

**Spectroscopic Insights into Metal Complexes: Toroidal Properties, Magnetism, and
Solvatochromism**

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DEDICATION

To Brooke, for your patience, love, and devotion.

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ABSTRACT

Compounds exhibiting quantum magnetic properties are of current interest for their potential use in quantum computing or spintronics. These magnetic properties, and the relaxation of magnetic excitations, are not fully understood and need further exploration for more widespread use in quantum information science applications. To further understand the magnetic relaxation and magnetic structure of these materials, they have been studied using advanced techniques such as magneto-couple spectroscopy and neutron scattering. The primary focus of this dissertation is the study of the magnetic structure, relaxation, and synthesis of molecular magnetic compounds such as single-molecule magnets (SMMs), a single-molecule toroic (SMT), and spin-1 Haldane topological chains. These are studied using a combination of routine and advanced techniques, such as inelastic neutron scattering, far-IR magneto spectroscopy, high-field and -frequency electron spin resonance, or polarized neutron diffraction to directly observe magnetic transitions or the magnetic structure. From these studies one can directly observe zero-field splitting parameters for the Co(II) complex **Co-MST-H₂O** ([Co(MST)(H₂O)][NEt₄]; MST³⁻ = *N,N',N''*-[2,2',2''-nitrilotris(ethane-2,1-diyl)]tris(2,4,6-trimethylbenzenesulfonamido), H₂O = water, NEt₄⁺ = tetraethylammonium) and phonon features of both **Co-MST-H₂O** and its Ni(II) analog **Ni-MST-H₂O** in Chapter 2. Using a combination of neutron diffraction techniques and magnetometry we have observed the atomic-scale spin configuration of Dy(III) ions in an SMT candidate in Chapter 3, which is a first for SMT compounds. Chapter 4 shows that through the use of multiple advanced techniques, we characterized two Ni(II)-based MOFs as spin-1 Haldane topological materials.

Chapter 5 is dedicated to synthesis and solvatochromism in Cu(II) compounds and the conversion of Cu(II) salts into CuO. This study was completed to teach the future generations of

chemists of multiple chemical theories and features, including the use of mechanochemistry, green chemistry, solvatochromic effects, solvent effects on synthesis, sol-gel reactions, and characterization of solid-state materials.

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List of Abbreviations

1-D	One-dimensional
2-D	Two-dimensional
3-D	Three-dimensional
AC	Alternate current
AF	Antiferromagnetic
AKLT	Affleck, Kennedy, Lieb, and Tasaki
AO	Atomic orbital
CP	Coordination polymer
CASSCF	Complete-active-space self-consistent field
CIF	Crystallographic information file
CShM	Continuous shape measure calculations
DC	Direct current
DFT	Density functional theory
EPR	Electron paramagnetic resonance
FIRMS	Far-IR magneto-spectroscopy
FT	Fourier transform
HFEP	High-frequency and -field EPR
INS	Inelastic neutron scattering
IR	Infrared
KD	Kramers doublet
LFT	Ligand-field theory
LMCT	Ligand-to-metal charge transfer

Ln	Lanthanide
MOF	Metal-organic-framework
NMR	Nuclear magnetic resonance
NIR	Near-IR
PND	Polarized neutron diffraction
PXRD	Powder X-ray diffraction
QTM	Quantum tunnelling of magnetization
Qubit	Quantum bit
SCXRD	Single-crystal X-ray diffraction
SH	Spin-Hamiltonian
SMM	Single-molecule magnet
SMT	Single-molecule toroics
SOC	Spin-orbit coupling
TM	Transition metal
TOF	time-of-flight
UV	Ultraviolet
VASP	Vienna <i>ab initio</i> simulation package
VH	Variable-field
VISION	Vibrational Spectrometer
VT	Variable-temperature
ZFS	Zero-field split(ting)

List of Symbols

A	Spin-phonon coupling constant
χ	Magnetic susceptibility
B	Magnetic field
D	Single-ion axial anisotropy parameter
E	Transverse or rhombic anisotropy parameter
g	g -factor or g -tensor
J	Total angular momentum
KD	Kramers doublet
$\mathbf{k_f}$	Momenta of outgoing neutrons
$\mathbf{k_i}$	Momenta of incoming neutrons
M_J	Total angular momentum quantum number
m_l	Magnetic quantum number
M_s or m_s	Electron spin quantum number
$\mathbf{Q}$	Momentum transfer
S	Spin
U_{eff}	Effective energy barrier separating bistable magnetic states
μ_{eff}	Effective magnetic moment (in the unit of μ_B or Bohr magneton)

List of Compounds

Co-MST	$[\text{M}(\text{MST})][\text{NEt}_4]$ ($\text{MST}^{3-} = N,N',N''\text{-}[2,2',2''\text{-nitrilotris(ethane-2,1-diyl)]tris(2,4,6-trimethylbenzenesulfonamido)}$, $\text{NEt}_4^+ =$ tetraethylammonium)
Co-MST-H₂O	$[\text{Co}(\text{MST})(\text{OH}_2)][\text{NEt}_4]$
Ni-MST-H₂O	$[\text{Ni}(\text{MST})(\text{OH}_2)][\text{NEt}_4]$
Dy₃-1	$[\text{Dy}_3(\mu_3\text{-OH})(\text{teaH}_2)_3(\text{paa})_3]\text{Cl}_2 \cdot \text{MeCN} \cdot 4\text{H}_2\text{O}$ [$\text{teaH}_3 =$ triethanolamine, $\text{paaH} = \text{N-(2-pyridyl)-acetoacetamide}$]
Dy₃-2	$[\text{Dy}_3(\mu_3\text{-OH})(\text{teaH}_2)_3(\text{paa})_3]\text{Cl}(\text{OMe}) \cdot \text{PhCN} \cdot 3\text{MeOH}$
NiBaO	$[\text{Ni}(\mu\text{-bpa})(\mu\text{-ox})]$ ($\text{bpa} = 1,2\text{-di(pyridin-4-yl)ethane}$; $\text{ox}^{2-} =$ oxalate)
NiBeO	$[\text{Ni}(\mu\text{-bpe})(\mu\text{-ox})]$ ($\text{bpe} = 1,2\text{-di(pyridin-4-yl)ethene}$)
NiBO	$[\text{Ni}(\mu\text{-4,4'-bpy})(\mu\text{-ox})]$ ($\text{bpy} =$ bipyridine)
NENP	$[\text{Ni}(\text{en})_2(\mu\text{-NO}_2)](\text{ClO}_4)$ ($\text{en} =$ ethylenediamine)
NENB	$[\text{Ni}(\text{en})_2(\mu\text{-NO}_2)](\text{BF}_4)$ ($\text{en} =$ ethylenediamine)
NDMAZ	$\text{Ni}(\text{dmpn})_2(\mu\text{-N}_3)](\text{ClO}_4)$ ($\text{dmpn} = 1,3\text{-diamino-2,2-dimethylpropane}$)
NINO	$[\text{Ni}(1,3\text{-propanediamine})_2(\mu\text{-NO}_2)](\text{ClO}_4)$

Chapter 1: Introduction

1.1. Molecular magnetic systems

Molecular quantum materials have gained significant research interest due to their promising use in spintronics, high-density data storage, and in quantum computing.¹⁻¹² These materials exhibit unique electronic structures and quantum entanglement of spins that could be used as qubits in quantum information science. Of these materials, this dissertation will discuss single-molecule magnets (SMMs), single-molecule toroics (SMTs), and Haldane topological spin-1 chains.

1.1.1 Single-molecule magnets

Single-molecule magnets (SMMs) are compounds with bi-stable magnetic states ($\pm M_s$) below a blocking temperature, as shown in **Figure 1.1**. These materials show a barrier to magnetization reversal ($+M_s$ to $-M_s$), commonly denoted as U_{eff} , leading to long magnetic relaxations in the absence of a magnetic field.¹³⁻¹⁶ For this relaxation to take place, there must be a mechanism that allows for either crossing over this barrier or tunneling through the barrier. These relaxation mechanisms are given in **Figure 1.2.**, showing that there are multiple mechanisms or a combination of mechanisms that might lead to this relaxation.

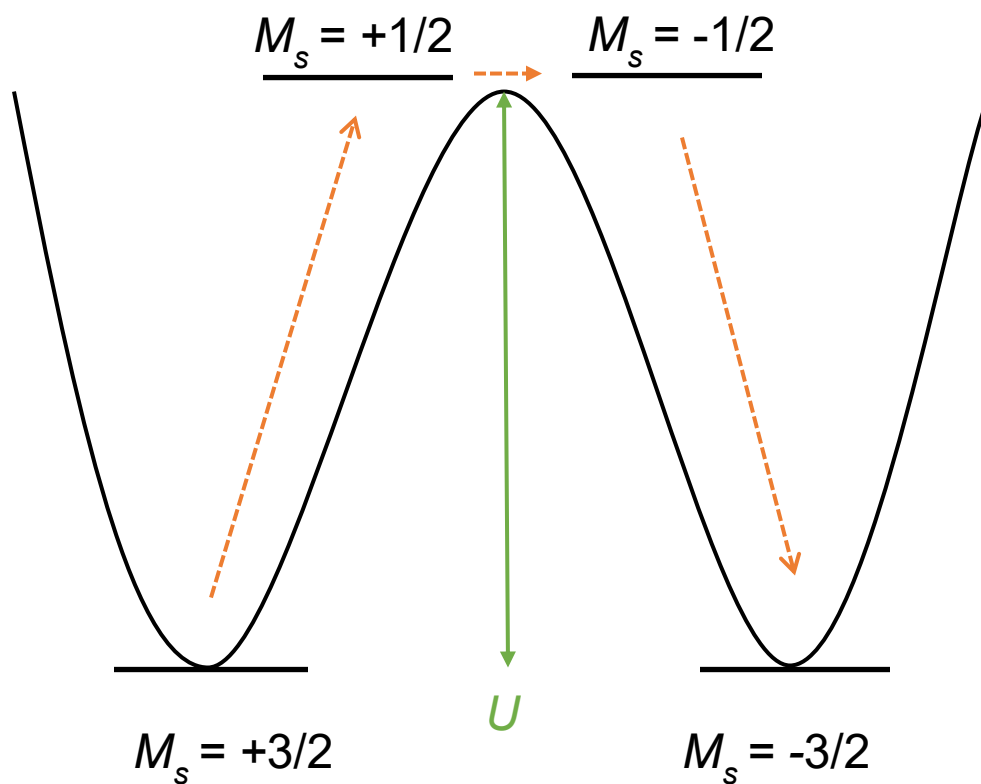


Figure 1.1. Double-well diagram showing the magnetic barrier (U) for a transition metal-based SMM with $S = 3/2$ and $D < 0$. If $D > 0$ the $M_s = \pm 1/2$ states are minimized. U is the barrier to magnetic reversal, with U_{eff} being the empirical equivalent of U when all relaxation mechanisms are considered. Dashed arrows indicate a simplified ideal pathway for magnetic relaxation.

