and 0.005
N from NCS	0.003
C	-0.002 0, 0.001, and 0.002
H	-0.001 and 0
Total	1.002

Appendix C. Supporting Information for Chapter 4

C1. Synthesis of NiBO and NiBO- d_8 and Characterization by Powder X-ray Diffraction and IR

For the discussion below, we will address the protonated version of $[\text{Ni}(\mu\text{-}4,4'\text{-bpy})(\mu\text{-ox})]_n$ as **NiBO** and the deuterated version as **NiBO- d_8** .

Polycrystalline samples of **NiBO** were prepared as reported in the literature.²⁰⁶ Repeated attempts at synthesizing **NiBO** were unsuccessful in obtaining single-crystals big enough for a single-crystal X-ray diffraction measurement but attempts at synthesizing **NiBO- d_8** yielded single-crystals for X-ray diffraction measurements, as discussed below. The powder X-ray diffraction (PXRD) patterns of **NiBO** compared to the reported calculated PXRD pattern from the reported structure²⁰⁶ can be seen in Figure C.1. The PXRD measurements for **NiBO** were taken at room temperature, while the reported calculated PXRD patterns were obtained from the reported single-crystal X-ray diffraction data taken at 295 K. The two compounds have similar PXRD patterns up to 50 degrees. Since we did not obtain single crystals for **NiBO**, we are unable to compare the unit cells to the reported structure. On the other hand, as we were successful at obtaining single-crystals of **NiBO- d_8** , we collected its single-crystal X-ray diffraction data and discussed them below, including a comparison to the reported structure.

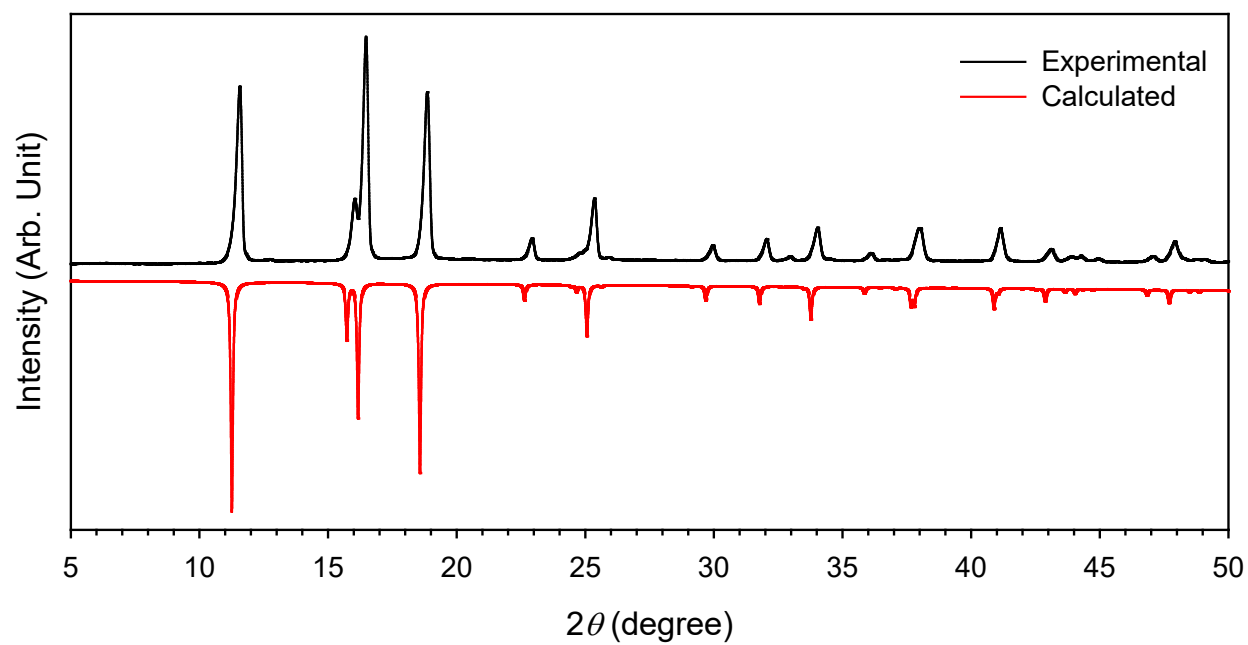


Figure C.1. Experimental PXRD patterns of **NiBO** at room temperature (296 K) compared to the reported calculated PXRD patterns at 295 K.²⁰⁶

As indicated above, we can only obtain polycrystalline samples from the synthesis of **NiBO**. On the other hand, single-crystal and polycrystalline samples of **NiBO-*d*₈** were prepared through hydrothermal synthesis by combining nickel(II) bromide trihydrate [$\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$, 0.2731 g, 1.002 mmol], oxalic acid dihydrate [$(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$], 0.1263 g, 1.002 mmol], and 4,4'-bipyridine-*d*₈ [$\text{C}_{10}\text{D}_8\text{N}_2$, 0.2469 g, 1.503 mmol] in 8 mL of deionized (DI) H_2O inside a 25 mL Teflon lined autoclave. The reaction was stirred for 2 minutes, and then the autoclave was sealed. The reaction was placed into a big furnace with proper insulation at 168 °C for 7 days. After 7 days, the furnace was turned off and the reaction was let to naturally cool down to room temperature inside the insulated furnace for 24 hours. The cool down process to room temperature only took about 10 hours, but the reaction vessel was left undisturbed for up to 24 hours after to let the single crystals grow bigger in size. After 24 hours, the reaction was filtered and washed with acetone and DI H_2O . The solid sample contains a mixture of single-crystal and polycrystalline forms. The filtrate has a dark blue color, the polycrystalline sample of **NiBO-*d*₈** MOF has a light blue color, and the single-crystals of **NiBO-*d*₈** MOF are blue plate-shaped crystals big enough for a single-crystal X-ray diffraction measurement. The total yield is 0.2014 g [66.36% based on the $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$ and $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$]. Figure C.2 shows a comparison between the experimental PXRD patterns of polycrystalline **NiBO-*d*₈** at room temperature and the calculated PXRD patterns from the single-crystal structure of **NiBO-*d*₈** at 100(2) K. The PXRD patterns are similar up to 50°. Figure C.3 shows the IR spectrum of the polycrystalline **NiBO-*d*₈** at room temperature.

The chemicals used in the synthesis of **NiBO** and **NiBO-*d*₈** were purchased commercially and used without further purification. Nickel(II) bromide trihydrate [$\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$, 98%, Alfa

Aesar], oxalic acid dihydrate $[(\text{COOH})_2 \cdot 2\text{H}_2\text{O}]$, 99.5+%, Acros Organics], 4,4'-bipyridine $[\text{C}_{10}\text{H}_8\text{N}_2]$, 98%, Acros Organics], 4,4'-bipyridine- d_8 $[\text{C}_{10}\text{D}_8\text{N}_2]$, 98%- d_8 , CDN Isotopes].

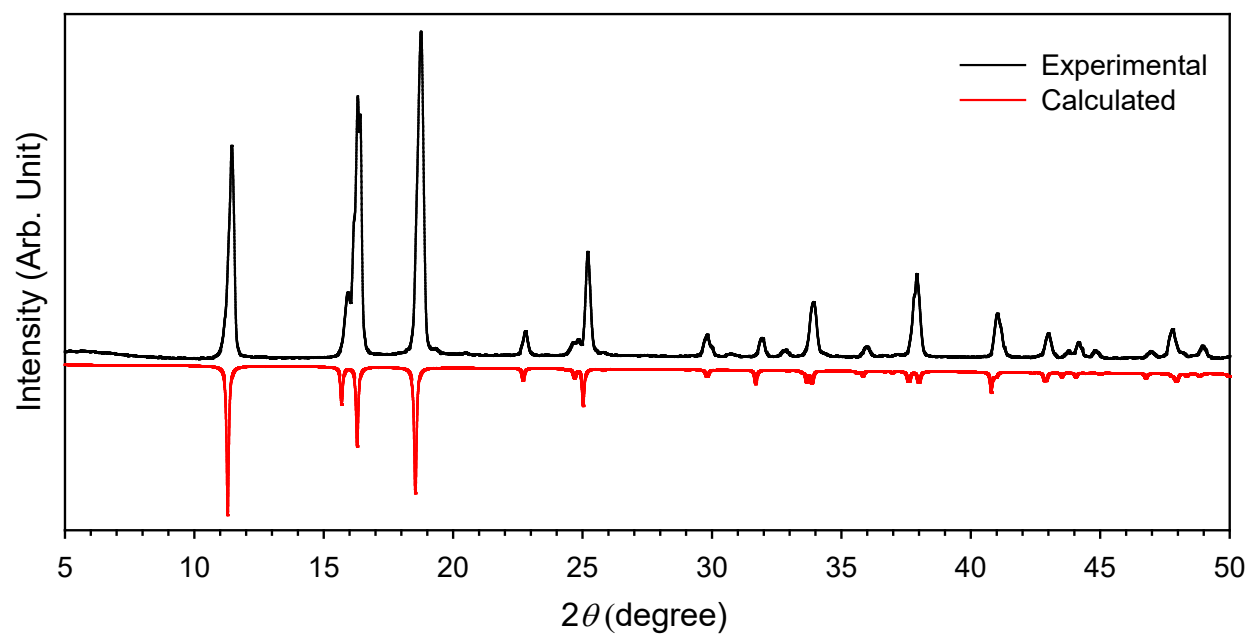


Figure C.2. Experimental PXRD patterns of NiBO-d_8 at 296 K compared to the calculated PXRD patterns based on the structure at 100(2) K.

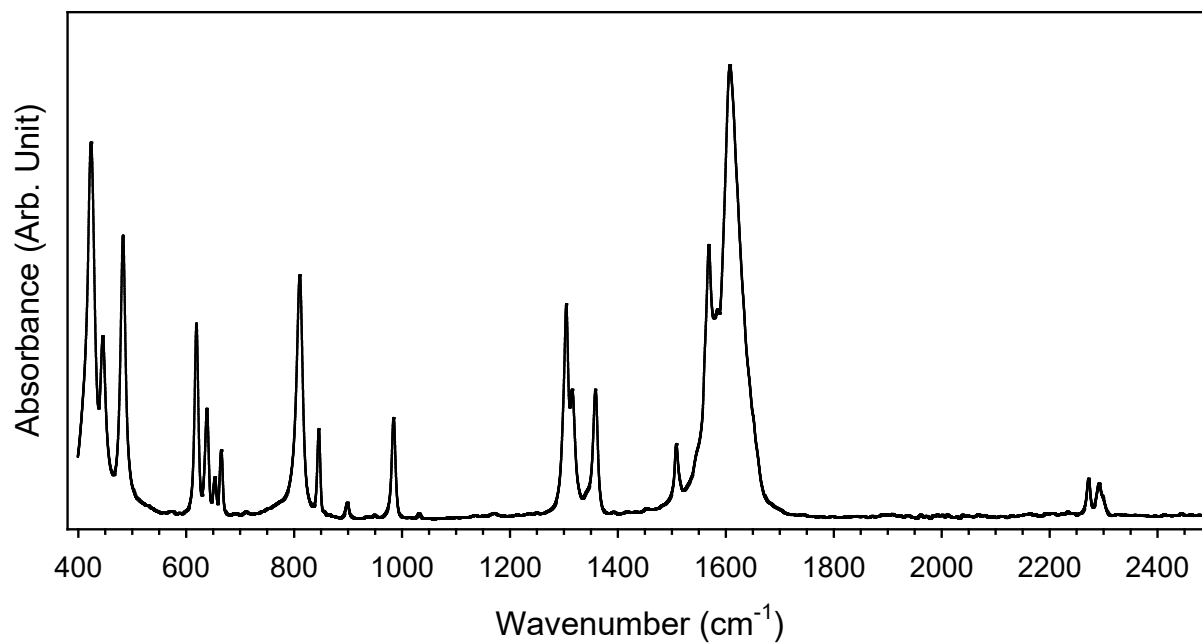


Figure C.3. IR spectrum of **NiBO-*d*₈** at room temperature from 400 to 2500 cm⁻¹.