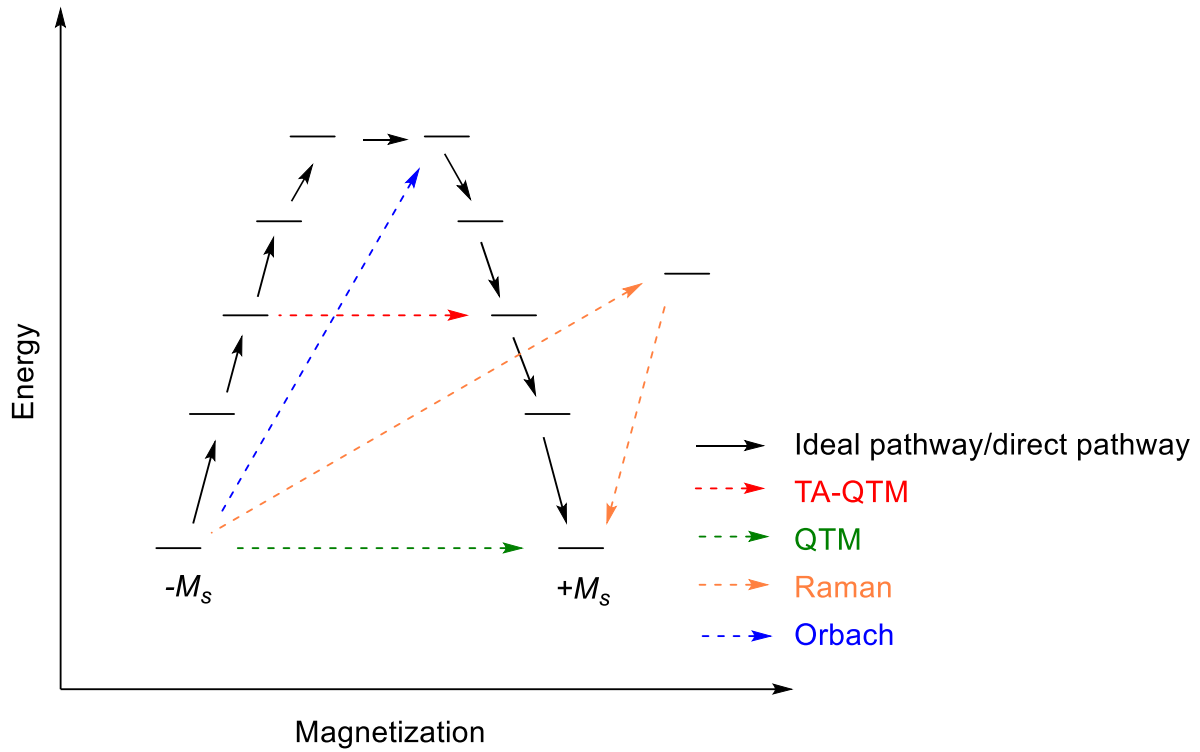


Figure 1.2. A schematic representation of the possible magnetic relaxation mechanisms in SMMs. Black lines indicate spin states. Color code of pathways: black = direct pathway, red = thermally assisted quantum tunnelling of magnetization (QTM), green = ground state QTM, orange = Raman relaxation, blue = Orbach relaxation.

To examine these mechanisms as well as what leads to the size of the barrier, we can look at Eqs. 1.1 and 1.2 that determine U_{eff} ,

$$U_{eff} = (S^2 - \frac{1}{4})|D| \quad (\text{Eq 1.1.})$$

for complexes with integer spins, or

$$U_{eff} = S^2|D| \quad (\text{Eq 1.2.})$$

for complexes with half-integer spins, where S is the spin of the ions within the complex and D is the axial anisotropy of the ion.¹⁷⁻¹⁹

We either increase the anisotropy of the metal ion or S to enlarge U_{eff} for a complex. This can be demonstrated comparing the first reported SMM $[\text{Mn}_{12}\text{O}_{12}(\text{AcO})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{AcOH}$ ($\text{AcO}^- = \text{CH}_3\text{COO}^-$), which is now commonly referred to as Mn_{12} ,¹⁵ with $[\text{TBA}][\text{Pc}_2\text{Ln}]$ ($\text{Pc}^{2-} =$ phthalocyanine dianion; $\text{Ln}^{3+} = \text{Tb}^{3+}, \text{Dy}^{3+}$; $\text{TBA}^+ =$ tetrabutylammonium), a lanthanide-based single-ion SMM. $[\text{TBA}][\text{Pc}_2\text{Ln}]$ shows a much larger barrier based on the high spin of a single Ln^{3+} ion combined with a high level of anisotropy.²⁰ Mn_{12} has U_{eff} of approximately 45 cm^{-1} with $S = 10$, while the U_{eff} of $[\text{TBA}][\text{Pc}_2\text{Tb}]$ is 230 cm^{-1} with much smaller $S = 3$.^{15, 20}

When examining the magnetic anisotropy of a metal ion, there are multiple effects to consider. These include the difference in spin states due to crystal field interactions, spin-orbit coupling (SOC) interactions, and the effects leading to zero-field splitting (ZFS).^{21, 22} There are two types of SOC: (1) Angular momentum of the ground state is unquenched, leading to first-order SOC. Here, the electron's magnetic dipole interacts with the electrostatic field of the nucleus, thus shifting its orbital motion. (2) Angular momentum is quenched. That is, the orbital motions of the unpaired electrons are quenched, and the ground state of the electronic structure mixes with low-energy excited electronic states, giving SOC properties to the ground state.²³⁻³⁰

As a result, the ground state splits inside non-cubic ligand fields, leading to ZFS. Crystal-field

split states are shown as ^{2S+1}L from Russell-Saunders coupling, as seen in **Figure 1.3(b)**. These degenerate ^{2S+1}L spin states, in compounds with $S > 1/2$ and quenched orbital angular momenta, are split by second-order SOC. This splitting is defined as ZFS, which defines magnetic levels according to the spin-Hamiltonian in Eq. 1.3:

$$\hat{H}_S = D \left[\hat{S}_z^2 - \frac{1}{3}S(S+1) \right] + E \left[\hat{S}_x^2 - \hat{S}_y^2 \right] + \mu_B (g_x B_x \hat{S}_x + g_y B_y \hat{S}_y + g_z B_z \hat{S}_z) \quad (\text{Eq. 1.3})$$

where $\hat{S}_i$ = components of the spin operator $\hat{S}$ in the x , y and z directions; D and E = axial and rhombic ZFS parameters, respectively; μ_B = electron Bohr magneton; g_i = components of the g -factor in the x , y and z directions; $\mathbf{B}$ = external magnetic field.³¹⁻³³ Inclusion of a C_3 axis, making x, y axes degenerate, lowers, or even eliminates rhombic anisotropy E . Reducing rhombic anisotropy is key for increasing quantum coherence times as it limits unwanted relaxation pathways such as quantum tunneling.

One can then see that there is an inherent correlation between the structure of an SMM compound, the anisotropy dictated by structure, and the U_{eff} of this compound. Due to the correlation, we have sought to study the impact of structure on magnetic relaxation using a combination of routine and advanced techniques. One of the most important forms of relaxation to study is the direct path or vibrationally coupled relaxation through phonons. In molecular solids, phonons refer to both internal and external vibrations, also described as intramolecular and intermolecular vibrations. Internal vibrations show large distortion of the molecule, while external vibrations have little molecular distortions but larger lattice vibrations and interactions. Lattice vibrations are typically much lower in energy than molecular distortions and are a primary driver of spin-reversal relaxations. In the current work, the term phonons will be used for both intramolecular and intermolecular vibrations. During molecular magnetic relaxation,

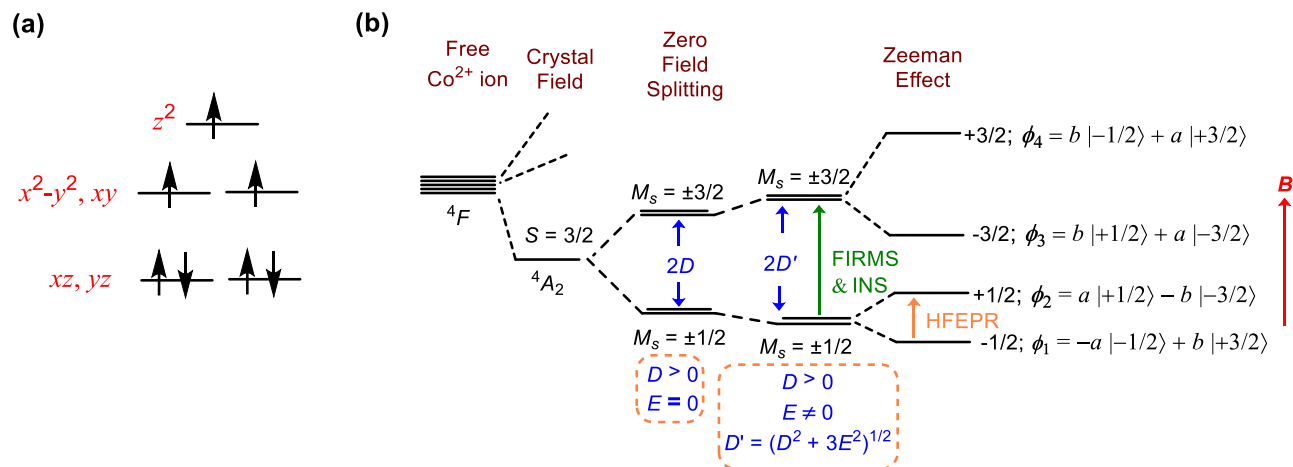


Figure 1.3. (a) Depiction of the ligand field splitting for a 5-coordinate, high-spin Co^{2+} complex with local C_{3v} symmetry. (b) Ground-state spin levels of a high-spin d^7 complex with C_3 or higher local symmetry of the metal site. When the symmetry is lower than C_3 , $E \neq 0$ and there is a mixing of spin states, giving ϕ_1 , ϕ_2 , ϕ_3 , and ϕ_4 . The mixing coefficients $a = \cos\beta$ and $b = \sin\beta$ are described by the mixing angle β obtained from the spin-Hamiltonian ($S = 3/2$). Mixing depends on the rhombicity as $\tan 2\beta = \sqrt{3}(E/D)$.

there is the possibility that these vibrations mix with the magnetic relaxation of the molecule, leading to spin-phonon couplings. Spin-phonon coupling may be observed in far-IR magneto-spectroscopy (FIRMS) in the form of an avoided crossing, as shown in **Figure 1.4**. Spin-phonon coupling occurs when the magnetic excited state ϕ_{magnetic} and phonon excited state ϕ_{phonon} have the same symmetry. When close enough in energy, these states interact to form two new, spin-phonon coupled states, one (Ψ_+) with higher energy and one (Ψ_-) with lower energy than the energies of ϕ_{magnetic} and ϕ_{phonon} states. These new states carry both magnetic and phonon features and are shifted by the Zeeman effect. This is shown through blue shifting of magnetic peaks that have repeated avoided crossings within the transition. A simple scheme is given in **Figure 1.4**. To determine the extent of spin-phonon couplings leading to magnetic relaxation, several spectroscopic methods may be used, including far-IR, Raman, and inelastic neutron scattering (INS). The current studies seek to probe spin-phonon couplings in SMMs.

1.1.2. Single-molecule toroics

A recent development in molecular quantum materials science has been SMT compounds. These compounds are bi-stable molecules with toroidal magnetic state, defined by a vortex arrangement of magnetic moments in a ferrotoroidic material. These vortex spin arrangements are formed by atomic magnetic moments coupling together within a metal cluster, showing geometric spin frustration that, at low temperatures, form a ferrotoroidic or vortex arrangement of spins as shown in **Figure 1.5**.^{34, 35} These materials show promises of slow magnetic relaxation and relatively large magnetic dipoles in comparison to other qubit candidates.^{4, 10, 36} While the family of these materials continue to grow, there has been strong

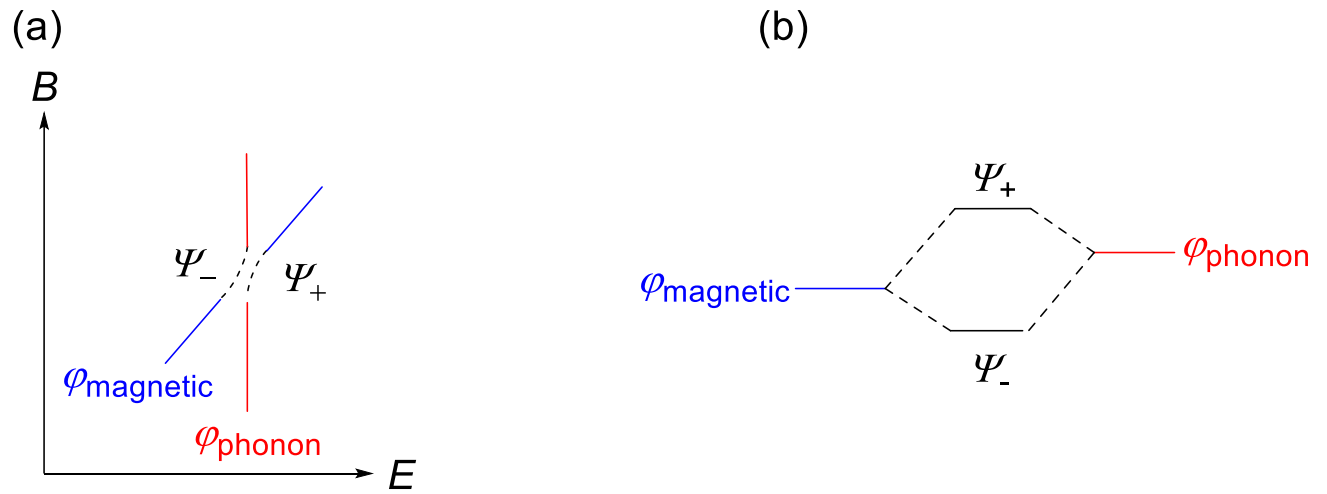


Figure. 1.4. (a) Schematic showing the Zeeman effect on magnetic excitations and the energy change (E) of the spin-phonon coupling with the external magnetic field B ($B = \text{magnitude of } \mathbf{B}$). (b) Schematic view of spin-phonon coupling. ϕ_{magnetic} and ϕ_{phonon} represent eigenfunctions of the magnetic state and phonon, respectively. Ψ_+ and Ψ_- are eigenfunctions of the two spin-phonon coupled states.

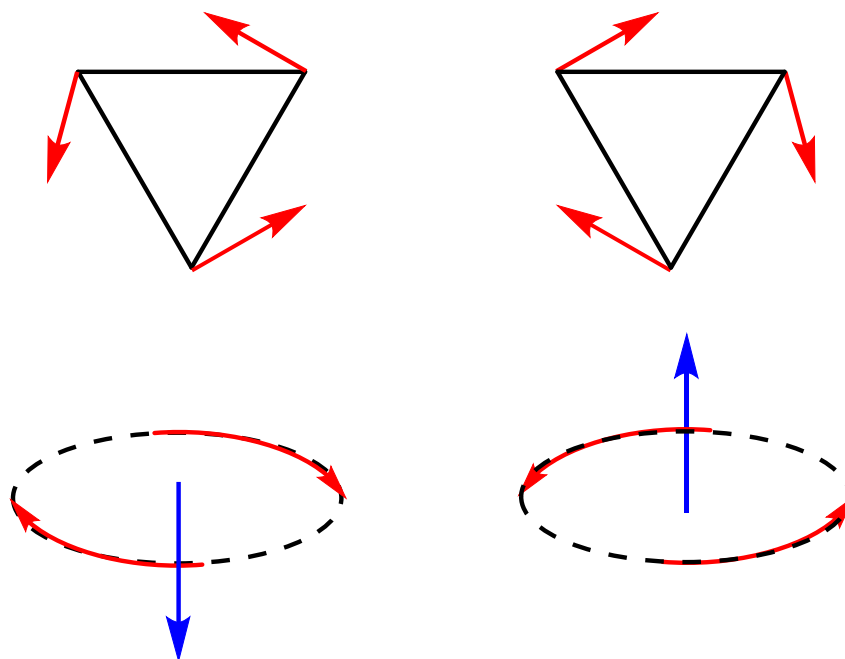


Figure 1.5. Planar spin alignment of coupled Dy^{3+} ions within an SMT.

interest to understand their physical and chemical properties or the driving force for the toroidal molecular moment alignment. The first SMT was reported in 2006 by Tang *et al.* and theoretically proven to be an SMT in 2008 by the work of Chibotaru *et al.*^{34,35} Since this development, there have been many SMTs synthesized and characterized, but there have been few if any studies to directly show the toroidal moment in SMTs.³⁷⁻⁴⁶ This dissertation will address the lack of direct observation of the toroidal spin arrangement.

1.1.3. Haldane topological materials

In 1983, Haldane suggested that antiferromagnetic (AF) Heisenberg chains with integer spin exhibit a disordered ground state along with a finite energy gap, whereas chains with half-integer spins are gapless.⁴⁷⁻⁵¹ This conclusion was based on effective-field theory and topological principles. **Figure 1.6** illustrates the energy structure of a Haldane spin-1 chain system, incorporating the effects of anisotropy (zero-field splitting or ZFS) and the Zeeman effect. The topological Haldane phase in the AF spin-1 chain is considered a key example of symmetry-protected topological states. Building on Haldane's work, Affleck, Kennedy, Lieb, and Tasaki (AKLT) developed an extended spin-1 Hamiltonian that describes the ground state of the Haldane phase, which includes one unpaired electron ($S = 1/2$) at each end of the chain, as depicted in **Figure 1.7**. The two electrons at the chain's ends can form singlet or triplet states, which are the edge states of the system.^{49, 50, 52-55} The topological Haldane phase is distinguished by its finite energy gap, which is protected by symmetry. As long as the symmetries are maintained, the Haldane phase remains stable and resilient to external disturbances. In contrast to typical antiferromagnetic materials, such as NiO, which exhibit long-range magnetic ordering, Haldane materials do not show such a behavior as the comparison in **Figure 1.7** shows. In NiO, a

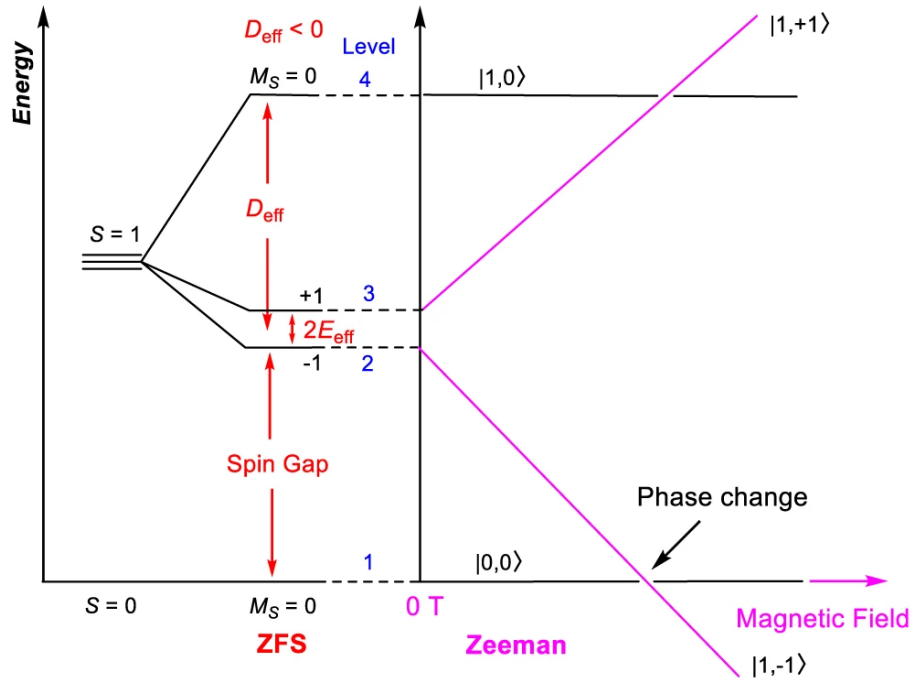


Figure 1.6. Energy diagram of a Haldane spin-1 chain system with the Zeeman effect on the magnetic states. Adapted from P. Tin, M. J. Jenkins et al.⁵⁶

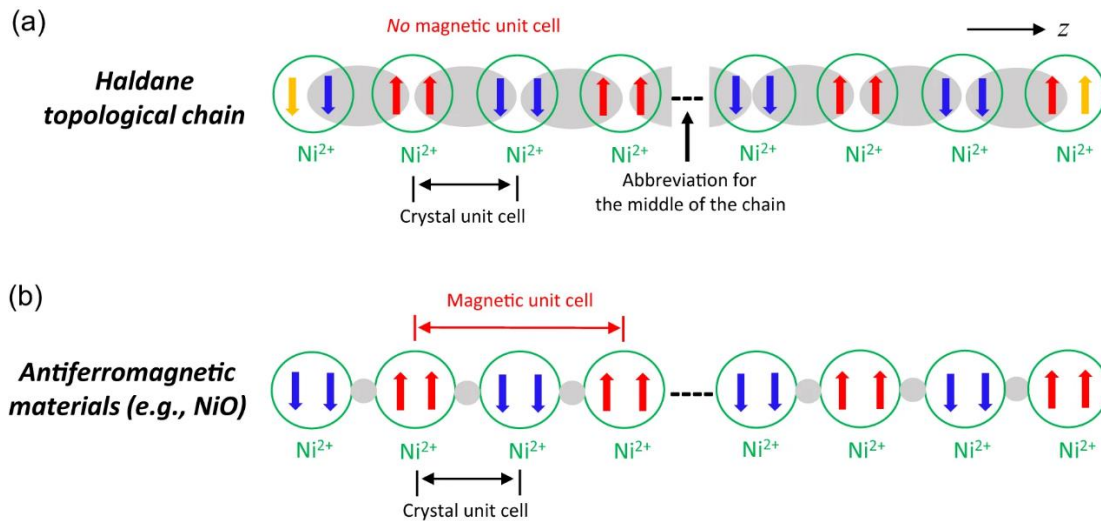


Figure 1.7. Scheme showing the differences between a Haldane topological chain and an antiferromagnetic material. Adapted from P. Tin, M. J. Jenkins et al.⁵⁶

magnetic unit cell forms in addition to the crystal unit cell, leading to Bragg reflections from both the magnetic and nuclear diffraction of the crystal's unit cell.⁵⁷

1.2. Experimental methods

Overviews of the experimental methods used in this dissertation are provided below with references for in-depth discussion.

1.2.1. DC magnetometry

One of the most widely used techniques to study magnetic materials is magnetometry, often implemented through a device known as the Superconducting QUantum Interference Device (SQUID). SQUID functions by exploiting the principles of flux quantization and Josephson tunneling. They consist of a superconducting loop interrupted by a Josephson junction, which permits the tunneling of Cooper pairs. This setup makes SQUIDs extremely sensitive to magnetic flux, effectively serving as flux-to-voltage transducers.

Direct current (DC) magnetization measurements are commonly carried out across a range of temperatures. As temperature decreases, higher-energy spin states become depopulated, providing insight into the energy separations between spin levels. A standard approach in such studies is to report the temperature-dependent magnetic susceptibility (χ) or the product χT . Plotting χT versus temperature (T) reveals deviations from ideal paramagnetic behavior, especially in systems of non-interacting spins. According to Curie's law, this relationship is described by:

$$\chi T = \frac{Ng^2\mu_B^2}{3k_B} S(S + 1) \quad (\text{Eq. 1.4})$$

where N is Avogadro's number, g is the g -factor (or g -tensor), μ_B is the Bohr magneton, and k_B is the Boltzmann constant.⁵⁸

1.2.2. Inelastic neutron scattering

In inelastic neutron scattering (INS), incident neutrons interact with a sample in such a way that energy is exchanged between the neutrons and excitations within the material. This interaction results in a change in both the energy and direction of the scattered neutrons, as shown in **Figure 1.8**. Energy transfer provides direct insight into the dynamic properties of the system, such as phonon modes or magnetic excitations. INS is a powerful technique for probing magnetic excitations in a material, owing to the interaction between the magnetic moment of the incident neutrons and the unpaired electron spins in the sample. This spin–spin interaction can induce transitions between discrete magnetic energy levels, resulting in a loss of energy by the scattered neutrons corresponding to the energy gap between these levels. In addition to magnetic excitations, INS can also couple to lattice vibrations through interactions with atomic nuclei, thereby providing access to the phonon spectrum. Neutrons exhibit high penetration depth, due to their lack of electric charge. One benefit of using INS is the lack of symmetry-based selection rules for vibrations, which govern Raman and IR spectroscopies. Thus, INS makes all phonon transitions observable. In addition, high-level density functional theory (DFT) phonon calculations can give calculated INS spectra and phonon modes to compare with the experimental spectra. “Subtracting” the calculated INS from the observed INS would leave just the magnetic transitions in the INS spectra.

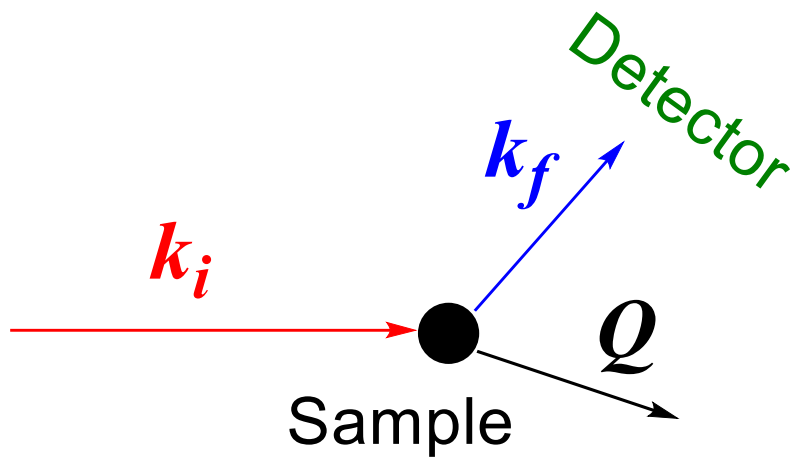


Figure 1.8. Schematic of the INS experiment. k_i = incident neutron momentum; k_f outgoing (final) neutron momentum; $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$ = vector of momentum transfer; Q = length of $\mathbf{Q}$.