C2. Additional Discussion of the Crystal Structure of NiBO-*d*₈

Table C.1 includes crystal information from the current measurements of NiBO-*d*₈ at 100(2) K and the reported measurements of NiBO at 295 K.²⁰⁶ The single-crystal X-ray structure of NiBO-*d*₈ were solved using hydrogen instead of deuterium due to the two isotopes with indistinguishable patterns in the X-ray diffraction. The reported crystal structures at 295 K and NiBO-*d*₈ at 100(2) K are mostly similar with some major differences. The β angle of the unit cell in the 100 K structure deviated from 90° to ~116° placing the crystal system of the 100 K structure into the monoclinic (C2, No. 5) system while the 295 K structure is in the orthorhombic (*Immm*, No. 71) system. Continuous shape measurement (CShM) was performed on the crystal structure at 100 K. The shape of the structure is 19.860 deviating from the perfect octahedral shape at 0. The local structure shows a Ni^{II} ion coordinates with two oxalate ligands in the *x-y* plane, while two 4,4'-bipyridine ligands coordinates in the *z*-direction. Figure C.4 shows the local structure around the Ni^{II} ion. The Ni^{II} ions across the oxalate ligands form the Haldane chains, while the 4,4'-bipyridine ligands connect the individual chains to form the 2-D framework. Some of the selected bond lengths and bond angles around the Ni^{II} ion at 100 K are in Table C.2. The Ni1 to N1 and N2 bond lengths are a bit longer than that of the Ni1 to O1 and O2 bond lengths. The bond angles of O1-Ni1-O1 and O2-Ni1-O2 are 179.4(2) and 179.5(2), respectively. The angles suggest that the two oxalate ligands are in the same plane (*x-y* plane) as one another. While the bond angles of O2-Ni1-N1 and O2-Ni1-N2 are very close to 90 degrees indicating that the two 4,4'-bipyridine ligands are in the axial positions. Figures 4.1 and C.5 show the inter- and intra-chain direction of the Haldane 1-D chain MOF as well as the view down the *a*-axis. The view of the crystal structure down the *b*- and *c*-axis can be seen in

Table C.1. Comparison of crystallographic data of $[\text{Ni}(\mu\text{-}4,4'\text{-bpy-}d_8)(\mu\text{-ox})]_n$ (**NiBO- d_8**) at 100 K (current studies) and $[\text{Ni}(\mu\text{-}4,4'\text{-bpy})(\mu\text{-ox})]_n$ (**NiBO**) at 295 K (reported)

	100(2) K	295 K²⁰⁶
Empirical formula	$\text{C}_{12}\text{D}_8\text{N}_2\text{NiO}_4$	$\text{C}_{12}\text{H}_8\text{N}_2\text{NiO}_4$
Fw	310.95	N/A
Temp (K)	100(2)	295
Crystal system	Monoclinic	Orthorhombic
Space group	$C2$ (No. 5)	$Immm$ (No. 71)
a , Å	12.096(2)	5.3030(11)
b , Å	11.288(2)	10.955(2)
c , Å	5.3238(10)	11.257(2)
α , °	90	90
β , °	115.995(5)	90
γ , °	90	90
V , Å ³	653.4(2)	653.968
Z	2	2
D_{calc} , g/cm ³	1.540	1.538
Crystal size (mm ³)	$0.062 \times 0.220 \times 0.258$	N/A
θ range (°)	2.601–30.993	N/A
Reflections collected	2079	N/A
Independent reflections	13697 [$R(\text{int}) = 0.0297$]	N/A
Completeness to θ	100%, 30.993°	N/A

Table C.1. Continued		
GOF on F^2	0.816	N/A
Final R indices	$R1 = 0.0160$	$R1 = 0.024$
$[I > 2\sigma(I)]^a$	$wR2 = 0.0394$	$wR2 = 0.024$
R indices (all data)	$R1 = 0.0161$	N/A
	$wR2 = 0.0394$	N/A
Largest diff. peak and hole, e.Å ⁻³	0.463 and -0.390	N/A

$$^a R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; R_w = (\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2])^{1/2}$$

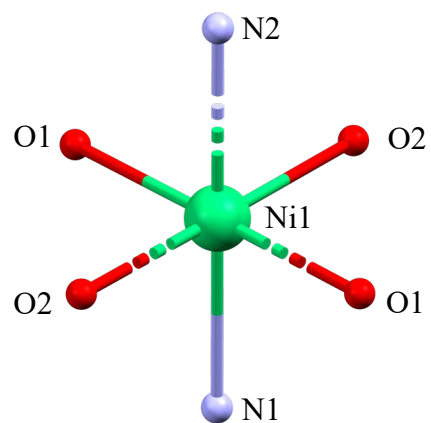


Figure C.4. The local structure around the Ni^{II} ion in **NiBO-*d*₈**. Green: Ni; Red: O; Purple: N; Gray: C.

Table C.2. Selected bond lengths and bond angles around the Ni^{II} ion in **NiBO-*d*₈** at 100 K

Bond Lengths (Å)	
Ni1-N1	2.092(5)
Ni1-N2	2.092(5)
Ni1-O1	2.0488(10)
Ni1-O1	2.0489(10)
Ni1-O2	2.0533(9)
Ni1-O2	2.0533(9)
Bond Angles (°)	
O1-Ni1-O1	179.4(2)
O1-Ni1-O2	97.47(4)
O1-Ni1-O2	82.53(4)
O1-Ni1-O2	82.53(4)
O1-Ni1-O2	97.47(4)
O2-Ni1-O2	179.5(2)
O1-Ni1-N1	90.32(11)
O1-Ni1-N1	90.32(11)
O2-Ni1-N1	89.73(11)
O2-Ni1-N2	89.73(11)
O1-Ni1-N2	89.68(11)
O1-Ni1-N2	89.68(11)
O2-Ni1-N2	90.27(11)

Table C.2. Continued	
O2-Ni1-N2	90.27(11)
N1-Ni1-N2	180.0

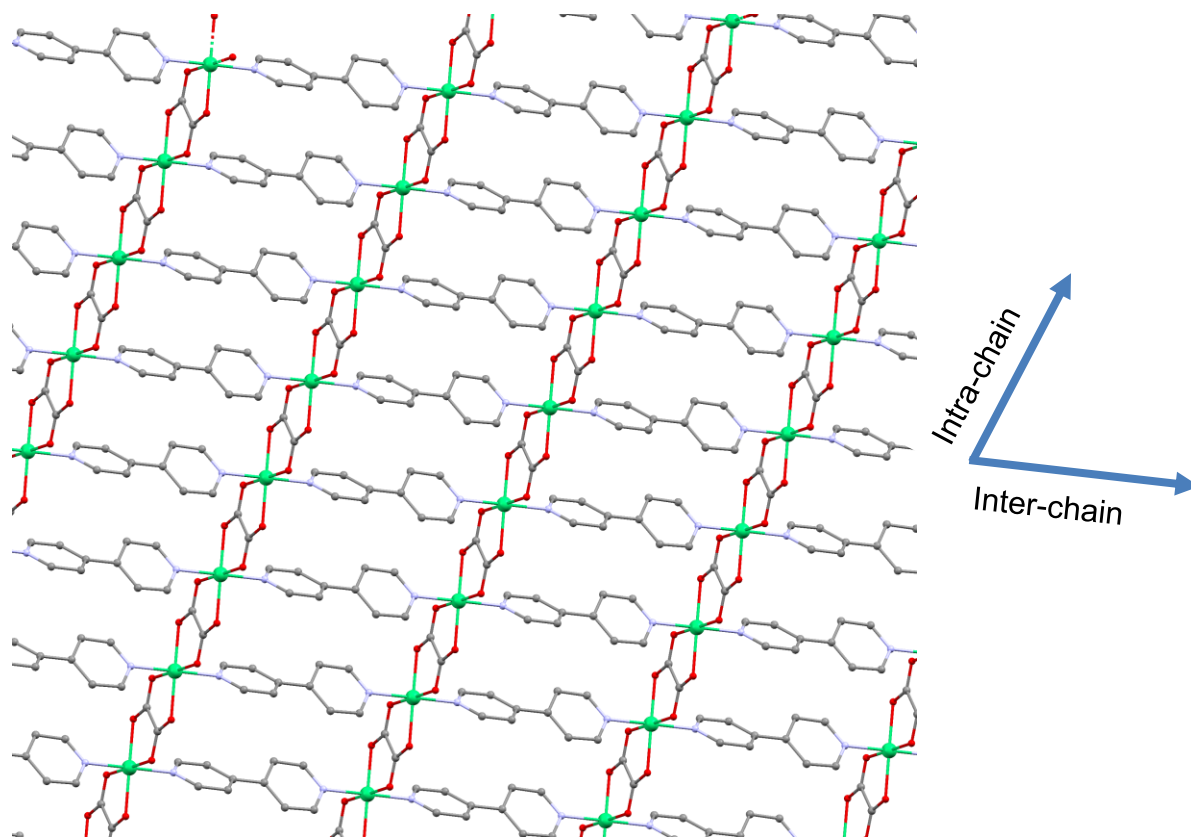


Figure C.5. Crystal structure of **NiBO-*d*₈** showing inter-chain and intra-chain directions. Green: Ni; Red: O; Purple: N; Gray: C. Deuterium atoms are omitted for clarity.

Figures C.6 and C.7.

At 100 K, the refinement of the crystal structure placed the two pyridine rings in the 4,4'-bipyridine ligands rotated at two different planes, while the reported structure (295 K) shows the bipyridine rings to be in the same plane. The freezing of the bipyridine rings rotation places the structure at 100 K into a lower symmetry than that of the structure at 295 K. The rotation of the two pyridine rings allows a better understanding of the magnetic coupling strength between the two nearest nickel atoms along the inter-chain direction. With the two pyridine rings rotated off the plane to one another, the magnetic coupling strength (J) in the inter-chain direction is expected to be negligible. The result is favorable for the Haldane phase to exist in the form of a 2-D MOF. Therefore, the nickel chains that form across the oxalate ligands can be effectively considered as individual isolated Haldane 1-D chains in the system.

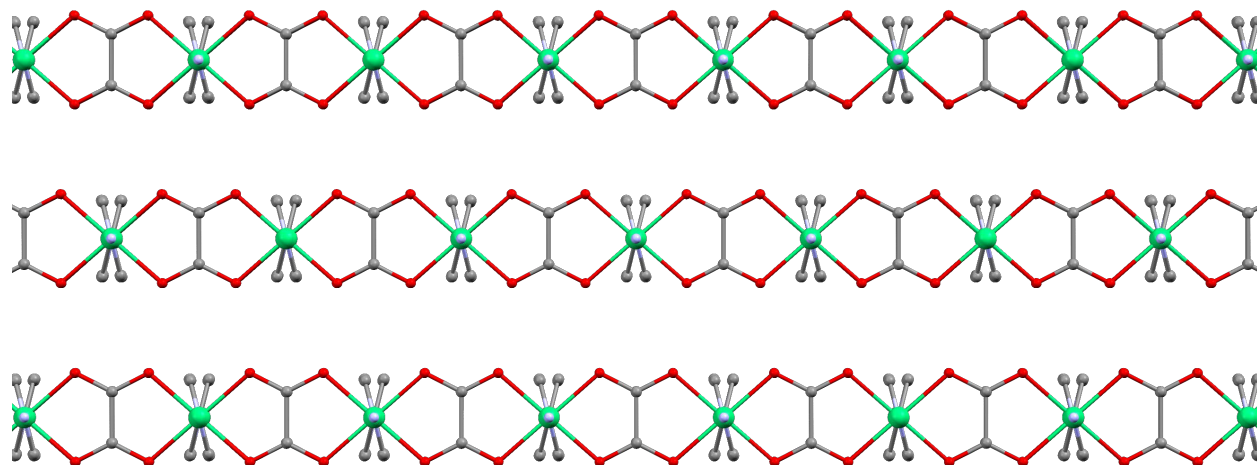


Figure C.6. Crystal structure of **NiBO-*d*₈** view down the crystallographic *b*-axis. Green: Ni; Red: O; Purple: N; Gray: C. Deuterium atoms are omitted for clarity.

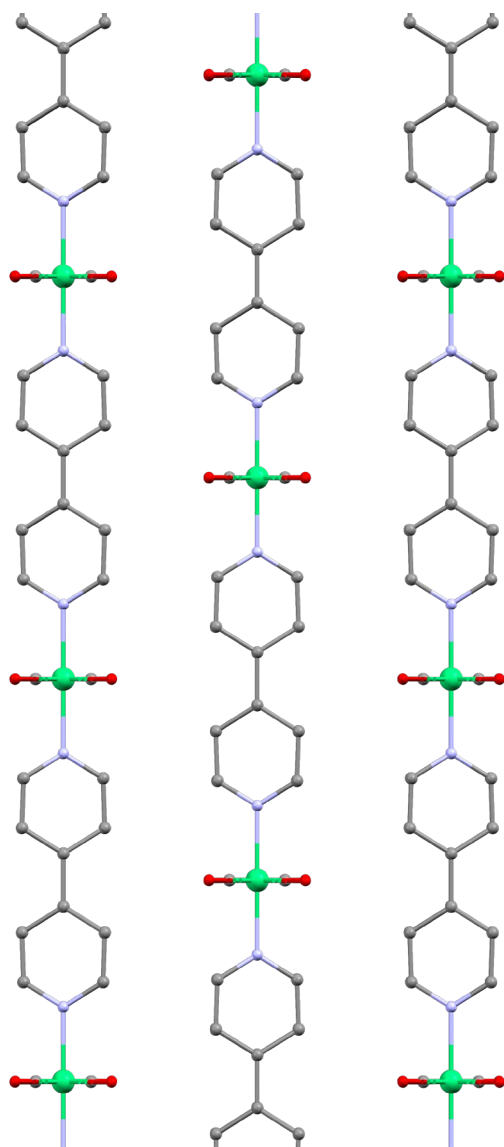


Figure C.7. Crystal structure of **NiBO-*d*₈** view down the crystallographic *c*-axis. Green: Ni; Red: O; Purple: N; Gray: C. Deuterium atoms are omitted for clarity.

C3. Additional Magnetic Susceptibility (DC) Data

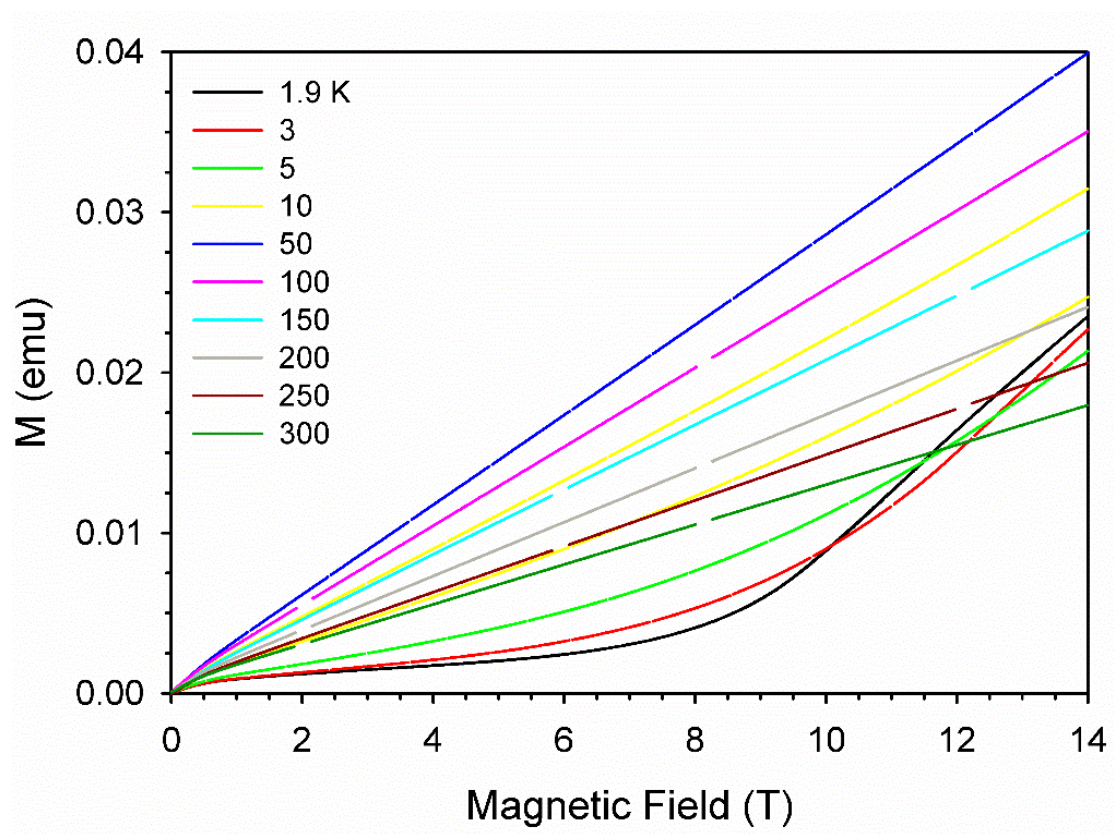


Figure C.8. Variable-field DC magnetization of **NiBO** at various temperatures.

Background subtraction of the DC magnetic susceptibility data were performed using the equation: $\chi = C/(T - \theta_{CW}) + \chi(0)$, where $\chi(0)$ is the paramagnetic contribution in the background.²⁰⁷ Figure C.9-Top shows the data after background subtraction and Figure C.9-Bottom before background subtraction for each of the magnetic field. $\chi(0)$ is constant and temperature-independent. $\chi(0)$ value is not only consisting of paramagnetic or diamagnetic contributions in the system but also the background noise of the instrument as well. Figure C.10 shows the fit to find $\chi(0)$ between 200 and 300 K for 0.1 T data. The same fitting process was performed for the data at other magnetic field strength.

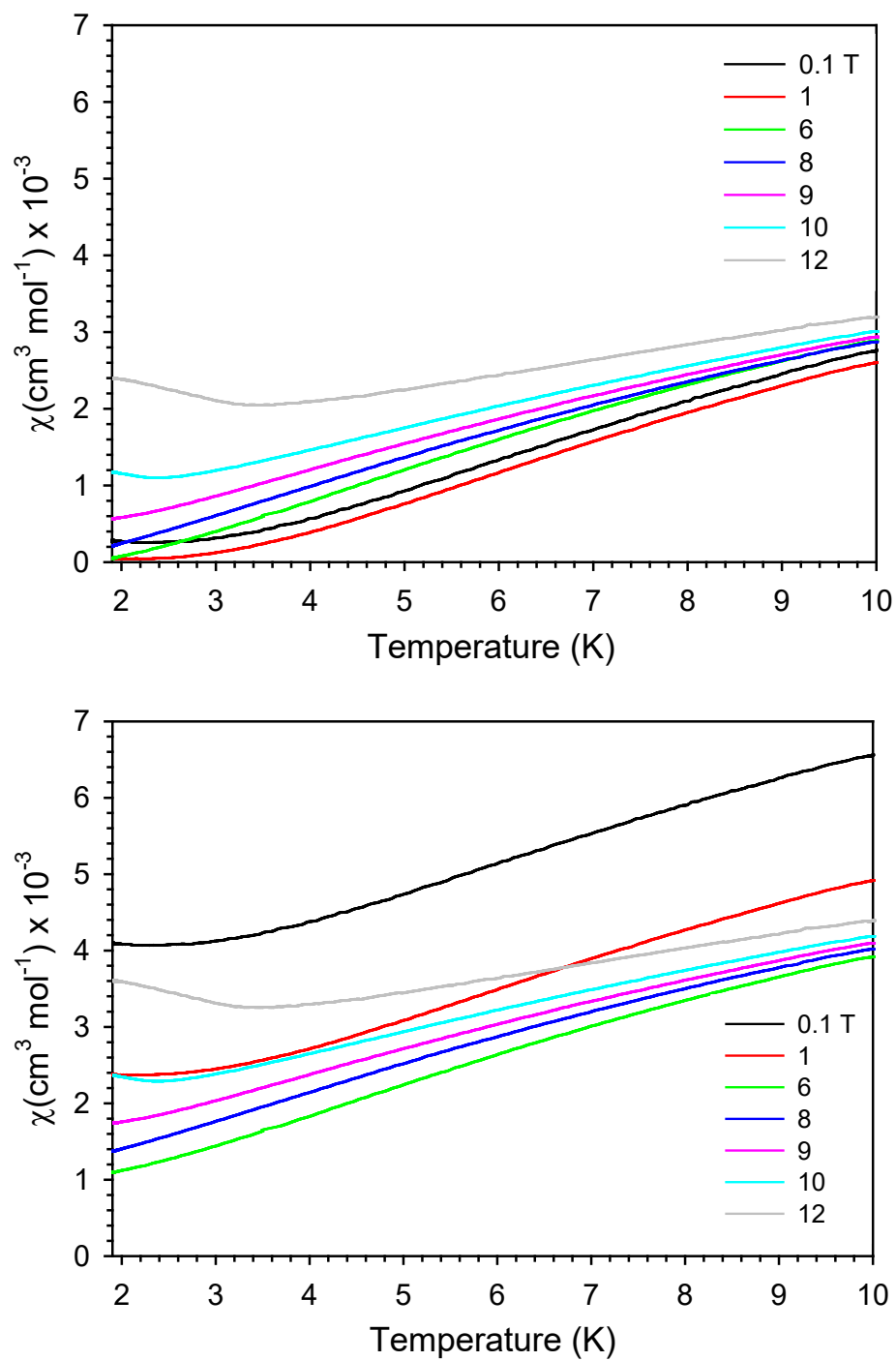


Figure C.9. Comparison between DC magnetic susceptibility data of **NiBO** (Top) after and (Bottom) before background subtraction using $\chi(0)$.

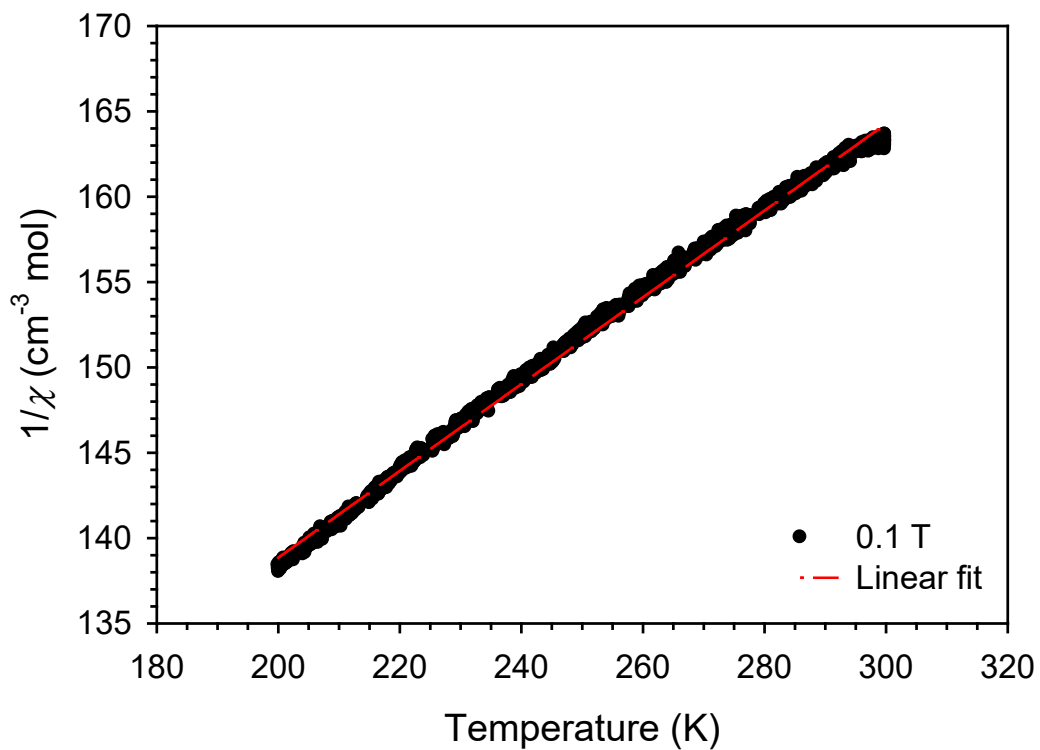


Figure C.10. DC magnetic susceptibility data of **NiBO** fitting between 200 and 300 K at 0.1 T.

The best fit value gives $\chi(0) = 0.0033 \text{ cm}^3 \text{ mol}^{-1}$.

C4. Additional Quantum Monte Carlo (QMC) Results

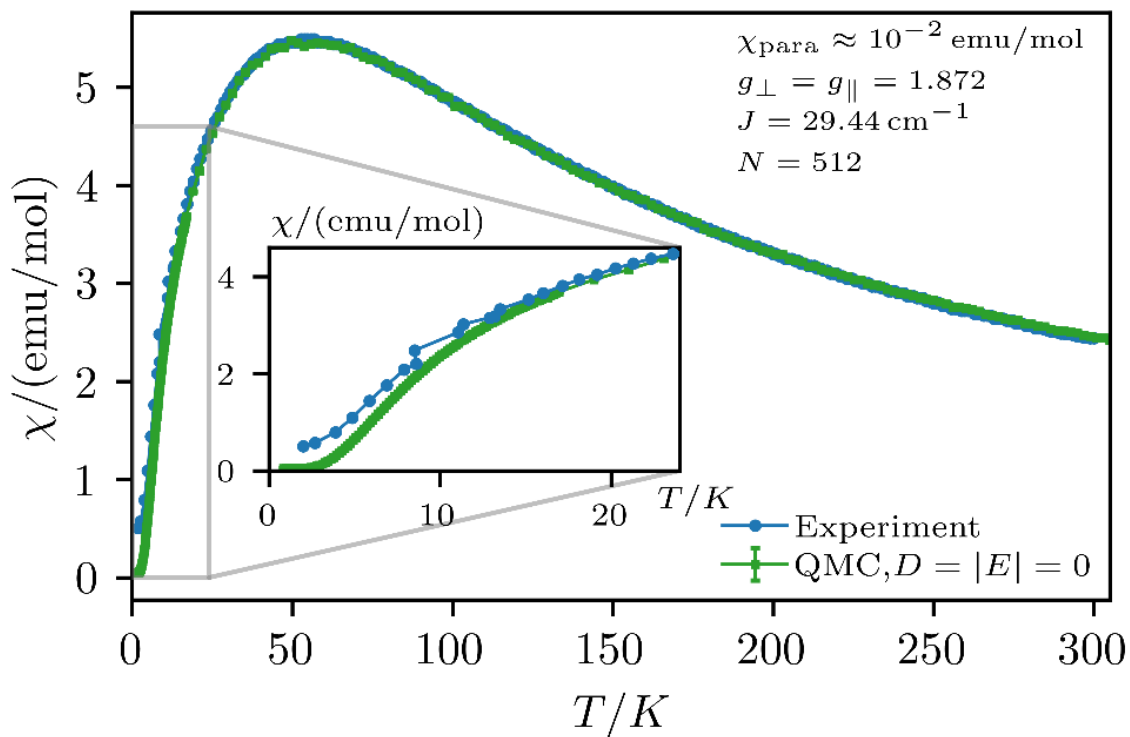


Figure C.11. Magnetic susceptibility as a function of temperature. The QMC simulations are carried out for $N = 512$ sites and without any additional anisotropies. Comparing the simulations to the experimental data, we obtained $J = 29.4 \text{ cm}^{-1}$, $g = 1.87$, and $\chi(0) = 10^{-5} \text{ cm}^3 \text{ mol}^{-1}$.