1.2.3. Far-IR magneto-spectroscopy

Far-infrared magneto-spectroscopy (FIRMS) is a powerful technique for probing magnetic transitions and spin–phonon coupling in molecular materials, particularly SMMs. FIRMS involves far-IR spectroscopy typically performed in the 12–720 cm^{-1} range under variable magnetic fields, a range well-matched to the energies of many magnetic excitations in metal complexes. Because numerous infrared-active phonons appear in this region and are largely field-independent, applying variable magnetic fields enables clear identification of magnetic transitions as features that shift in response to the magnetic field, distinguishing them from phonon modes. The experimental setup is similar to conventional IR spectroscopy, with the key difference being that the sample is placed within a magnet. Spectra are first collected at zero field, followed by measurements at increasing fields to track the evolution of spectral features. Magnetic transitions in FIRMS arise from magnetic dipole–allowed processes, governed by transition moment operators with the symmetry of rotational operations (R_x , R_y , R_z) as defined in molecular point group character tables. FIRMS serves two primary roles: (1) direct observation and quantification of magnetic transitions, commonly used to extract ZFS parameters such as $2D' = 2(D^2 + 3E^2)^{1/2}$ for $S = 3/2$ complexes; (2) identification and analysis of spin–phonon coupling. Notably, FIRMS can resolve ZFS transitions beyond the frequency limits of traditional electron paramagnetic resonance (EPR), making it a valuable tool for characterizing relaxation dynamics and magnetic anisotropy in systems where EPR is insufficient. The technique has become increasingly important in the study of SMMs, enabling precise determination of magnetic energy levels and offering insight into potential relaxation pathways driven by spin–lattice interactions.

1.2.4. High-field and -frequency electron paramagnetic resonance

EPR is a technique well established for probing the electronic structure of metal complexes and investigating magnetic properties, particularly transitions between $M_S = -1/2$ to $+1/2$ states. These transitions arise from the Zeeman splitting of spin states in an external magnetic field and occur when the energy difference between states matches the energy of the applied microwave frequency, described by Eq. 1.5:

$$\Delta E = h\nu = g\mu_B B \quad (\text{Eq. 1.5})$$

where ν is the applied frequency, g is the g -tensor, μ_B is the Bohr magneton, and $B = |\mathbf{B}|$ is the applied magnetic field. The g -tensor components (g_x, g_y, g_z), which reflect the magnetic anisotropy of the system, can be determined from single-crystal measurements or, more broadly, from powder or frozen solution samples with isotropic orientation distribution. EPR additionally provides information on the local chemical environment and SOC at the paramagnetic centers.

However, conventional EPR methods, typically operating at X- or Q-band frequencies (~ 0.3 or $\sim 1.2 \text{ cm}^{-1}$), are limited in their ability to detect large magnetic transitions or measure zero-field splitting (ZFS) parameters D and E when $h\nu < D$. To overcome these limitations, high-field and -frequency EPR (HFEPR) has been developed, operating at frequencies up to $\sim 1 \text{ THz}$ (33 cm^{-1}) and magnetic fields as high as 35 T. HFEPR extends the applicability of EPR to systems with large ZFS or those that are EPR-silent at lower fields and frequencies. Importantly, HFEPR also enables determination of the sign of D and the E/D ratio in the spin-Hamiltonian, providing deeper insight into magnetic anisotropy and the spin dynamics of high-spin or strongly anisotropic systems.

1.2.7. Polarized neutron diffraction

Direct determination of spin configuration within SMTs is challenging due to the weak interactions of the inter-molecule magnetic spins. While other techniques might determine spin numbers or the magnetic moments of a compound, the only technique to determine spin configurations is polarized neutron diffraction (PND). PND provides an atomic magnetic susceptibility tensor showing the spatial aspects of the wavefunction and bonding within a compound. Examining the spin of a single ion is completed by defining the local susceptibility tensor for each magnetic atom within the unit cell. To experimentally determine the susceptibility tensor, the flipping ratios are measured and compared to determine the orientation as well as the magnitude of the magnetic moment of the atoms within the unit cell. The flipping ratios, defined in Eq. 1.6, are the diffracted intensities for the up-or-down spin of the polarized incident neutron beam in the Bragg reflections.

$$R(k) = R(hkl) = \frac{I^+}{I^-} = \frac{F_N^2 + 2pq^2F_NF_M + q^2F_M^2}{F_N^2 - 2epq^2F_NF_M + q^2F_M^2} \quad (\text{Eq. 1.6})$$

where I^+ and I^- are the diffracted intensities at a fixed point for the two different polarization states, q is the sine of the angle between the scattering vector and the magnetic field direction, p is the polarization of the incident beam, and e is the flipping intensity.

The molecular structures from single-crystal crystallographic data can be used to subtract the nuclear structure factors and allow for the determination of the magnetic structure. This crystallographic magnetic structure can be broken down into individual atomic spin densities and local susceptibility tensors for each atom.

To determine the independent tensor components, the simultaneous refinements of spin flip ratios from orthogonal directions must be used (this can be changed based on symmetry).

The atomic magnetic moment (m_i) of an atom i within an applied magnetic field $\mathbf{B}$ can be expressed in Eq. 1.7:

$$m_i = \vec{\chi}_i \mathbf{B} \quad (\text{Eq. 1.7})$$

where χ_i is the magnetic susceptibility tensor of the atom i , which has six independent components as shown in Eq. 1.8.

$$\vec{\chi}_i = \begin{pmatrix} \chi_{11} & \chi_{12} & \chi_{13} \\ \chi_{12} & \chi_{22} & \chi_{23} \\ \chi_{13} & \chi_{23} & \chi_{33} \end{pmatrix} \quad (\text{Eq. 1.8})$$

PND has been used to determine spin density of complexes such as $[\text{Fe}_8\text{O}_2(\text{OH})_{12}(\text{tacn})_6]^-$ (tacn = 1,4,7-triazacyclononane) where it was found that spins of six Fe^{3+} ions were up spin, while the remaining two had down spin. PND has also been used to examine magnetic anisotropy within a compound showing alignment and susceptibility for individual atoms.⁵⁹⁻⁶⁹

1.2.8. Powder neutron diffraction

Powder neutron diffraction can show both structural and magnetic features of materials. The common basis of powder neutron diffraction is that as a monochromatic neutron beam diffracts through a material, diffraction occurs to give Bragg peaks. These are described through Bragg's law:

$$n\lambda = 2d\sin\theta$$

where n is an integer representing the diffraction order, λ is the incident neutron central wavelength, d is the space between the lattice plane of the sample, and θ is the Bragg angle or angle between the neutron beam and the lattice plane.⁷⁰ If instead of a monochromatic neutron

beam, a white neutron beam is used, this law must be adapted to account for time-of-flight (TOF) neutron diffraction. This then changes Bragg's law to be:

$$\frac{n(ht)}{m_n L} = 2d \sin \theta$$

where h is Planck's constant, m_n is a neutrons mass, t is TOF, and L is the path length. These changes allow to determine the d-spacing of the crystal lattice by measuring the TOF of the diffracted neutrons at know angles.^{71, 72} Using variable temperature powder neutron diffraction one can then examine the dependence of Bragg peaks on temperature. If a compound is a traditional antiferromagnetic material, then at a temperature below the Neel point there should arise new Bragg peaks within the powder neutron diffraction spectra.⁵⁷ These new peaks are related to the magnetic structure of the material, with magnetic peaks showing at twice the d-spacing of Bragg peaks associated with the metal ions within the sample. These magnetic peaks can then be modeled to show the magnetic structure of the material. A lack of magnetic Bragg peaks within an antiferromagnetic sample, with data collected below the Neel point, is indicative of short-range coupling contained within the crystal lattice. This is an important note when examining Haldane spin-1 chains, as the short-range coupling should not show long range antiferromagnetic coupling that would be indicated by new Bragg peaks in variable temperature powder neutron diffraction.⁵⁷

1.3. Current dissertation

1.3.1. Chapter 2

The use of advanced spectroscopies are applied to two single-molecule magnet candidates, $[M(MST)(OH_2)][NEt_4]$ (where $M^{2+} = Co^{2+}$ or Ni^{2+} ; $MST^{3-} = N,N',N''$ -[2,2',2''-nitrilotris(ethane-2,1-diyl)]tris(2,4,6-trimethylbenzenesulfonamido)), to examine the magnetic

excitations and vibrational spectra. The use of INS, coupled with VASP and Phonopy calculations, gives phonon spectra and visual representations of the phonons. Magnetic transitions between ZFS levels are probed by FIRMS, INS, and HFEPR to give ZFS parameters of D , E , and g -values as well as give magnetic excitation spectra. DFT was used to calculate spin densities, showing that more localized spin density on the metal center corresponds with larger ZFS splitting. Hirshfeld surface analysis was used to examine the intermolecular interactions and their intensities to further understand the potential for phonon coupled relaxations of magnetic excitations.

1.3.2. Chapter 3

The combined use of DC magnetometry and polarized neutron diffraction unambiguously determines the atomic magnetic tensor of Dy^{3+} ions within an SMT molecule. Within this chapter is the design, synthesis, and comprehensive characterization, including by polarized neutron diffraction (PND), of a trinuclear dysprosium cluster, $[\text{Dy}_3(\mu_3\text{-OH})(\text{teaH}_2)_3(\text{paa})_3]\text{Cl}(\text{OMe})\cdot\text{PhCN}\cdot 3\text{MeOH}$ [teaH_3 = triethanolamine, paaH = N-(2-pyridyl)-acetoacetamide]. DC magnetometry confirms anisotropic antiferromagnetic coupling normal to the molecular plane and mixed ferromagnetic/antiferromagnetic in-plane coupling, which is consistent with a toroidal ground state. The use of PND at 5 K gives an atomically resolved mapping of the local magnetic susceptibility tensor for each Dy^{3+} ion, showing the head-to-tail spin arrangement that defines a toroidal moment.

1.3.3. Chapter 4

The use of DC magnetometry and neutron scattering is applied to two metal-organic frameworks (MOFs) with Ni-oxalate spin-1 chains showing Haldane topological properties. Magnetometry is used to probe the gapped state and understand the stability to external

perturbation. Powder neutron diffraction examines the magnetic unit cell, showing that there is no magnetic unit cell within the temperature range of the Haldane phase. HFESR is used to examine the magnetic excitations within the gapped states.

1.3.4. Chapter 5

Solvatochromism, green chemistry, and CuO nanoparticle synthesis are discussed. The use of multiple types of nanoparticle synthesis is explored to help understand synthetic pathways to CuO and green chemistry.

Chapter 2: Probing magnetic and vibrational properties of trigonal-bipyramidal Co(II) and Ni(II) complexes using advanced spectroscopies

This chapter is based on the following paper:

Michael J. Jenkins, Mykhaylo Ozerov, J. Krzystek, Luke L. Daemen, Yongqiang Cheng, Zi-Ling Xue, Probing magnetic and vibrational properties of trigonal-bipyramidal Co(II) and Ni(II) complexes using advanced spectroscopies. *New J. Chem.*, **2025**, 49, 5740-5756.

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Author Contributions:

M. J. Jenkins and M. Ozerov performed the FIRMS experiments. Jenkins interpreted FIRMS results and conducted simulation of transitions using *EasySpin* package. J. Krzystek performed HFEPR experiments as well as analyzed and interpreted the results. L. L. Daemen and Y. Cheng collected VT-INS data, and Y. Cheng conducted VASP calculations of the INS spectra and spin density. Jenkins analyzed the INS data and interpreted results. Z.-L. Xue initiated the project and supervised the research. Jenkins, Xue, and Krzystek wrote the manuscript with input from all authors.