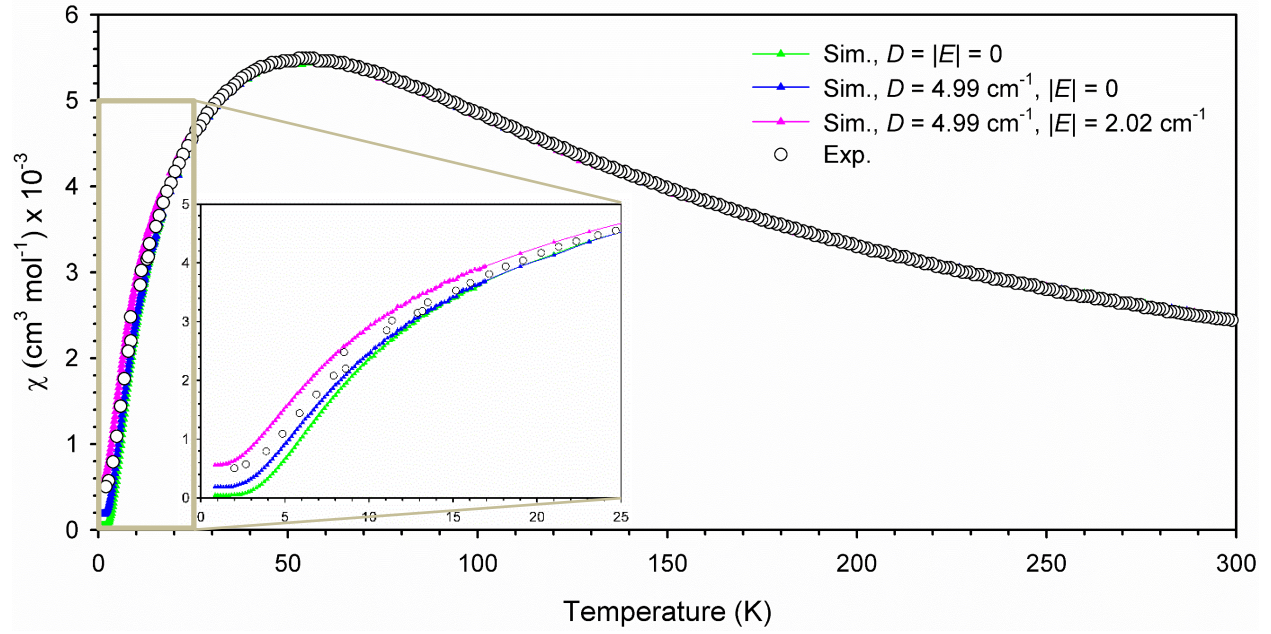


Figure C.12. Magnetic susceptibility as a function of temperature. The QMC simulations are carried out for $N = 512$ sites and with a D and E term. We further show the results without any anisotropies. For J , $g_{\perp} = g_{\parallel}$ and $\chi(0)$ we used the same values (with and without anisotropies).

Before analyzing the low temperature behavior of the magnetic susceptibility, we note that due to the transverse contribution in the powder averaging the susceptibility goes to a finite value in the zero-temperature limit, as shown in Figure 4.5. Therefore, we expect the following (asymptotic) low temperature behavior:

$$\chi = \chi(T = 0) + \alpha e^{-\Delta_1/T}$$

where α denotes some constant and Δ_1 is the spin gap. Therefore, we expect on a log-scale, a linear behavior:

$$\log(\chi - \chi(T = 0)) = -\frac{\Delta_1}{T} + \text{const.}$$

The zero-temperature limit $\chi(T = 0)$ can be readily extracted from the QMC simulations. In Figure C.13, the spin gap (Δ_1) is in good agreement with the experimental susceptibility data, excluding the lowest two data points.

Regarding the spin gap splitting with a magnetic field in a powder sample, one obtains in first order perturbation theory the gaps outlined in Eq. 4.5.^{211, 212} If additional magnetic field is applied to the energy splitting of the spin states, at first order, the singlet ground state is not affected, and all changes affect only the triplet excited state. One may now consider in the canonical basis an additional Zeeman term of the form, which leads to a perturbation of the form:²¹²

$$H_s + \mu_B g h \cdot S = \begin{pmatrix} \Delta_x & -i\mu_B g h_z & i\mu_B g h_y \\ i\mu_B g h_z & \Delta_y & -i\mu_B g h_x \\ -i\mu_B g h_y & i\mu_B g h_x & \Delta_z \end{pmatrix}$$

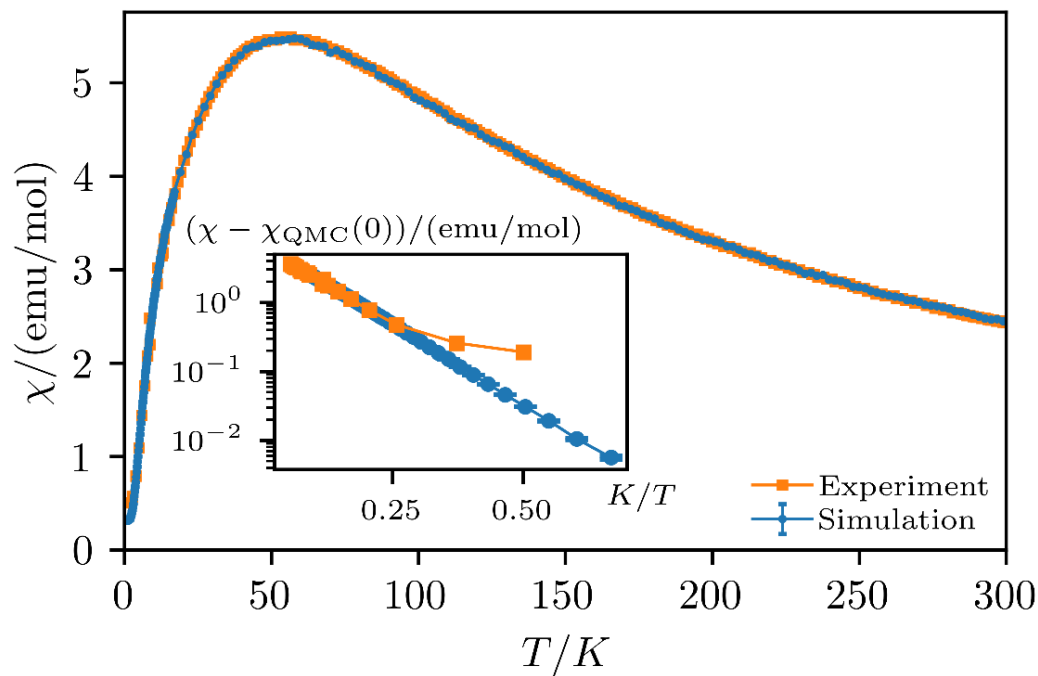


Figure C.13. Magnetic susceptibility as a function of temperature as obtained from experiments and QMC simulations. The inset shows the susceptibility subtracted by the zero-temperature limit on a logarithmic scale as a function of inverse temperature.

where h denotes the magnetic field in Tesla. From diagonalizing the effective Hamiltonian above, one can get the corrections of the triplet states in the canonical basis for an arbitrary direction of the field as shown in Figure C.14 and C.15.

For a powder sample, we must average over all field directions. Therefore, we drew 1000 random samples at each field strength to sample different directions yielding the following gaps as shown in Figure C.16. In Figure C.14 and C.15, we expect at field strengths over (roughly) 4 T a broad distribution when averaging over the different directions, which agrees with the data shown in Figure C.16.

In addition, QMC simulations extracted HFESR parameters that can be used to compare to the experimental HFESR data. In theory, both Δ_1 and Δ_2 contain mixing of the terms $|1, \pm 1\rangle$. Due to the clear splitting of the gaps, we expect Δ_1 to be the thermally more occupied relevant level, such that the signal seen in HFESR should mainly show the energy difference between $\Delta_3 - \Delta_1$. A comparison between QMC simulation results and HFESR experimental data is in Figure C.17. The results show an excellent agreement between theory and experiment.

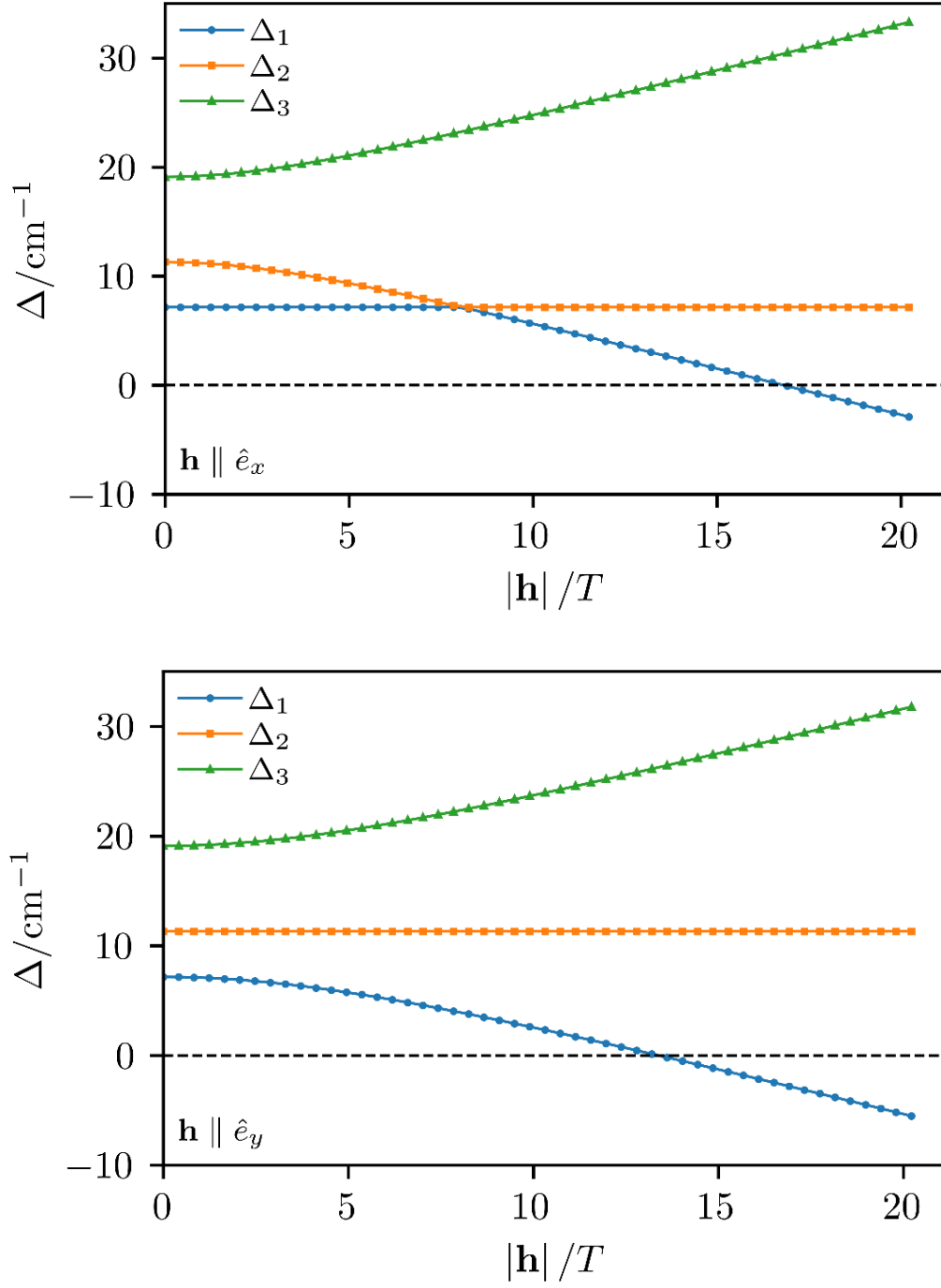


Figure C.14. Eigenvalues Δ_1 , Δ_2 , Δ_3 as a function of magnetic field strength for (Top) $h \parallel \hat{e}_x$ and (Bottom) $h \parallel \hat{e}_y$.

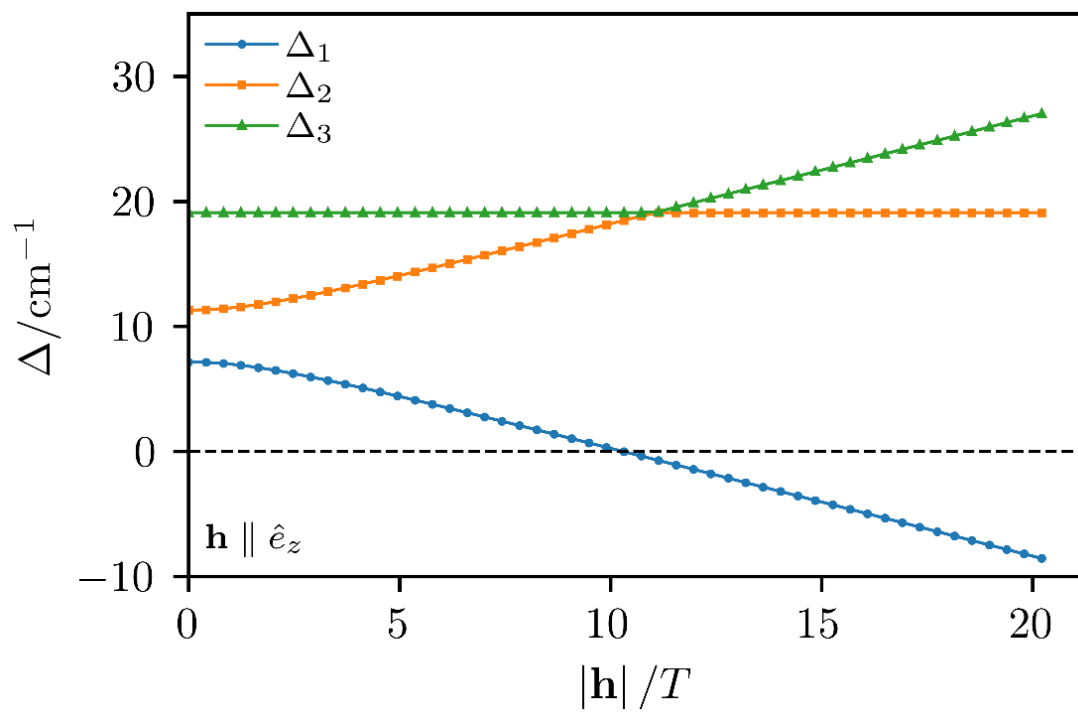


Figure C.15. Eigenvalues Δ_1 , Δ_2 , Δ_3 as a function of magnetic field strength for $h \parallel \hat{e}_z$.

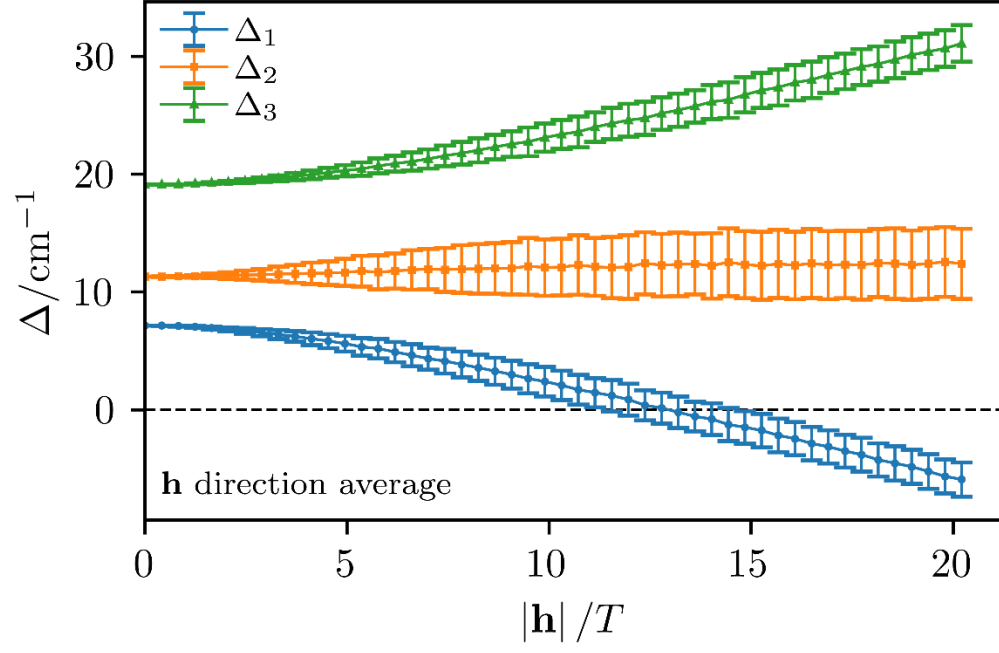


Figure C.16. Δ_1 , Δ_2 , Δ_3 as a function of magnetic field strength averaged over all directions. The error bars denote the standard deviation, while the markers denote the mean of the distribution.

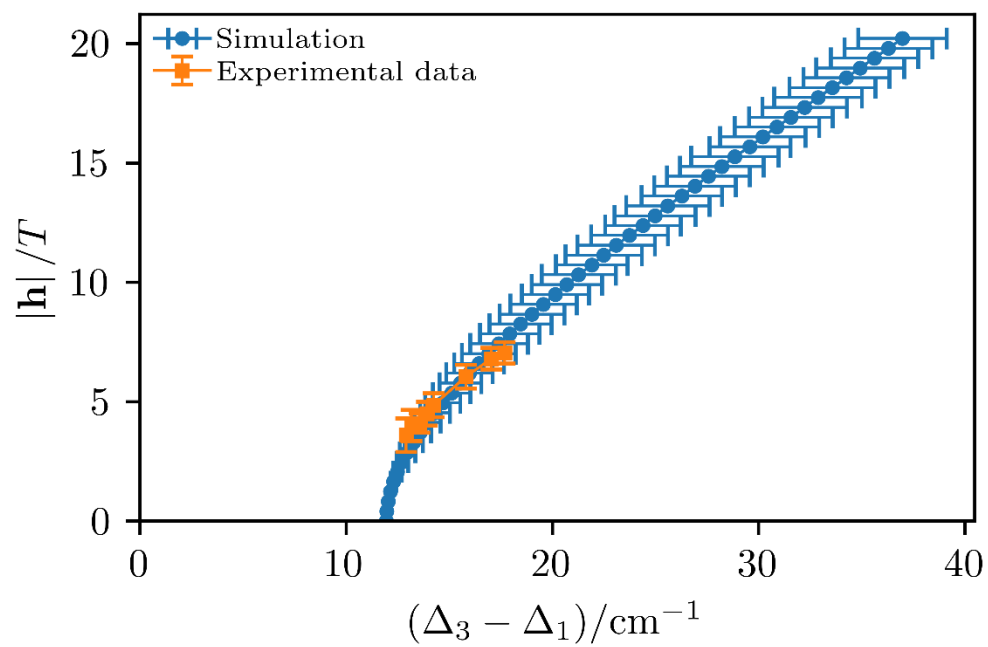


Figure C.17. Magnetic field strength vs. difference $\Delta_3 - \Delta_1$ compared to HFESR experimental data.

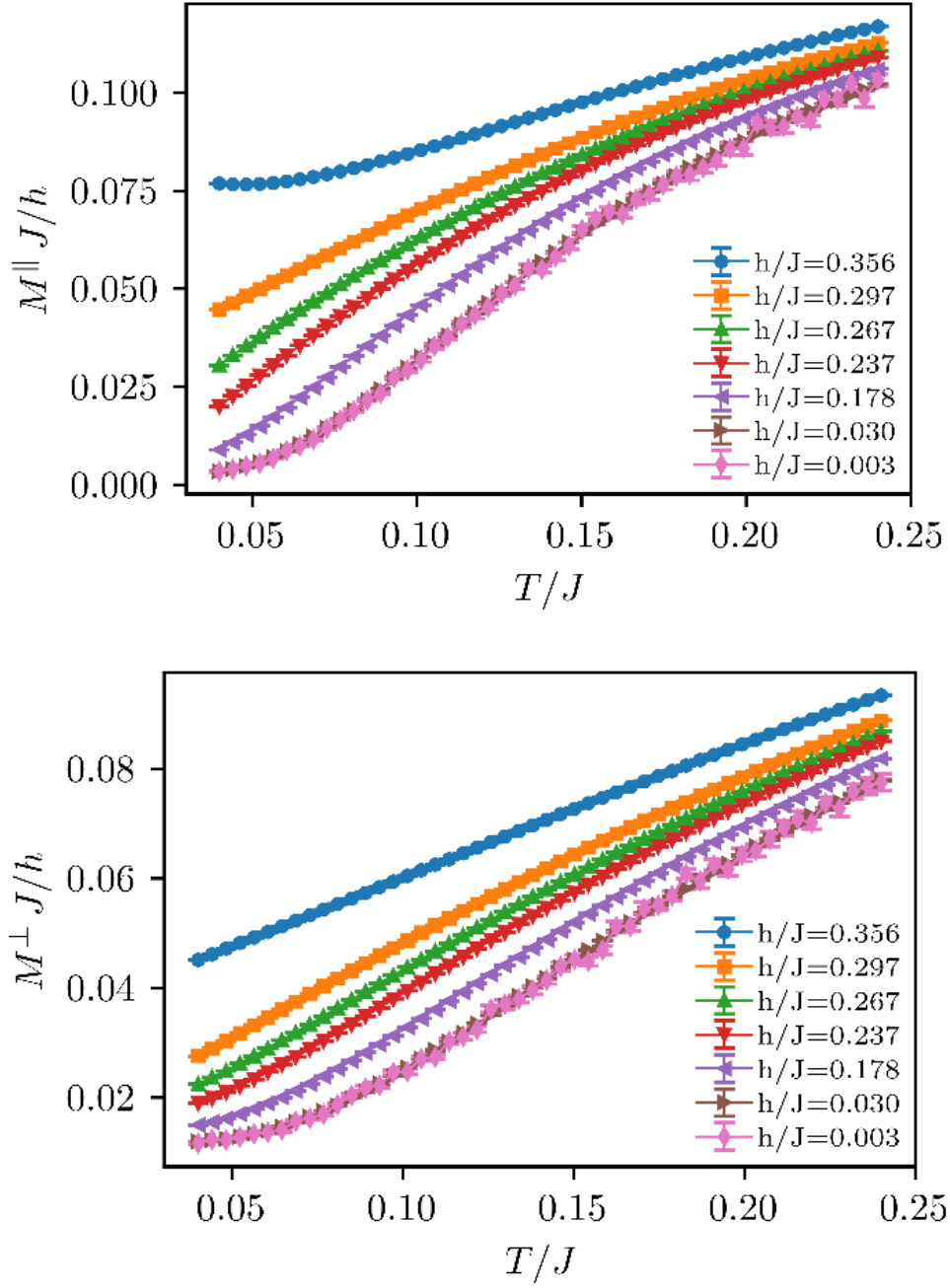


Figure C.18. (Top) QMC results for the temperature-dependent of the magnetization divided by the field strength h for finite magnetic fields oriented parallel to the easy-axis direction. (Bottom) QMC results for the temperature-dependent of the magnetization divided by the field strength h for finite magnetic fields oriented perpendicular to the easy-axis direction.

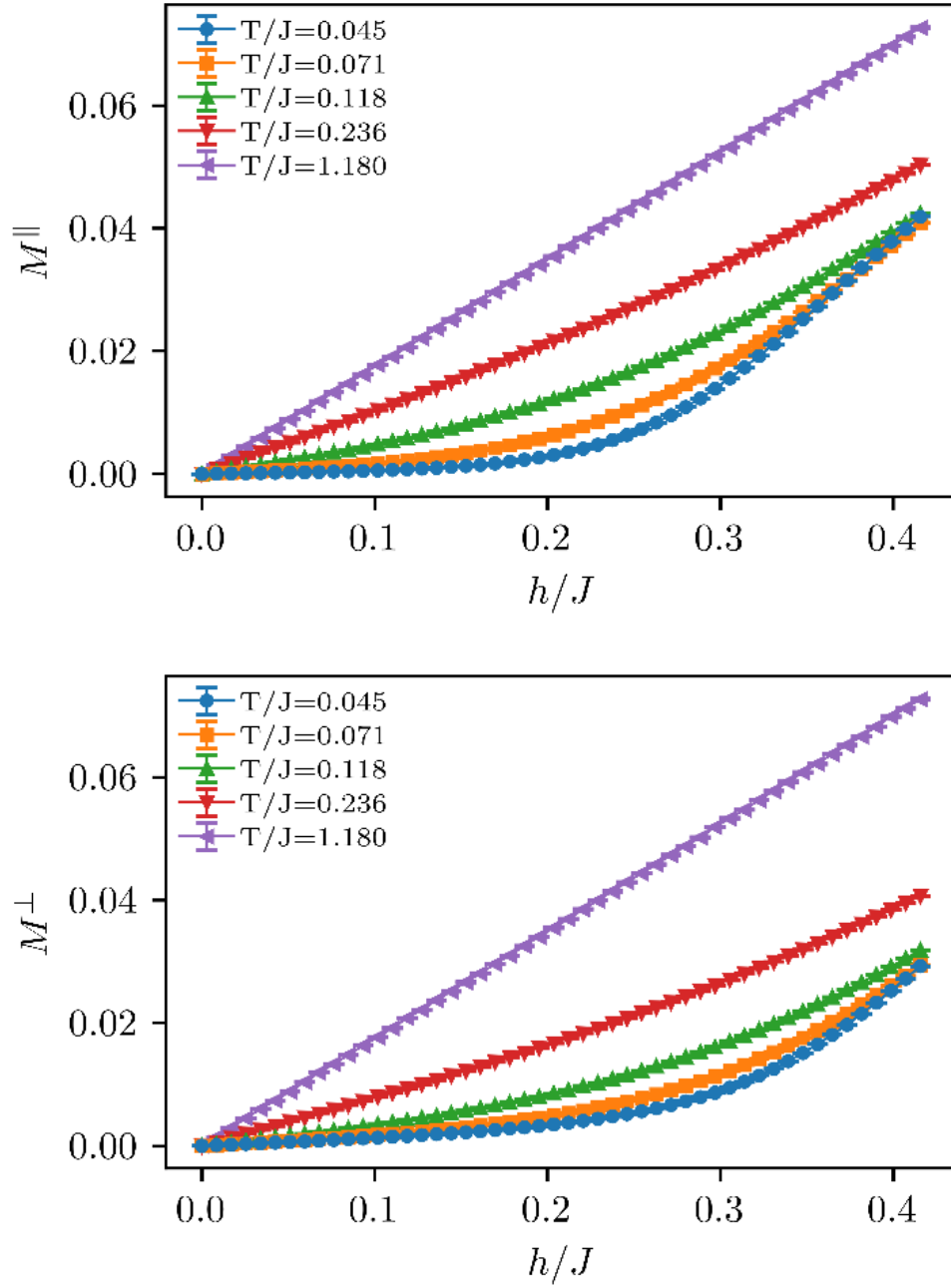


Figure C.19. (Top) QMC results for the field-dependent of the magnetization in finite magnetic fields oriented parallel to the easy-axis direction at various temperatures. (Bottom) QMC results for the field-dependent of the magnetization in finite magnetic fields oriented perpendicular to the easy-axis direction at various temperatures.

C5. Additional Specific Heat Data

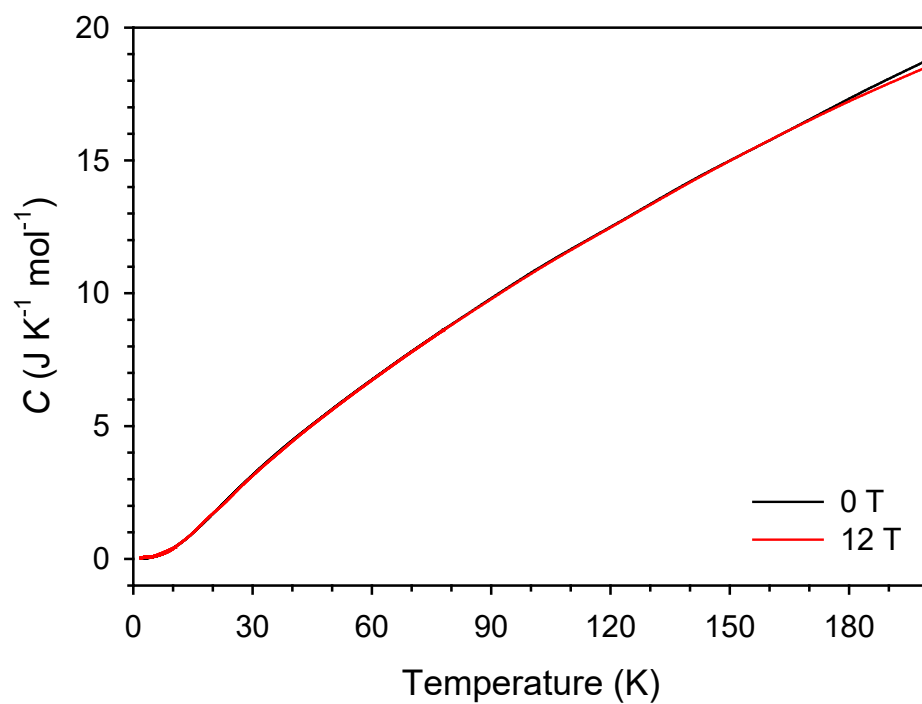


Figure C.20. Specific heat of **NiBO** at zero-field and 12 T between 1.92 K and 202 K.