2.1. Abstract

Transition metal-based single-molecule magnets (SMMs) with local C_3 or higher symmetries on the metal centers have garnered significant interest due to their unique magnetic properties. With rhombic anisotropy parameters $E =$ (or $\approx$) 0 for such highly symmetric complexes, quantum tunneling in magnetic relaxation is eliminated or reduced, enhancing the

performance of the SMMs. Zero-field splitting (ZFS) in metal complexes has been probed by various advanced methods, including spectroscopies such as far-infrared magneto-spectroscopy (FIRMS), high-frequency and -field electron paramagnetic resonance (HFEPR), and inelastic neutron scattering (INS). Studies of the trigonal bipyramidal SMM complex with local C_{3v} symmetry, $(\text{Me}_4\text{N})[\text{Co}(\text{MST})(\text{OH}_2)]$ (**Co-MST-H₂O**, $\text{MST}^{3-} = N,N',N''\text{-}[2,2',2''\text{-nitrilotris(ethane-2,1-diyl)]tris(2,4,6-trimethylbenzenesulfonamido)}$), give the following spin-Hamiltonian parameters: axial ($D = 25.3 \text{ cm}^{-1}$) and rhombic ($E = 0$) ZFS values, $g_{\perp} = 2.230$, and $g_{\parallel} = 2.045$. Phonon properties of **Co-MST-H₂O** have been studied by INS and DFT phonon calculations, yielding phonon symmetries, energies, and movies. Phonons here refer to either molecular vibrations (internal modes) or lattice vibrations (external modes or intermolecular vibrations) in the crystalline solid. Intermolecular interactions in **Co-MST-H₂O** have been probed by Hirshfeld surface analysis, revealing strong interactions between the $[\text{Co}(\text{MST})(\text{OH}_2)]^{-}$ anion and solvents (H_2O and CH_2Cl_2) in the crystal lattice. The DFT phonon calculations of **Co-MST-H₂O** have also generated the spin density on the Co^{2+} ion and other atoms in the molecule. For $(\text{Me}_4\text{N})[\text{Ni}(\text{MST})(\text{OH}_2)]$ (**Ni-MST-H₂O**), FIRMS and INS studies did not show the magnetic transitions among the spin sublevels. Spin-Hamiltonian parameters (D , E , and g value) of **Ni-MST-H₂O**, determined by magnetometry, were reported earlier (K.A. Schulte, K.R. Vignesh, K.R. Dunbar, *Chem. Sci.*, **2018**, 9, 9018). In the absence of magnetic resonance or INS results for the magnetic transitions in **Ni-MST-H₂O**, magnetometry is the only viable technique to determine spin-Hamiltonian parameters for the compound. Hirshfeld surface analysis of **Ni-MST-H₂O** shows strong interactions of the $[\text{Ni}(\text{MST})(\text{OH}_2)]^{-}$ anion with lattice solvent H_2O and the cation Me_4N^{+} .

2.2. Introduction

Magnetic properties of transition metal complexes have been of intense recent interest for their potential uses as quantum materials with applications in spintronics, data storage, and quantum computing.^{2, 4, 7, 10, 12-14, 16, 21, 22, 36, 73-81} d-Block complexes with at least two unpaired electrons ($S \geq 1$) and quenched first-order spin-orbit coupling (SOC), showing a barrier (U) to spin reversal (or magnetic relaxation) are considered single-molecule magnets (SMMs).^{15, 16} One research area is to find SMMs with large and tunable U . Magnetic anisotropy of transition metal complexes is far more tunable than lanthanide complexes, as the ligand field effects are more easily tuned in the former than the spin-orbit coupling (SOC) in the latter.^{13, 74, 79, 80, 82-84} Transition metal complexes with many unpaired electrons (and thus large spins) are favored, as the increase in the spin (S) leads to the increase in the energy barrier (U) for spin reversal. Because of ligand field or Jahn-Teller distortion, many transition metal complexes have quenched angular orbital momentum of the unpaired electrons. The magnetic properties of such complexes are governed by the second-order SOC, as represented by zero-field splitting (ZFS).^{23-30, 85-88} The magnitude of the ZFS for a transition metal complex is given by axial (D) and rhombic (E) anisotropy parameters, as defined by spin Hamiltonian in Eq. 1:

$$\hat{H}_S = D[\hat{S}_z^2 - \frac{S(S+1)}{3}] + E(\hat{S}_x^2 - \hat{S}_y^2) + \mu_B g_x B_x \hat{S}_x + \mu_B g_y B_y \hat{S}_y + \mu_B g_z B_z \hat{S}_z \quad (2.1)$$

where $\hat{S}$ is the spin operator, μ_B is the electron Bohr magneton, $g_{x,y,z}$ are the g -factor components, and $B = (B_x, B_y, B_z)$ is the applied magnetic field vector.³¹⁻³³ In Eq. 1, the last three terms show the Zeeman effect on the zero-field split states.

For complexes with at least C_3 crystallographic point group symmetry at the metal site (or the paramagnetic center), spin Hamiltonian is given in Eq. 2:

$$\hat{H}_S = D[\hat{S}_z^2 - \frac{S(S+1)}{3}] + \mu_B g_{\parallel} B_z \hat{S}_z + \mu_B g_{\perp} (B_x \hat{S}_x + B_y \hat{S}_y) \quad (2.2)$$

where $g_{\parallel}$ and $g_{\perp}$ are the g -tensor components parallel and perpendicular, respectively, to the unique z axis.

Using the ZFS parameters, the energy barrier (U) for a compound is given by Eqs. 3-4:

$$U = |D|(S^2 - \frac{1}{4}) \text{ for non-integer spins} \quad (2.3)$$

$$U = |D|S^2 \text{ for integer spins} \quad (2.4)$$

Penta-coordinate Co^{2+} complexes have been actively studied to use their magnetic anisotropies in the search of SMMs.^{30, 31, 82, 84, 85, 89-105} For complexes with at least C_3 crystallographic point group symmetry of the metal site (or the paramagnetic center), the rhombic ZFS parameter $E = 0$.^{31, 84, 104, 105} Five-coordinate Co^{2+} -based SMMs with such crystallographic symmetries are typically trigonal bipyramidal in the C_{3v} ^{98, 102, 103} or D_{3h} ²⁹ point group. These symmetries give d orbital configuration in **Figure 2.1a** with quenched first-order SOC. Thus, mixing of the $M_S = \pm 1/2$ and $M_S = \pm 3/2$ states (to give ϕ_1 , ϕ_2 , ϕ_3 , and ϕ_4 , as shown in **Figure 2.1b** which leads to quantum tunneling) does *not* occur. Five-coordinate Co^{2+} -based SMMs with crystallographic C_{3v} or D_{3h} symmetry through the metal ion are therefore highly desirable. However, there are few five-coordinate Co^{2+} SMMs with such high symmetries.^{29, 98, 102, 103} Instead, some five-coordinate Co^{2+} SMMs have *approximate* (or *local*) C_3 ^{82, 87, 94, 102, 106-108} or C_4 ^{85, 109} symmetries of the metal sites. Either crystallographic space groups^{85, 87, 94, 102, 106-108} in, *e.g.*, monoclinic unit cells (with C_2 or C_{2h} symmetry), or the ligands^{82, 109} such as N_3^- or NCS^- with bent structures, lower the symmetries of the complexes. In addition, five-coordinate Co^{2+} SMMs with planar, tri-dentate ligands such as $\text{Co}(\text{terpy})\text{X}_2$ (terpy = terpyridine)^{110, 111} or analogs^{101, 112-117} have approximately

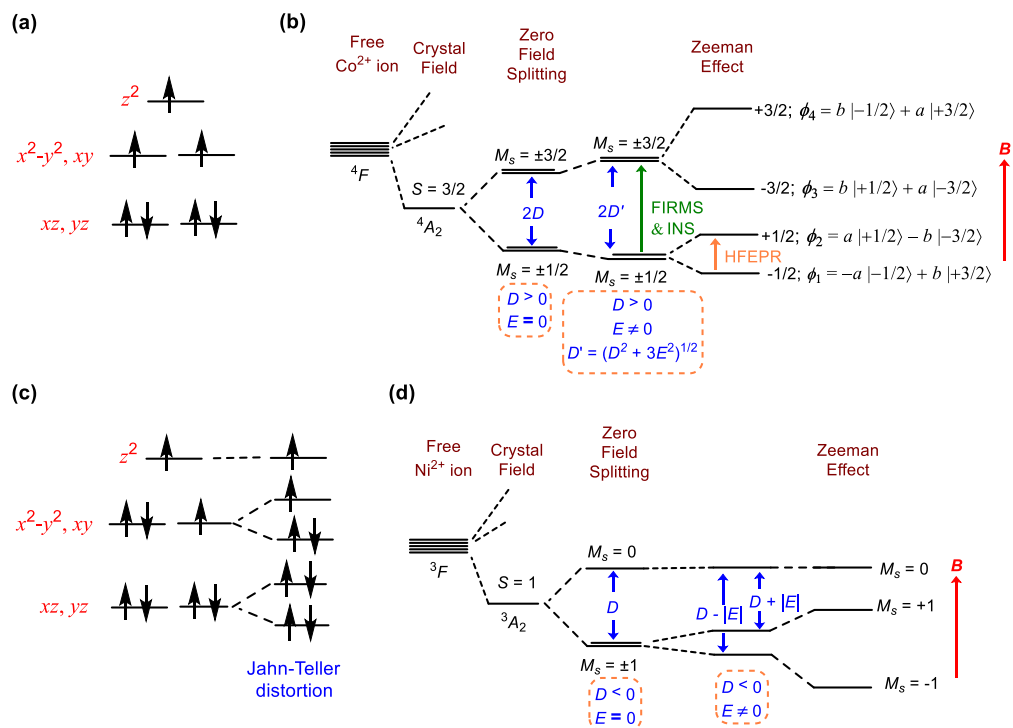


Figure 2.1. (a) Ligand field splitting diagram for a 5-coordinate, high-spin Co^{2+} complex in crystallographic C_{3v} or D_{3h} symmetry through the metal ion. (b) Ground-state quartet spin levels in high-spin, d^7 complexes with at least C_3 crystallographic point group symmetry of the metal site ($D > 0$; $E = 0$) and lower symmetry ($D > 0$; $E \neq 0$). When the symmetry is lower than C_3 , $E \neq 0$ and there is a mixing of states to give ϕ_1 , ϕ_2 , ϕ_3 , and ϕ_4 . The mixing coefficients $a = \cos \beta$ and $b = \sin \beta$ are described by the mixing angle β obtained from the spin-Hamiltonian ($S = 3/2$).^{33, 118} Mixing depends on the rhombicity as $\tan 2\beta = \sqrt{3} (E/D)$. (c) Ligand field splitting diagram for a high-spin Ni^{2+} complex in C_{3v} geometry with the Jahn-Teller distortion.^{81, 119} (d) Ground-state quartet spin levels in high-spin, d^8 complexes with at least C_3 crystallographic point group symmetry of the metal site ($D < 0$; $E = 0$ before the Jahn-Teller distortion) and lower symmetry ($D < 0$; $E \neq 0$) after the Jahn-Teller distortion.

C_{2v} symmetry around the metal ions. For such complexes in which the crystallographic point group symmetry of the metal site is lower than C_3 , $E \neq 0$ and $2D' = 2(D^2 + 3E^2)^{1/2}$, giving the ground-state quartet level in **Figure 2.1b**, in which mixing of the $M_S = \pm 1/2$ and $M_S = \pm 3/2$ states (to give ϕ_1 , ϕ_2 , ϕ_3 , and ϕ_4) occurs, potentially leading to quantum tunneling and fast magnetic relaxation. These are undesirable properties for SMMs.

Penta-coordinate $d^8 \text{Ni}^{2+}$ complex with crystallographic C_{3v} symmetry through the metal ion has been reported.^{81, 119} However, Jahn-Teller distortion leads to the splitting of degenerate d orbitals (**Figure 2.1c**). There are also penta-coordinate Ni^{2+} complexes with *approximate* (or *local*) C_{3v} ^{30, 106, 120-124} or C_{4v} ^{125, 126} symmetries. Their crystal structures or ligands lower the symmetries of the complexes.

A series of transition metal complexes containing the tripodal ligand N,N',N'' -[2,2',2''-nitrilotris(ethane-2,1-diyl)]tris(2,4,6-trimethylbenzenesulfonamido) (MST^{3-} , **Figure 2.2**) were reported by Lacy, Lau, Borovik and coworkers, revealing catalytic activities.^{123, 127, 128} Later, magnetic properties of $[\text{NMe}_4][\text{Co}(\text{MST})(\text{OH}_2)]$ (**Co-MST-H₂O**) and $[\text{NMe}_4][\text{Ni}(\text{MST})(\text{OH}_2)]$ (**Ni-MST-H₂O**) were reported by Schulte, Vignesh, and Dunbar, showing slow magnetic relaxation and SMM properties.¹⁰⁶ Although the local symmetry for both $[\text{NMe}_4][\text{Co}(\text{MST})(\text{OH}_2)]$ (**Co-MST-H₂O**) and $[\text{NMe}_4][\text{Ni}(\text{MST})(\text{OH}_2)]$ (**Ni-MST-H₂O**) is C_{3v} , the crystallographic symmetry of the two complexes at 100 K is triclinic $P\bar{1}$ (No. 2; point group C_i).¹⁰⁶ ZFS parameters were determined from reduced magnetization data, giving spin-Hamiltonian parameters for **Co-MST-H₂O** ($D = 24 \text{ cm}^{-1}$, $|E| = 0.001 \text{ cm}^{-1}$, $g = 2.40$) and **Ni-MST-H₂O** ($D = -209 \text{ cm}^{-1}$, $|E| = 1.8 \text{ cm}^{-1}$, $g = 2.81$).