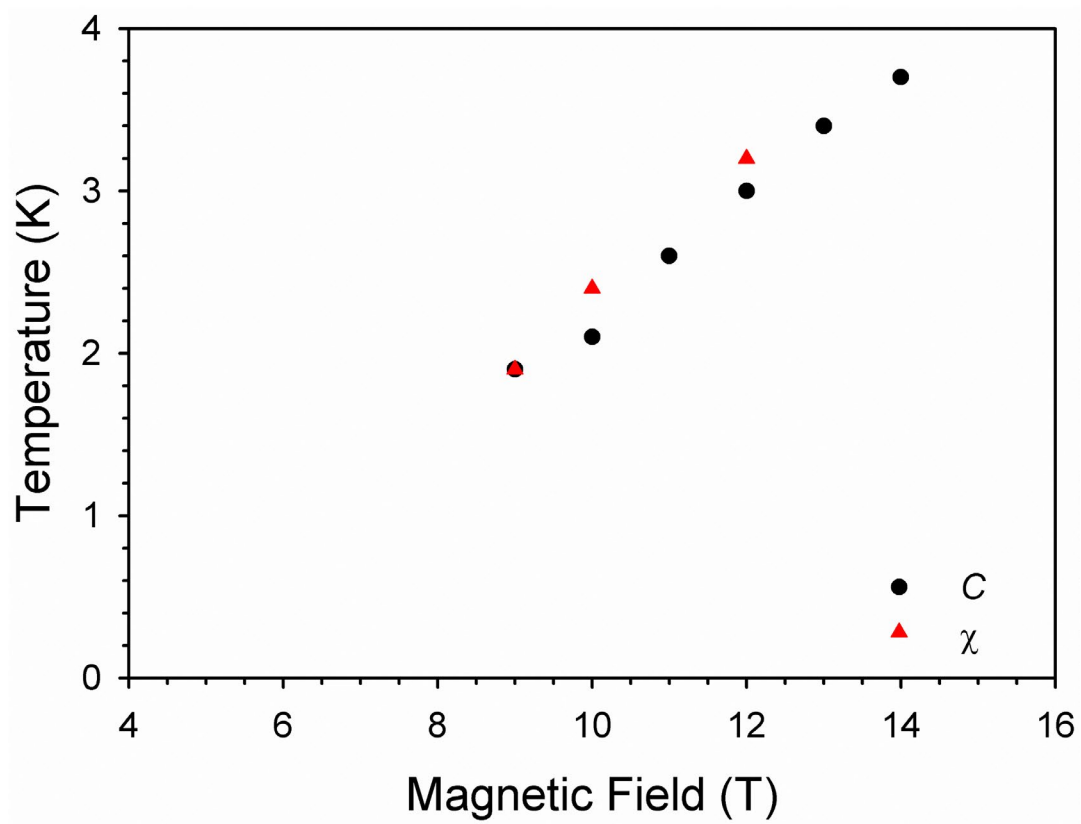


Figure C.21. Transition points estimated from specific heat and magnetization data for magnetic field beyond 9 T.

C6. Additional Inelastic Neutron Scattering (INS) Data of NiBO and Tables of Calculated Phonon Symmetries and Spin Densities

The comparison of the phonon features of **NiBO** between the 5 and 40 K is given in Figure C.22. At 40 K, the INS data fluctuate more in intensity than the 5 K data. The intensity fluctuation is due mostly to the thermal energy contribution. The data at both temperatures have similar phonon features.

Figure C.23 shows the comparison between the experimental INS spectrum of **NiBO** at 5 K and the calculated phonon spectrum in the low-energy region around the Haldane gap. The calculated phonon spectrum compares reasonably well with the experimental data. Table C.3 contains a list of phonon symmetries and modes of **NiBO** extracted from the phonon calculation.

In addition to the calculated phonon spectrum, spin densities of the compound were also obtained from the DFT calculations using VASP. Spin density provides insight into the localization of spin in the metal ions and the ligands in the system. The calculation does not include the spin densities in the bonds, but rather only shows the spin densities in individual atoms inside a unit cell. The full list of spin densities is given in Table C.4. The results show that most of the spin densities are concentrated at the Ni^{II} ion, containing 1.781 (89.1%) of the 2 unpaired electrons. The rest of the spin densities are dispersed among the ligands (oxalate and 4,4'-bipyridine). We recently found that in **Co-TODA**,³⁰ the spin densities concentrated in the Co^{II} ions are 2.68-2.69 (89.3-89.7%) of the 3 unpaired electrons on the metal ions. The percentage of the spin concentration is comparable to the spin densities in the current Ni^{II} system, which is possibly due to both compounds having only nitrogen and oxygen coordinating atoms.

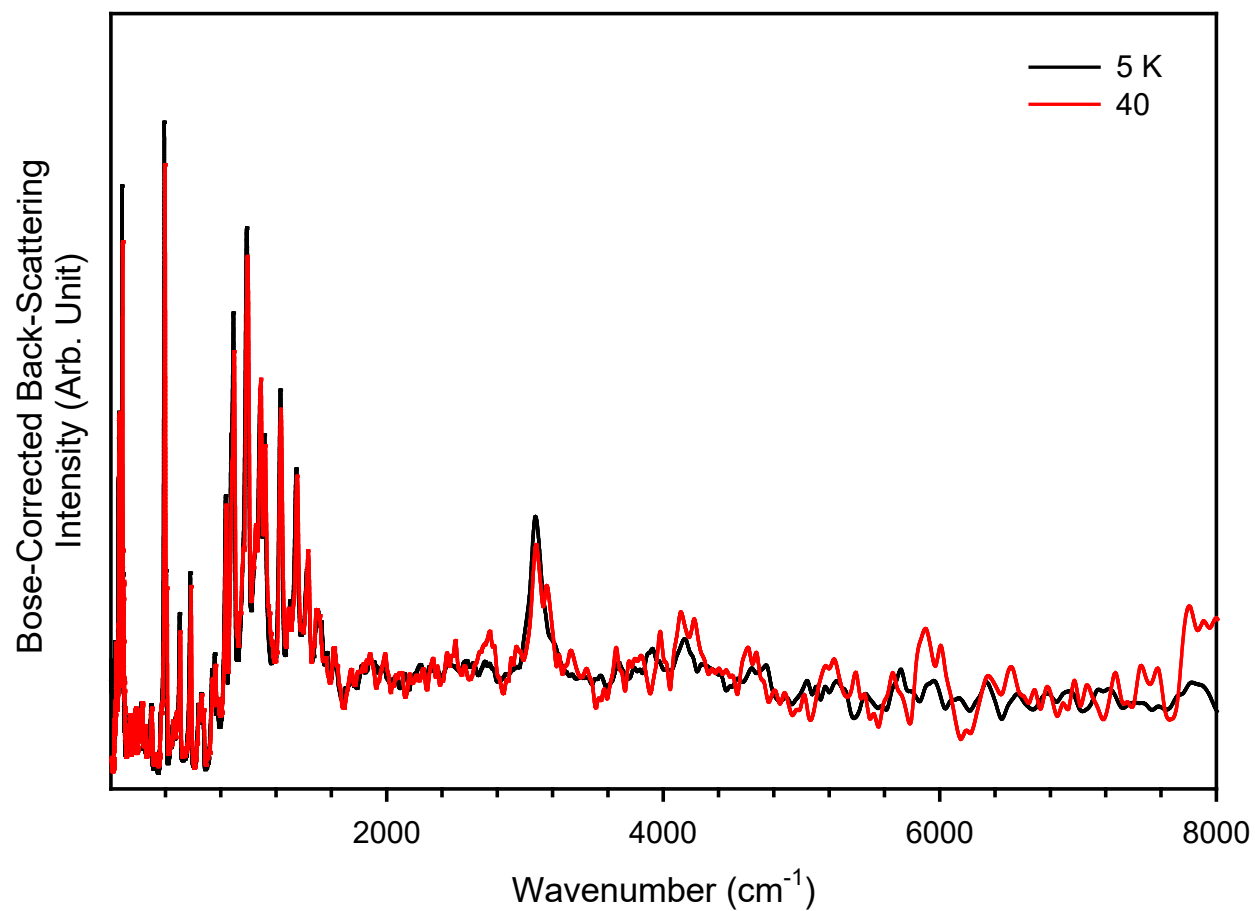


Figure C.22. INS spectra of **NiBO** at 5 and 40 K. The two spectra are similar with the 40 K spectrum having more vibrational intensity due to the increase in thermal energy compared to the 5 K spectrum.

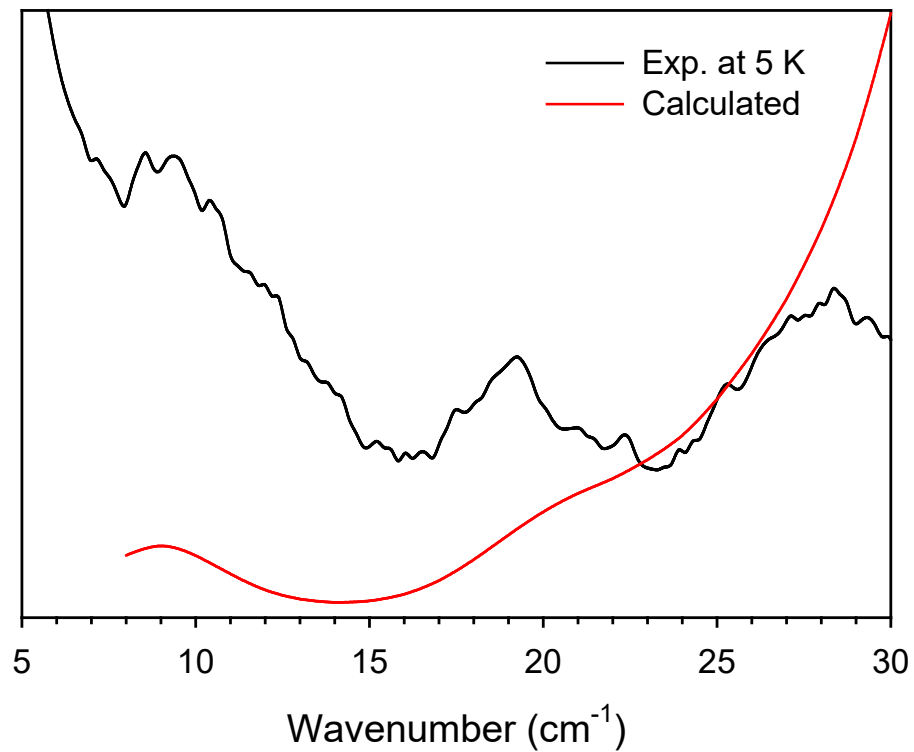


Figure C.23. Experimental INS spectrum of **NiBO** at 5 K in comparison with the calculated phonon spectrum (5-30 cm⁻¹ region).