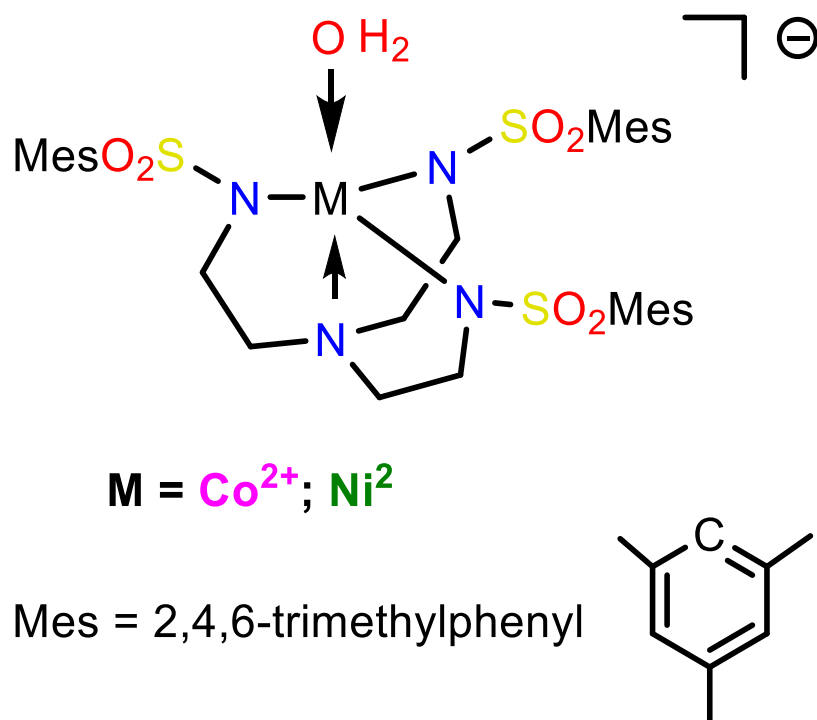


Figure 2.2. Structures of the anions in **Co-MST-H₂O** and **Ni-MST-H₂O**. Both show local C_{3v} symmetry. The crystallographic point groups of **Co-MST-H₂O** and **Ni-MST-H₂O** are C_i (for triclinic space group $P\bar{1}$, No. 2) and C_{2h} (for monoclinic space group $C2/c$, No. 15), respectively.

Magnetometry is an indirect, non-resonant method for determining ZFS parameters. There are several reported spectroscopic techniques for directly determining ZFS,^{129, 130} including high-frequency and -field electron paramagnetic resonance (HFEPR),^{25, 27, 85, 88, 95, 103, 114, 116, 131-136} far-IR magneto-spectroscopy (FIRMS),^{25, 96, 119, 137-149} and inelastic neutron scattering (INS).¹⁵⁰⁻¹⁶⁶ HFEPR is a powerful tool to measure ZFS up to approximately 32 cm⁻¹ for non-Kramers ions, and 15 cm⁻¹ for Kramers spin species using, e.g., the facilities at the US National High Magnetic Field Laboratory (NHMFL).^{129, 131, 140, 167} For ZFS >32 cm⁻¹, a combined use of HFEPR and FIRMS¹³⁰ has been adopted to determine large spin-Hamiltonian parameters.^{25, 95, 114, 116, 133, 141, 142, 144-147} FIRMS is far-IR spectroscopy conducted with variable magnetic fields, helping reveal magnetic transitions in the spectra.¹³⁰ Phonon properties of metal complexes and intermolecular interactions are important to the understanding of spin-phonon coupling and magnetic relaxation. Indirect-geometry time-of-flight (TOF) INS spectroscopy has been widely used to probe both magnetic and vibrational transitions.¹⁵² Incident neutrons (with spin ½) interact with both unpaired electrons and nuclei of atoms in the sample, leading to magnetic and vibrational transitions, respectively.¹⁵² Unlike HFEPR and FIRMS that use external magnetic fields to probe magnetic transitions, indirect-geometry INS spectroscopy can distinguish magnetic transitions in spectra from vibrational transitions (also known as phonons) *without* the use of external magnetic fields. Phonons here refer to either molecular vibrations (internal modes) or lattice vibrations (external modes or intermolecular vibrations) in crystalline solids of compounds. Phonons are bosons following Bose-Einstein statistics, while electrons, giving magnetic transitions, are fermions following Boltzmann statistics. Thus, in variable-temperature (VT) INS spectra, magnetic and phonon peaks show different temperature profiles, leading to their identifications. Another unique feature of INS is that it does not have symmetry-

based selection rules for phonons/vibrations, unlike optical IR and Raman spectroscopies each with its own selection rules.¹⁵² Thus, *all* phonons are observed in INS spectra. In addition, powerful DFT phonon calculations give calculated phonon symmetries, energies, and INS *phonon* spectra. Thus, INS and the calculations together are very useful to probe magnetic and phonon properties of metal complexes.¹⁵² Direct determination of ZFS and spin-Hamiltonian parameters by the advanced spectroscopies has led to their increased use.^{23, 131, 133, 139, 150, 153, 168-172} The DFT phonon calculations also give spin densities on atoms in the molecules.

Hirschfeld surface analysis is a unique technique to probe intermolecular interactions in the context of crystal packing.^{170, 173} It has been extensively used to probe such interactions in metal complexes, including SMMs and other magnetic compounds.^{117, 174-196} Thus, Hirschfeld surface analysis and phonon studies, which include lattice vibrations (external modes), provide an understanding of intermolecular interactions from two perspectives.

We have studied **Co-MST-H₂O** and **Ni-MST-H₂O** to answer the following: (1) Could the ZFS and other spin-Hamiltonian parameters be determined using advanced spectroscopies? How are the results compared with those from DC magnetic susceptibility and reduced magnetization? (2) What are the phonon properties of the two complexes, including their symmetries, as revealed by inelastic neutron scattering (INS) spectroscopy and DFT phonon calculations? (3) How do molecules of the two complexes interact in their crystalline solids? Our studies are reported here.

2.3. Results and discussion of [NMe₄][Co(MST)(OH₂)] (Co-MST-H₂O)

Co-MST-H₂O has been probed by far-IR magneto-spectroscopy (FIRMS), HFEPR, INS, DFT-phonon calculations, and Hirschfeld surface analysis.

2.3.1. FIRMS

The FIRMS we have used has a typical energy range of 12–720 cm^{-1} . Since the energy gaps between the spin sublevels in SMMs are often in that energy range, far-IR (i.e., FIRMS) is selected to probe them. A transition from ground $M_S = \pm 1/2$ sublevel to the excited $M_S = \pm 3/2$ sublevel is magnetic dipole-allowed.^{130, 197, 198} IR-active phonons are also observed in far-IR. To identify the magnetic peaks from phonon peaks in far-IR spectra, variable magnetic fields are used. The former shift with the fields because of Zeeman effect (**Figure 2.1**), while the latter do not. The experimental set up in FIRMS is analogous to that of a typical IR experiment, except that the sample is placed inside a magnet and, in our studies, at 5 K. Powders of the samples were made into a mull in *n*-eicosane, a waxy substance transparent in the far-IR range.

Changes by the external magnetic fields in FIRMS spectra of **Co-MST-H₂O** at 0 and 17 T are observable in **Figure 2.3a**. To distinguish the magnetic transitions from the phonon peaks, all spectra were normalized to the reference spectrum, which is the average spectrum for all magnetic fields at 0–17 T. **Figure 3b** shows the normalized 2D plot (known as a heatmap or contour map). In the 2D plot, a magnetic peak is clearly observed at 50.6(6) cm^{-1} , which blue-shifts as a result of transitions from the Zeeman-split sublevels. The magnetic peak at zero field is the $M_S = \pm 1/2 \rightarrow M_S = \pm 3/2$ transition (**Figure 2.1b**). That is, ZFS for **Co-MST-H₂O**: $2D' = 2(D^2 + 3E^2)^{1/2} = 50.6(6) \text{ cm}^{-1}$. However, determining the *D* and *E* values requires additional results from HFEPR discussed below. Also, there is no obvious spin-phonon coupling, as no avoided crossing is clear in **Figure 2.3b**. In addition to the dominant zero-field transition at 50.6(6) cm^{-1} , another broad transition was observed at 65(1) cm^{-1} (**Figure 2.3c-d**).

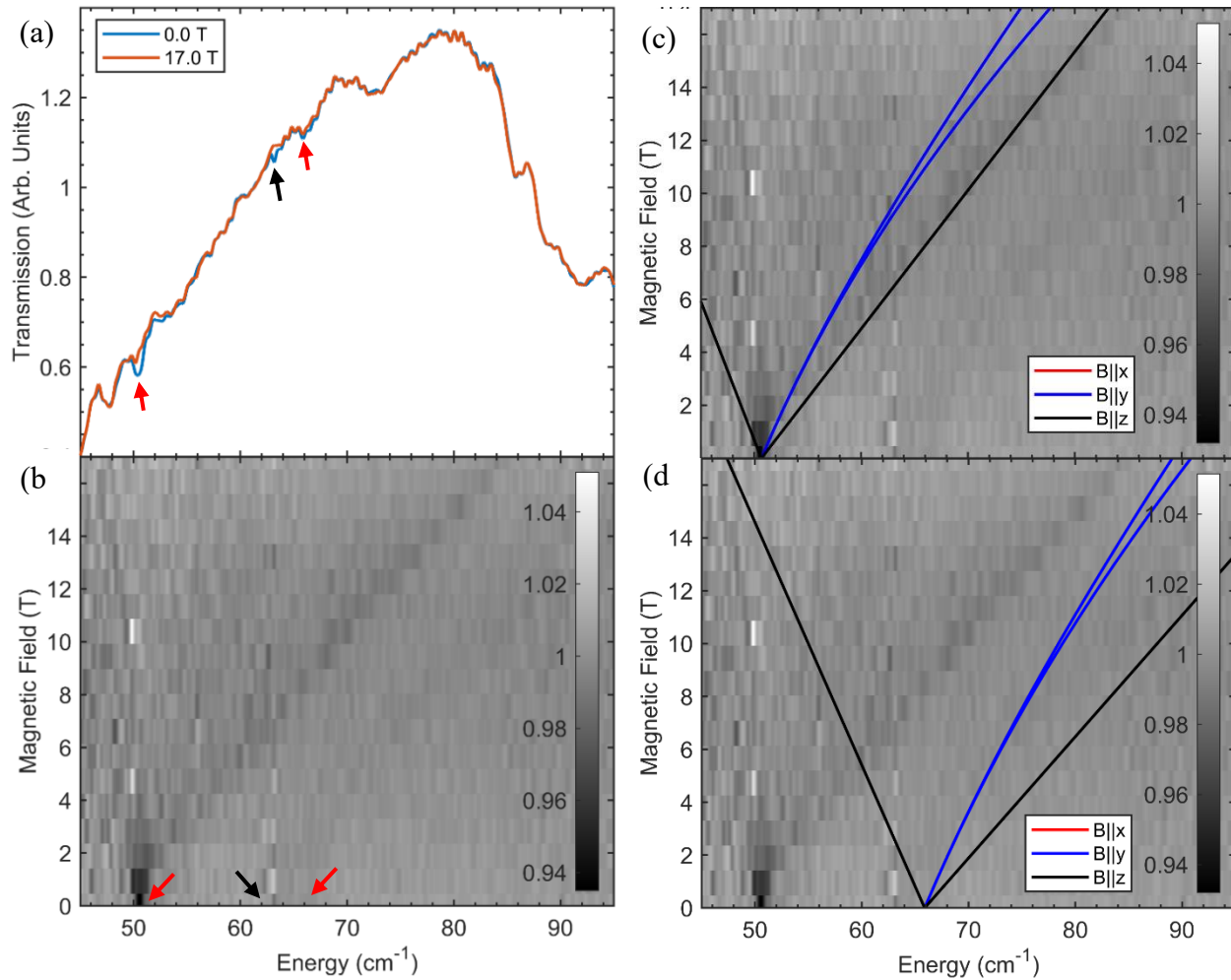


Figure 2.3. FIRMS of a powder sample of **Co-MST-H₂O**. (a) Spectra at 5 K and 0 and 17 T. (b) Contour plot of the normalized (by average) transmission, showing blue shifting of the magnetic peak at 50.6(6) cm⁻¹. The red arrows point to the magnetic transitions. The black arrow points to a shot noise in the spectra. There is no clear spin-phonon coupling or avoided crossings. (c) Turning points for the magnetic peak at 50.6(6) cm⁻¹ as solid lines simulated by *EasySpin* in the powder spectra using *g*-values from HFEPR. (d) Turning points for the weak magnetic peak of **Co-MST** at 65(1) cm⁻¹ as solid lines simulated by *EasySpin* in the powder spectra using *g*-values from HFEPR. Additional FIRMS results of **Co-MST-H₂O** are given in **Figure A2.2**.

It has a very low signal/noise (S/N) ratio and we would be reluctant to claim it is a real resonance, but it coincides very well with the magnetometric result for D of the de-hydrated complex $[\text{NMe}_4][\text{Co}(\text{MST})]$ (**Co-MST**) ($2D' = 66 \text{ cm}^{-1}$)¹⁰⁶ and is corroborated by HFEPR (see below). We thus tentatively identify it as originating from the dehydrated derivative **Co-MST**. Given the propensity of **Co-MST-H₂O** to lose the coordinated water molecule, it is conceivable that the sample of **Co-MST-H₂O** partially lost water during the sample cooling process which involves pumping on it, to give a small amount of **Co-MST**.

2.3.2. HFEPR

HFEPR is a field-domain version of magnetic resonance, and can deliver information complementary to FIRMS. When applied to compound **Co-MST-H₂O** in a loose polycrystalline form, at low temperatures, it delivers spectra such as shown in **Figure A2.4** in the addenda. The shape of the spectra strongly suggests that the compound torques (aligns) with magnetic field, a phenomenon well known to HFEPR spectroscopists.¹³² The spectra are thus similar to those of a single crystal. However, in such a case one would expect a single resonance corresponding to the intra-Kramers transition between the $M_S = \pm 1/2$ sublevels while two resonances of unequal intensities are actually observed. This observation suggests the presence of two different spin species. The frequency dependence of the two resonances (**Figure A2.5**) shows that the two species differ by their g -values. We can thus tentatively attribute the resonances to complexes **Co-MST-H₂O** and its anhydrous derivative $(\text{Me}_4\text{N})[\text{Co}(\text{MST})]$ (**Co-MST**) produced by the loss of the axial water ligand. We tentatively attribute the lower-intensity resonance with higher $g_{\perp}$ value to the anhydrous species.

Given that the field-aligned spectra were uninformative with regard to spin-Hamiltonian parameters, we proceeded to prevent the torquing by pressing **Co-MST-H₂O** in a pellet with n -

eicosane. The resulting spectra at 203 GHz are shown in **Figure 2.4** and can be recognized as originating from a powder rather than a single crystal. At low temperatures (10 K in **Figure 2.4a**), the powder pattern corresponds to a single species, which is assigned to $[\text{NMe}_4][\text{Co}(\text{MST})(\text{OH}_2)]$ (**Co-MST-H₂O**), as proved by the simulation that uses the $2D'$ -value obtained from FIRMS, 50.6 cm^{-1} . The other spin-Hamiltonian parameters used in the simulation are: $E = 0$, $g_{\perp} = 2.230$, $g_{\parallel} = 2.045$. The ZFS and g -tensors are thus strictly axial and the D' value obtained from FIRMS is equal to D .

Raising the temperature (40 K in **Figure 2.4b**) causes an emergence of a second parallel turning point in the spectrum at ca. 6.2 T, of lower intensity. The perpendicular turning point remains unsplit at the same position (3.3 T). This corresponds to a second spin species whose spin-Hamiltonian parameters were obtained through simulation: $E = 0$, $g_{\perp} = 2.23$, $g_{\parallel} = 2.33$. Apparently, embedding the sample in an *n*-eicosane pellet did not fully prevent it from losing water under vacuum. Alternatively, the pressure exerted on the sample while making the pellet may have caused a release of coordinated water, creating the de-hydrated species **Co-MST**. The simulation of that extra species used the tentative D -value of the second spin species, i.e., 32.5 cm^{-1} observed by FIRMS. This species thus has a much larger $g_{\parallel}$ value than the first one but the same $g_{\perp}$ value. For both species, the rhombicity factor E/D remains zero within the linewidth of the perpendicular turning point. Results here show that, although the crystallographic point group of C_i for **Co-MST-H₂O** is low, the local molecular symmetry of C_{3v} likely plays a critical role, leading to $E = 0$ (or it is too small to be detected) by HFEPR, a desired property in SMMs.

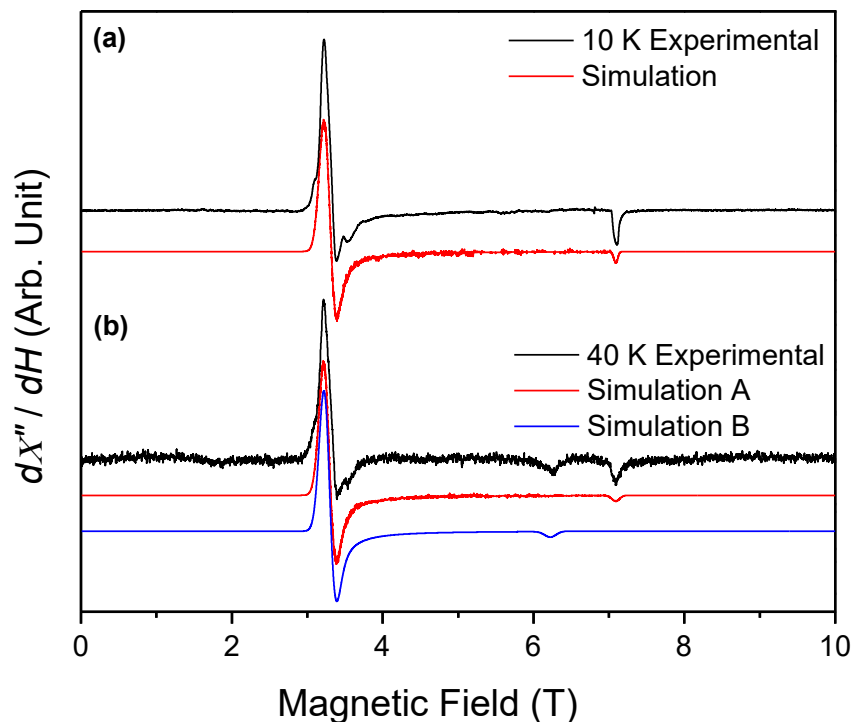


Figure 2.4. (a) HFEPR spectrum of **Co-MST-H₂O** embedded in an *n*-eicosane pellet at 10 K and 203 GHz (black trace) accompanied by a powder simulation (red trace) using spin-Hamiltonian parameters: $D = 25.3 \text{ cm}^{-1}$, $E = 0$, $g_{\perp} = 2.230$, $g_{\parallel} = 2.045$. (b) HFEPR spectrum of the same sample at 40 K (black trace) accompanied by simulations. For species A (red trace), the simulation parameters are the same as at 10 K; for species B (blue trace), the parameters are: $D = 32.5 \text{ cm}^{-1}$, $E = 0$, $g_{\perp} = 2.23$, $g_{\parallel} = 2.33$. dX''/dH is the first derivative of the absorption X'' vs the external magnetic field H .

2.3.3. INS

As discussed earlier, variable-temperature (VT) INS (without using external magnetic fields) is required to differentiate between the local molecular vibrational/phonon and magnetic excitations. As phonons and electrons respond differently to temperature changes, the use of Bose-corrected VT-INS may determine which excitations are magnetic or phonon/vibrational.¹⁵²

INS of **Co-MST-H₂O** was conducted using Vibrational Spectrometer (VISION) at Oak Ridge National Laboratory (ORNL). There are forward- and back-scattering detectors at VISION, which are 45° and 135° from the incident neutrons, respectively.¹⁵² The sample was sealed inside a can under a helium atmosphere in a glovebox and spectra were collected at 5, 25, 50, 75, 100, and 125 K. Bose-corrected VT INS are given in **Figure 2.5**, where Bose correction is a numerical normalization that highlights non-phonons by applying normalization to phonons that follow Bose-Einstein statistics. The peak at 48.5 cm⁻¹ is assigned to the magnetic transition in **Co-MST-H₂O**, which is slightly shifted from 50.6 cm⁻¹ observed in FIRMS likely due to instrument errors. Spin-Hamiltonian parameters determined by the advanced techniques: $D = 25.3 \text{ cm}^{-1}$, $E = 0$, $g_{\perp} = 2.230$, and $g_{\parallel} = 2.045$, are very close to $D = 24 \text{ cm}^{-1}$, $|E| = 0.001 \text{ cm}^{-1}$, $g = 2.40$ determined using magnetometry by Schulte, Vignesh, and Dunbar.¹⁰⁶

2.3.4. DFT phonon and spin density calculations

The phonon INS spectrum for **Co-MST-H₂O** was calculated using the periodic DFT VASP (Vienna Ab Initio Simulation) program. The calculated INS spectrum is compared with the experimental INS spectrum at 5 K. *Ab initio* (also known as first-principle) DFT calculations allow for predictions of interatomic force constants. For **Co-MST-H₂O**, the calculated spectrum overall matches experimental spectrum well.

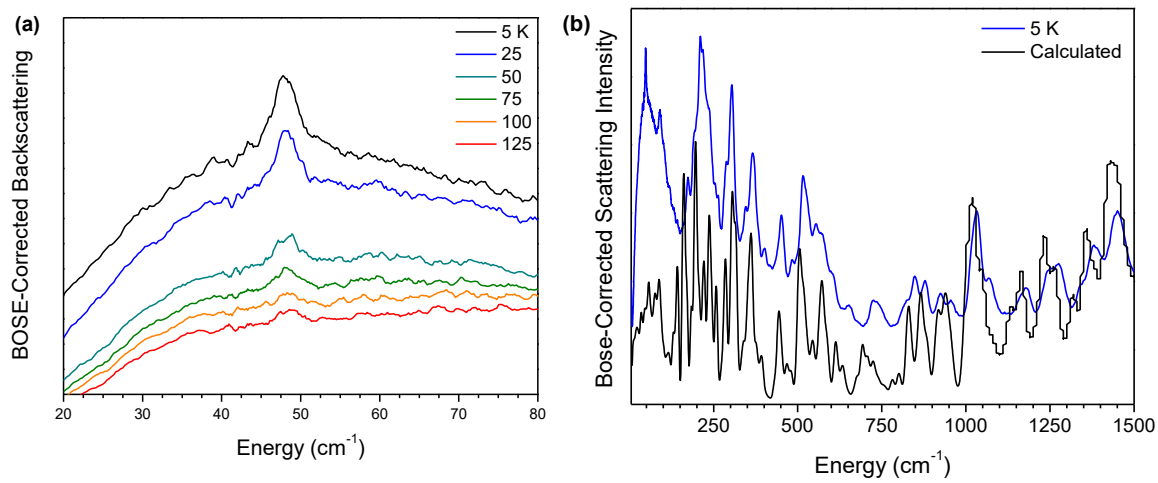


Figure 2.5. (a) Bose-corrected INS spectra of **Co-MST-H₂O** at 20-80 cm⁻¹. Forward-scattering spectra are given in **Figure A2.6**. (b) INS spectrum at 5 K in comparison to the calculated INS spectrum in the 5-1500 cm⁻¹ range.

Calculated symmetries and energies of phonons are given in **Table A2.1** in the addenda for Chapter 2. There are four phonons (47.65, 50.62, 53.95, and 54.59 cm⁻¹) near the magnetic excitation at 48.5 cm⁻¹, as predicted by VASP calculations. Among the four phonons (listed in **Table 2.1**), only the 54.59 cm⁻¹ phonon has the *u* symmetry which is far-IR active. However, there is no observable spin-phonon coupling with this phonon in FIRMS (**Figure 2.3**) as avoided crossing.