Table C.3. Calculated phonon symmetries and modes of **NiBO**

Wavenumber (cm ⁻¹)	Symmetries of the modes	Wavenumber (cm ⁻¹)	Symmetries of the modes
68.853	<i>B</i>	887.178	<i>A</i>
78.699	<i>B</i>	975.925	<i>B</i>
78.873	<i>A</i>	980.973	<i>A</i>
82.731	<i>A</i>	1002.163	<i>A</i>
108.143	<i>B</i>	1008.519	<i>A</i>
115.883	<i>B</i>	1033.115	<i>A</i>
182.689	<i>B</i>	1075.207	<i>A</i>
183.123	<i>A</i>	1077.428	<i>A</i>
192.065	<i>B</i>	1106.668	<i>B</i>
197.872	<i>B</i>	1108.590	<i>B</i>
211.306	<i>A</i>	1211.672	<i>A</i>
224.928	<i>B</i>	1223.726	<i>A</i>
244.372	<i>A</i>	1271.586	<i>B</i>
279.673	<i>A</i>	1284.012	<i>A</i>
282.652	<i>B</i>	1285.602	<i>B</i>
297.328	<i>B</i>	1313.346	<i>B</i>
318.915	<i>B</i>	1326.318	<i>B</i>
382.149	<i>A</i>	1331.750	<i>B</i>
391.352	<i>A</i>	1403.771	<i>B</i>

Table C.3. Continued			
393.596	<i>B</i>	1405.542	<i>A</i>
415.794	<i>B</i>	1417.434	<i>B</i>
448.006	<i>A</i>	1475.766	<i>A</i>
498.541	<i>B</i>	1499.908	<i>A</i>
501.982	<i>A</i>	1523.854	<i>B</i>
569.796	<i>A</i>	1550.712	<i>B</i>
574.936	<i>B</i>	1588.764	<i>B</i>
628.673	<i>A</i>	1594.705	<i>A</i>
648.740	<i>B</i>	1596.594	<i>A</i>
664.476	<i>B</i>	1598.219	<i>A</i>
733.178	<i>B</i>	3068.039	<i>A</i>
749.623	<i>B</i>	3069.185	<i>B</i>
766.278	<i>A</i>	3070.673	<i>B</i>
773.847	<i>B</i>	3072.682	<i>A</i>
813.957	<i>B</i>	3079.726	<i>B</i>
817.366	<i>B</i>	3080.780	<i>B</i>
866.603	<i>B</i>	3081.382	<i>A</i>
868.397	<i>A</i>	3083.977	<i>A</i>
881.198	<i>A</i>		

Table C.4. Calculated spin densities of atoms in **NiBO** [one Ni(μ -4,4'-bpy)(μ -ox) unit]

Atom	Spin Density
Ni atom	1.781
All O atoms	0.035
Both N atoms	0.035
C (in oxalate)	-0.001
C (<i>ortho</i> from the N atoms in bpy)	-0.001
C (<i>para</i> from the N atoms in bpy, i.e., C atom linked to the other ring)	-0.001
C (<i>meta</i> from the N atoms in bpy)	0.002
All H atoms	<0.001
Total	1.995

Appendix D. Supporting Information for Chapter 5

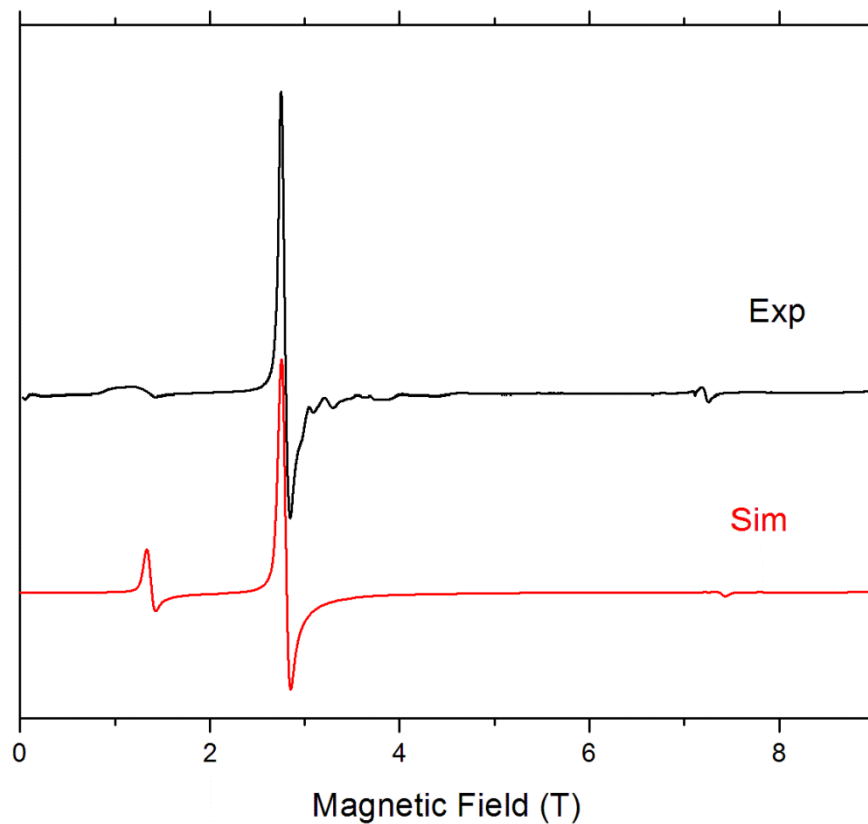


Figure D.1. Experimental HFEPR spectrum of **Fe(TPP)F** at 10 K and 203.2 GHz (black trace) and its powder-pattern simulation (red trace) using spin-Hamiltonian parameters: $D = 4.67 \text{ cm}^{-1}$, $E = 0$, $g_{\text{iso}} = 1.98$.

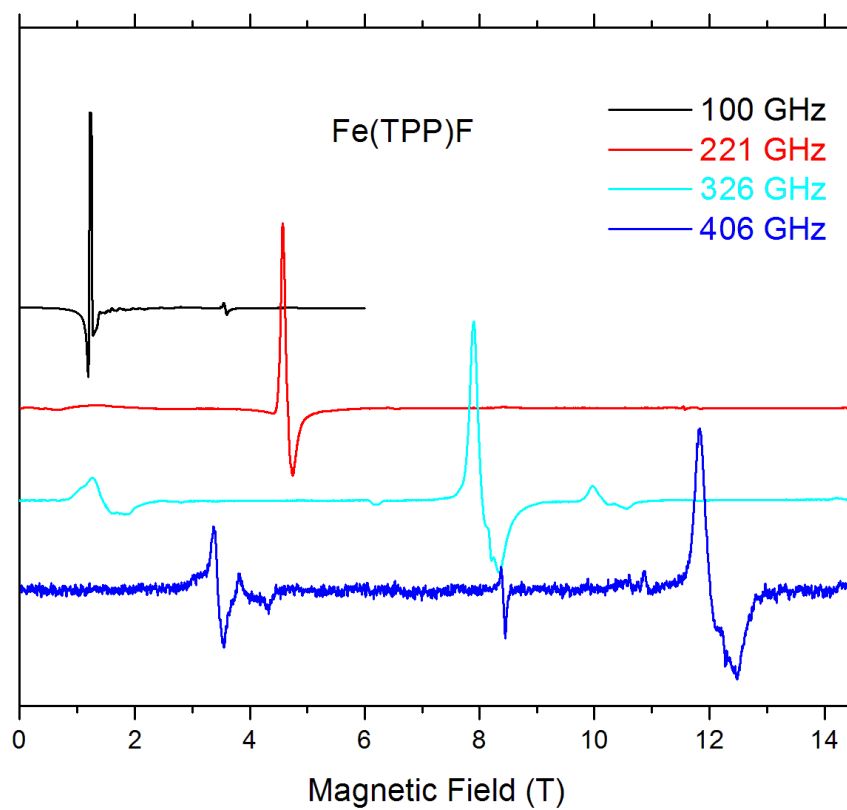


Figure D.2. A collection of multi-frequency, low-temperature (5 K) experimental HFEPR spectra of **Fe(TPP)F** eicosane mull.

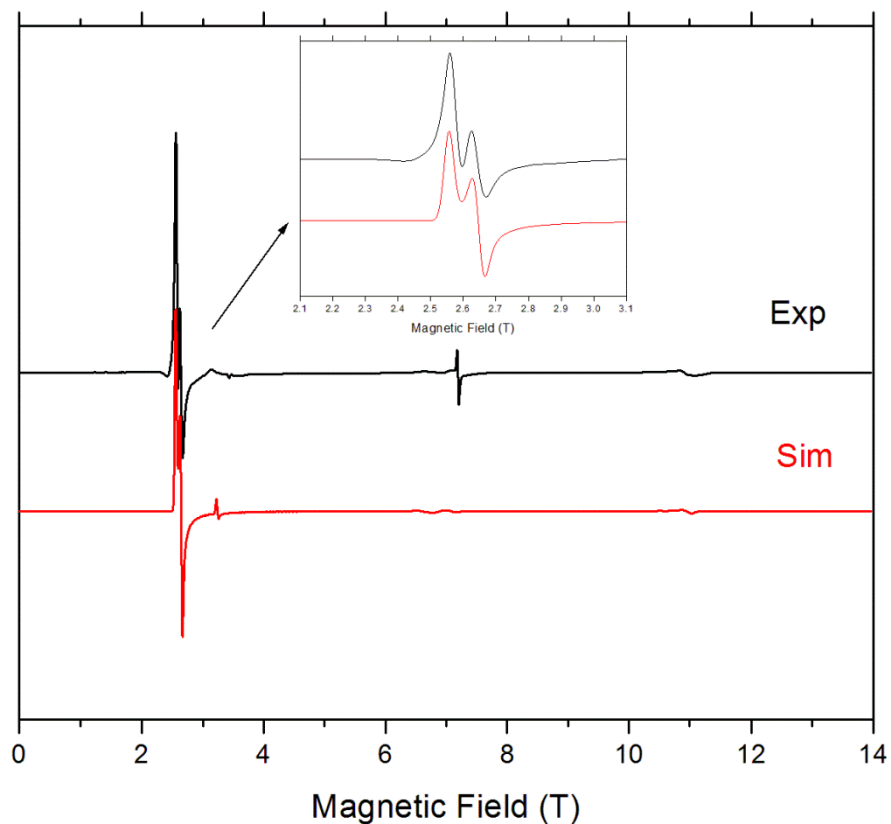


Figure D.3. Main plot: An experimental HFEPR spectrum of **Fe(TPP)Cl** at 10 K and 203.2 GHz (black trace) and its simulation (red trace) using spin-Hamiltonian parameters: $D = 6.45 \text{ cm}^{-1}$, $E = 0.025 \text{ cm}^{-1}$, $g_{\perp} = 1.985$, $g_{\parallel} = 2.02$. Inset: a zoom-in of the perpendicular intra-Kramers turning point. The splitting is indicative of a very small ($E/D \sim 0.004$) yet measurable rhombicity of the ZFS tensor. The resonance at 7.1 T is from an unidentified $g = 2.00$ species and is not simulated.

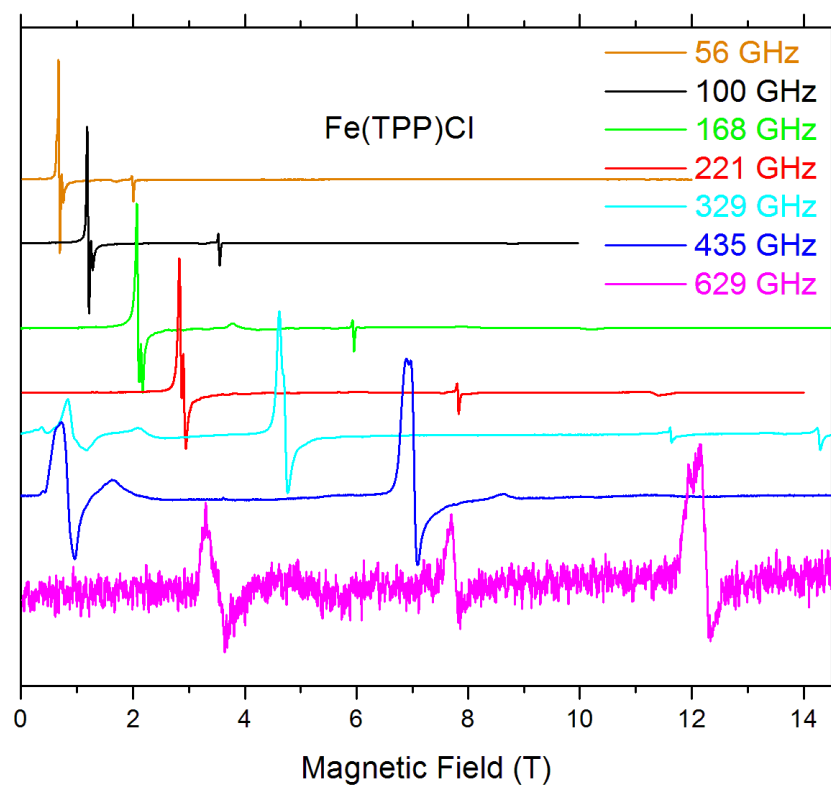


Figure D.4. A collection of multi-frequency, low-temperature (10 K) experimental HFEPR spectra of Fe(TPP)Cl eicosane mull.

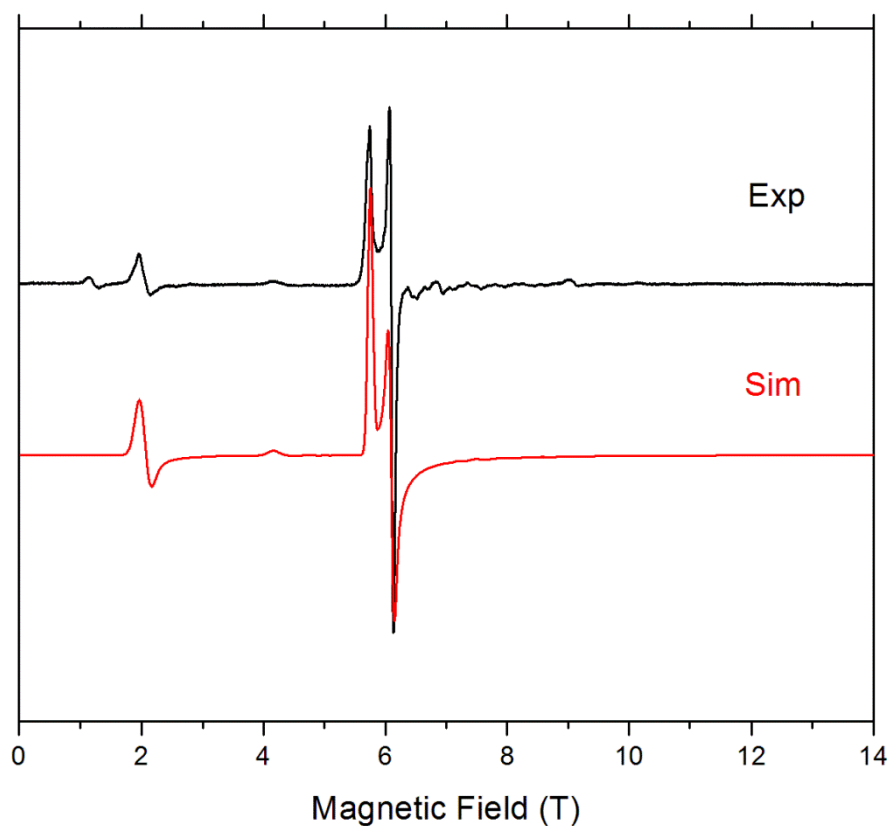


Figure D.5. An experimental HFEPR spectrum of **Fe(TPP)Br** at 10 K and 424 GHz (black trace) and its simulation (red trace) using spin-Hamiltonian parameters: $D = 9.01 \text{ cm}^{-1}$, $E = 0.056 \text{ cm}^{-1}$, $\mathbf{g} = [1.98, 1.98, 2.00]$. The weak resonance at 1.5 T originates from an unknown impurity and is not simulated.

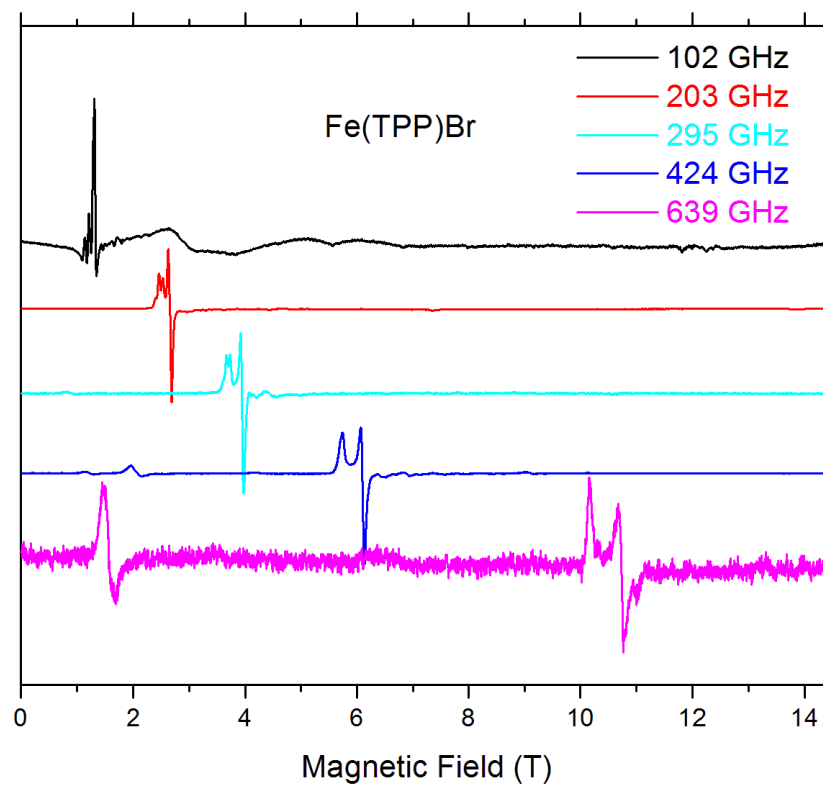


Figure D.6. A collection of multi-frequency, low-temperature (10 K) experimental HFEPR spectra of $\text{Fe}(\text{TPP})\text{Br}$ as in eicosane pellet.

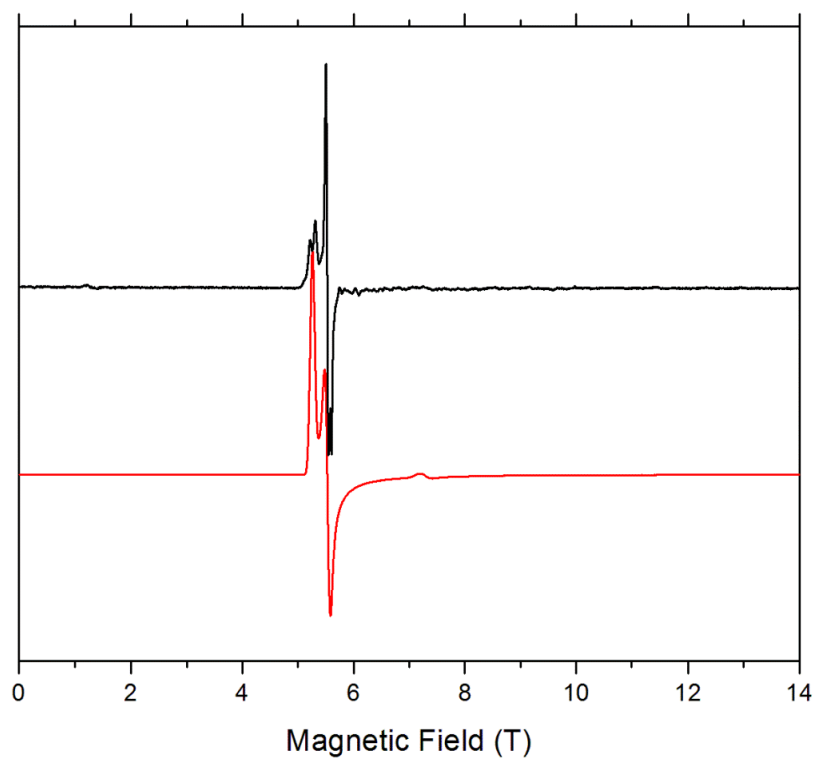


Figure D.7. An experimental HFEPR spectrum of **Fe(TPP)I** at 10 K and 423 GHz (black trace) and its simulation (red trace) using spin-Hamiltonian parameters: $D = 13.84 \text{ cm}^{-1}$, $E = 0.08 \text{ cm}^{-1}$, $\mathbf{g} = [1.985, 1.985, 2.00]$.

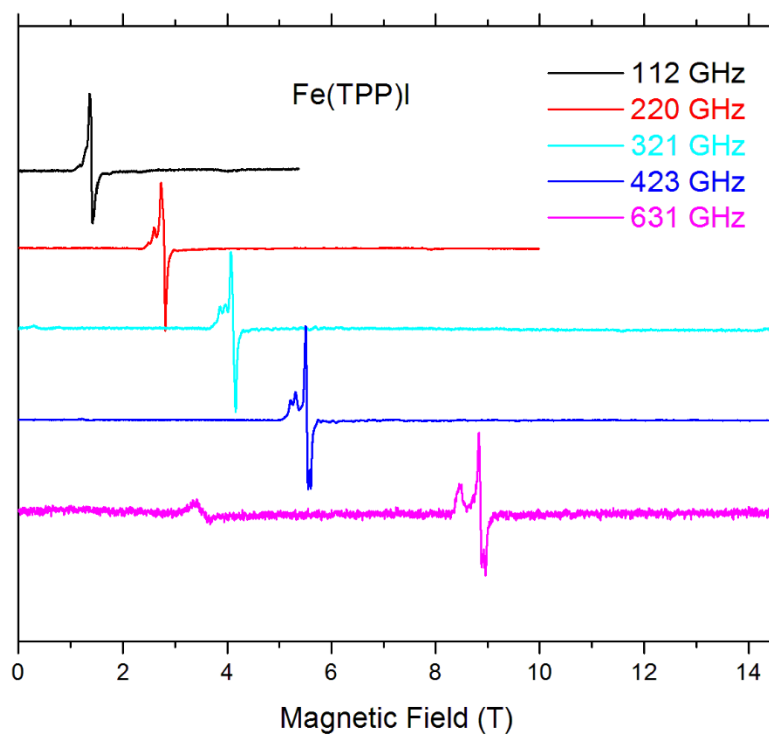


Figure D.8. A collection of multi-frequency, low-temperature (10 K) experimental HFEPR spectra of **Fe(TPP)I** as in eicosane pellet.

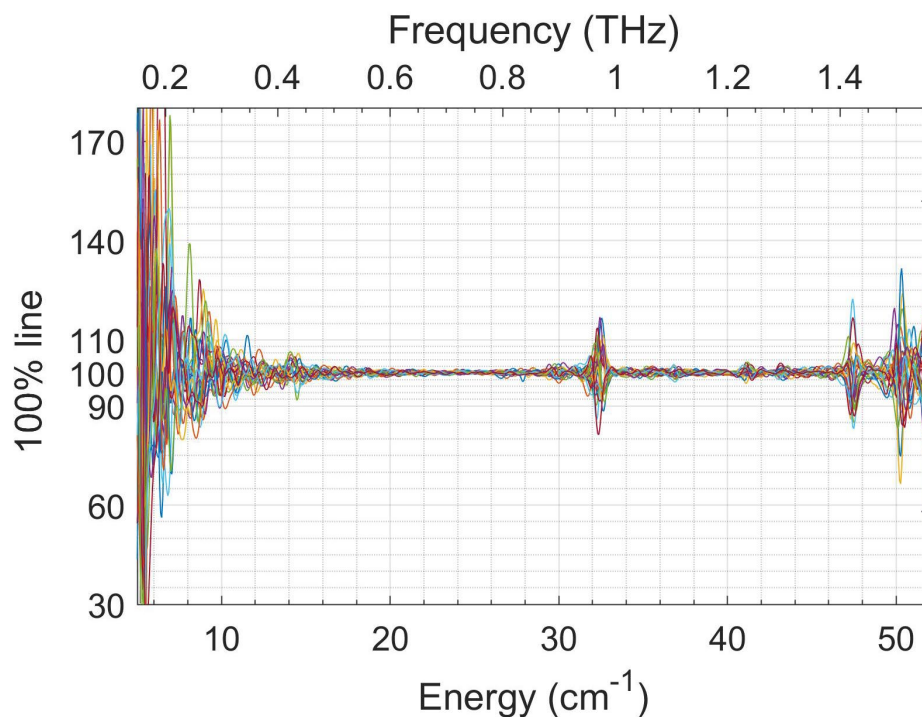


Figure D.9. The signal-to-noise of FIRMS measurements of **Fe(TPP)I**. The 100% line is calculated as a ratio of two transmission spectra recorded under identical conditions for each magnetic field. Ideally, the result should be a flat line at 100% transmission and the deviation from this value characterizes the validity of spectroscopic measurements in the real set-up. In this case, any field-induced changes above 2% in the transmission can be detected in the vicinity of 25 cm^{-1} , but at lower frequencies the noise level is rising which is attributed simply to the vanishing power of the THz source at these frequencies, so that the region below $\sim 15 \text{ cm}^{-1}$ is unreliable. In contrast, the higher frequency range (above $\sim 47 \text{ cm}^{-1}$) suffers by a combination of non-magnetic spectral features, such as vibrational absorptions and instrumental artefacts.

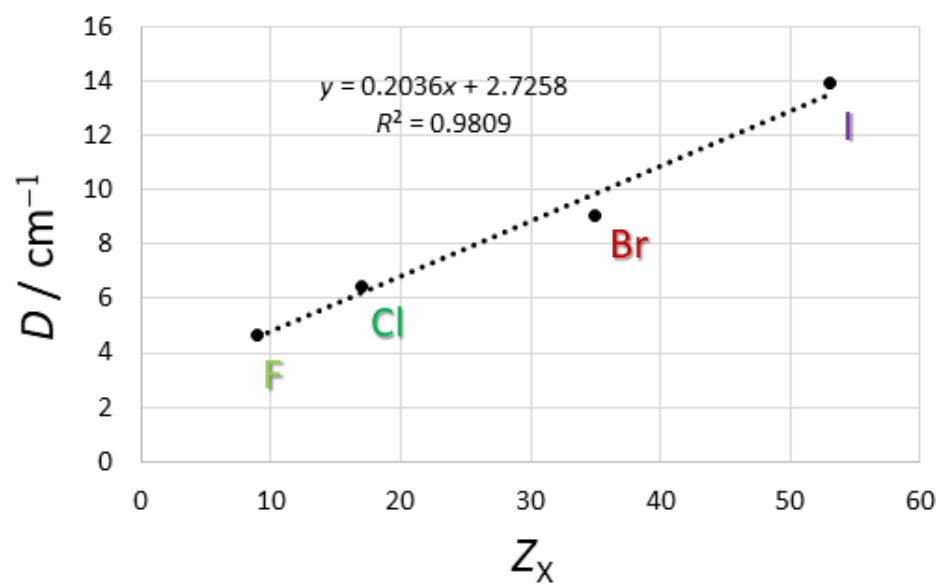


Figure D.10. Plot of D values of $\text{Fe}(\text{TPP})\text{X}$ versus Z_X (atomic number of the halides X).

VITA

Pagnareach Tin was born in Phnom Penh, Cambodia to Samedy S. Tin and Ponloeu Young. He immigrated to Durham, NC in March 2010 with his family. Afterward, he attended C.E. Jordan High School in Durham, NC. After graduating from high school in May 2014, he moved to Asheville, NC to attend the University of North Carolina, Asheville and graduated in May 2018 with a Bachelor of Science degree in Chemistry. During his undergraduate years, he obtained a summer laboratory internship position with Doble Engineering Company and conducted research with Dr. Bert E. Holmes on the study of the trichloroethylene decomposition pathway in the gas phase using ultraviolet light. He joined the graduate school program at the University of Tennessee, Knoxville in August 2018, where he studied molecular magnetism with Dr. Zi-Ling Xue. Since then, he received the Shull Wollan Center Graduate Research Fellowship in 2021 and was awarded the Graduate Fellowship for Achievement in Inorganic Chemistry in Spring 2023 by the Department of Chemistry, University of Tennessee, Knoxville.

As of April 2023, Pagnareach has published the following two papers from his Ph.D. studies:

1. Tin, P. et al. Advanced Spectroscopic and Computational Studies of a Cobalt(II) Coordination Polymer with Single-Ion-Magnet Properties. *J. Phys. Chem. C* **2022**, *126*, 13268.
2. Tin, P. et al. Advanced Magnetic Resonance Studies of Tetraphenylporphyrinatoiron(III) Halides. *Appl. Magn. Reson.* **2020**, *51*, 1411.