The DFT calculation of phonons produced phonon movies for the four phonons in **Table 2.1**, which are attached to this dissertation. These phonon movies of the anion (**Co-MST-H₂O**⁻) in **Co-MST-H₂O** show small changes in the location of the Co²⁺ ion of the molecule. Larger changes in the mesityl positions in the MST³⁻ ligand and shifting of the water molecule are more noticeable in the phonon movies.

The DFT phonon calculations also determined the spin density, ρ_s , on the Co²⁺ ion in **Co-MST-H₂O**, providing a quantitative scale, revealing how the spin is dispersed onto Co²⁺ ion and atoms in the ligand.¹⁹⁹ VASP partitions electrons according to the Wigner-Seitz radius a_e in Eq. 5:²⁰⁰

$$a_e = (3/4\pi n_e)^{1/3} \quad (2.5)$$

where n_e is the particle density of electrons; a_e is the radius “occupied” by one atom in a sample, and each atom is considered as a sphere.

Table 2.1. List of calculated phonons near the magnetic transition in **Co-MST-H₂O** and their symmetries from VASP calculations.

Frequency (cm ⁻¹)	Symmetry
47.65	A_g
50.62	A_g
53.95	A_g
54.59	A_u

The calculations do not include the spin densities residing in the bonds, but rather just the densities in individual atoms. The range of spin densities for each atom type is presented in **Table 2.2**. Detailed spin densities are given in **Table A2.2**. The total spin density (sum of those on all atoms) on the **Co-MST-H₂O** molecule is 2.863 which is lower than 3 (= 3 unpaired electrons). The total spin density here is similar to those in, e.g., in Co(PPh₃)₂Cl₂ (2.797),¹³³ Co(PPh₃)₂Br₂ (2.783),¹³³ and Co(PPh₃)₂I₂ (2.747).¹³³ The remaining spin densities are dispersed in the *bonds* in the **Co-MST-H₂O** molecule. *No spin densities are present in the atoms of the cation NMe₄⁺ or lattice solvents (H₂O and CH₂Cl₂). In other words, the unpaired electron spins appear to be entirely on the Co²⁺-containing anion [Co(MST)(OH₂)]⁻.* We have used the current DFT calculation method to obtain spin densities in several Co²⁺ SMMs (**Table 2.2**).^{95, 133} It is the first time that spin densities entirely on the metal-containing anion have been observed.

Most of the spin densities, 2.627 (87.6% of the 3 unpaired electrons) of the total 2.863, is concentrated on the Co²⁺ ion. This is understandable as the unpaired electrons are in the Co²⁺ ion. Then, the axial N atom (N3 in **Table A2.2**) bound to the Co²⁺ ion has the next highest spin density of 0.045, followed by the 3 equatorial N atoms (N1, N5, N7; spin densities: 0.036-0.037) and the O atom of the water ligand (O3; 0.030) that all bind directly to the Co²⁺ ion. After these α atoms (bound to Co²⁺), β atoms have much smaller or no spin densities, including 0.004-0.005 for S atoms, -0.001 for the C atoms (C13, C23, C33) bound to the 3 equatorial N atoms, -0.001 to 0 for the C atoms (C5, C21, C31) bound to the axial N atom, and 0 for the 2 H atoms of the water ligand. The negative spin densities here indicate that these (small) spins are in the

Table 2.2. Correlation between calculated spin densities on the Co²⁺ ions and ZFS parameters of the complexes/coordination polymer (CP).

Complexes	Spin densities on the Co ²⁺ ions (and percentage of 3 unpaired electrons)	<i>D'</i> values (cm ⁻¹)	Refs
Co(PPh ₃) ₂ I ₂	2.553 (85.1%)	13.63(10)	133
Co(AsPh ₃) ₂ I ₂	2.558 (85.3%)	27	^a
Co(PPh ₃) ₂ Br ₂	2.570 (85.7%)	13.83(2)	133
Co(PPh ₃) ₂ Cl ₂	2.585 (86.2%)	14.89(2)	133
Co-MST-H₂O	2.627 (87.6%)	25.3	Current work
Co-TODA (CP)	2.68-2.69 (89.3%-89.7%)	40.2	95
Co(acac) ₂ (H ₂ O) ₂	2.81 (93.7%)	57.0	199
[Co(12-crown-4) ₂](I ₃) ₂	2.82 (94.0%)	24.7	^a

^a SMM behaviors of [Co(12-crown-4)₂](I₃)₂ and Co(AsPh₃)₂I₂ were probed by Saber and Dunbar in ref. 201 and by Chen et al. in ref. 202, respectively. Their *D'* values determined by advanced spectroscopies were reported in refs. 96 and 139, respectively. Spin densities of [Co(12-crown-4)₂](I₃)₂ and Co(AsPh₃)₂I₂ have been calculated and are reported here for comparison. Tables listing the spin densities for these complexes are given in **Tables A2.3-A2.6**.

opposite direction as the 3 unpaired electrons on the molecule. Some of the other atoms of the ligand, including a few H atoms, carry small spin densities (**Table A2.2**). A comparison of calculated spin densities on Co²⁺ ions in a few complexes and their ZFS *D'* values are given in **Table 2.2**.

2.3.5. Hirshfeld surface analysis

Hirshfeld surface analysis^{170, 173} is especially effective to examine which parts of a molecule interact most strongly with neighboring molecules in the crystal solid.^{117, 174-196} A Hirshfeld surface is an isosurface calculated from the weight function $w(\mathbf{r})$ of the sum of spherical atom electron densities (Eq. 6):

$$w(\mathbf{r}) = \frac{\rho_{promolecule}(\mathbf{r})}{\rho_{procrystal}(\mathbf{r})} = \frac{\sum_{A \in molecule} \rho_A(\mathbf{r})}{\sum_{A \in crystal} \rho_A(\mathbf{r})} \quad (2.6)$$

where $\rho_{promolecule}(\mathbf{r})$ is the sum of the molecular electron density over the atoms in the molecule or ions under consideration (the promolecule) and $\rho_{procrystal}(\mathbf{r})$ is the similar sum over the crystal (the procrystal).^{170, 173}

The isosurface here separates a molecule (promolecule) or ion from its nearest neighbors (procrystal) at a given density level. Distances to the nearest atoms outside (external), d_e , and inside (internal), d_i , are defined from the Hirshfeld surface, giving a 3-*D* representation of the intermolecular, close contacts in the crystal using the *CrystalExplorer* software by Spackman and coworkers.^{170, 173} Also, the Hirshfeld surface could be made into a 2-*D* histogram with a unique fingerprint plot for intermolecular interactions.

Surfaces (**Figure 2.6**) and fingerprint plots (**Figure A2.12**) for the [Co(MST)(OH₂)]⁻ anion (named **Co-MST-H₂O⁻**) show interactions with neighboring molecules, cation Me₄N⁺, and lattice solvents (CH₂Cl₂ and H₂O), while the average surface reveals low to moderate intensity.

The strongest interactions are from those of the O atoms of the sulfonyl groups interacting with solvents in the lattice (CH_2Cl_2 and H_2O through hydrogen bonds), as shown by the red spots in **Figure 2.6b**. The interactions of the anion with the cation NMe_4^+ are present but not strong, as there are no nearby red spots near NMe_4^+ in **Figure 2.6b**. Interactions of H atoms with other **Co-MST-H₂O** molecules, the solvents, and the cation NMe_4^+ take the largest share (83.9%) of close interactions with neighboring molecules, as shown in **Table 2.3**.

2.4. Results and discussion of $[\text{NMe}_4][\text{Ni}(\text{MST})(\text{OH}_2)]$ (Ni-MST-H₂O)

Phonon properties of **Ni-MST-H₂O** have been studied by INS, DFT-phonon calculations, and Hirschfeld surface analysis. HFEPR was not used for **Ni-MST-H₂O** as the effective range for HFEPR using current instrumentation is up to $\sim 30 \text{ cm}^{-1}$, while the expected transition from previously reported magnetometry is near 209 cm^{-1} .¹⁰⁶ Repeated attempts to probe powder samples of **Ni-MST-H₂O** by FIRMS (**Figure A2.13**) did not show any magnetic peaks. VT INS spectra of powder samples in **Figure 2.7** also did not clearly reveal magnetic peaks in the spectra. VT profile of the shoulder peak at $\sim 208 \text{ cm}^{-1}$ indicates that it is mostly phonon in nature with possible magnetic contributions to the intensity. Both FIRMS and INS spectra show strong, broad phonon peaks at $\sim 210 \text{ cm}^{-1}$. We speculate that the following may lead to the results in the current studies: (1) The magnetic transitions among the ZFS states in **Figure 2.1d** are possibly too weak to be observed by both FIRMS and INS; (2) The magnetic transitions undergo spin-phonon couplings with the nearby strong phonons, dividing the magnetic features over several phonons, making the direct observation of the magnetic transition difficult. For future spectroscopic studies, the use of single crystals in FIRMS and deuterated **Ni-MST-H₂O** samples in VT INS is expected to help reveal magnetic transitions in **Ni-MST-H₂O**.

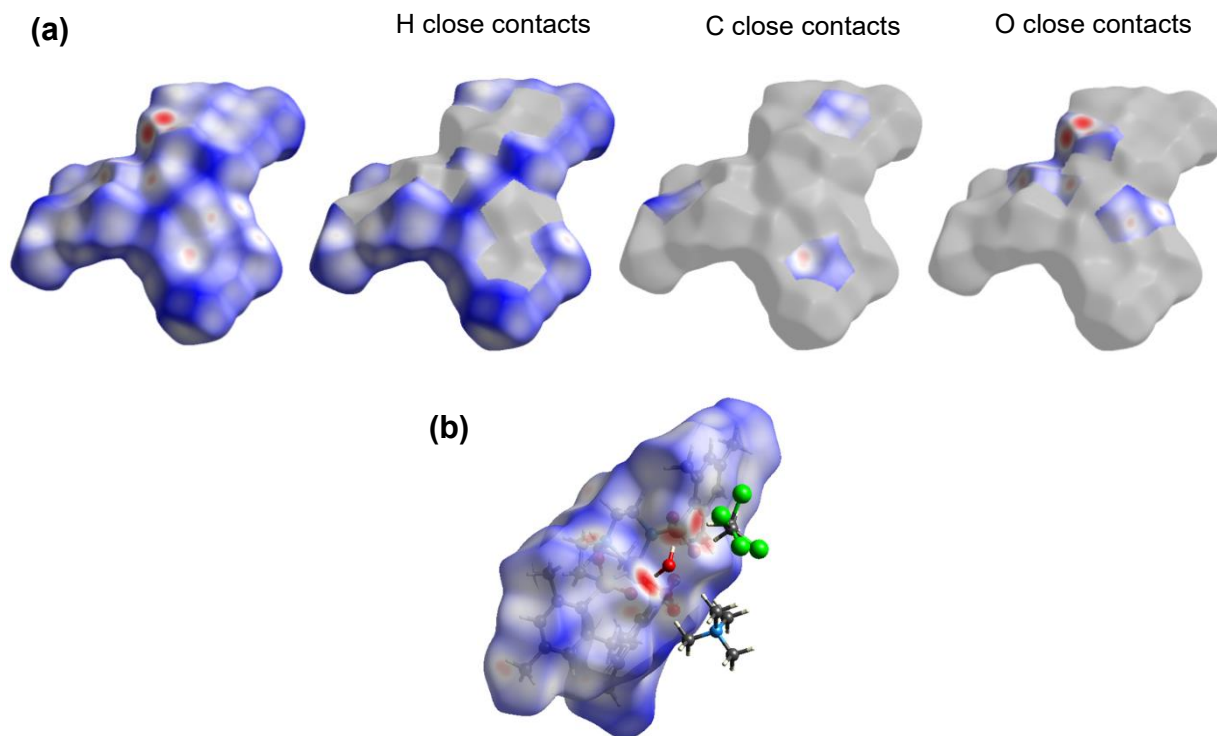


Figure 2.6. (a) Hirshfeld surfaces of the **Co-MST-H₂O⁻** ion showing surface interactions as heat maps. Red zones indicate strong interactions with closer distances between d_e and d_i atoms, while blue zones are indicative of larger distances and less strong interactions. (b) Representations of the closest and more intense interactions of the **Co-MST-H₂O⁻** Hirshfeld surface, showing that lattice H₂O forms hydrogen bonds with the O atoms in the MST³⁻ ligand. The H atoms of lattice CH₂Cl₂ also interact strongly with O atoms of ligand. The CH₂Cl₂ molecule is disordered.

Table 2.3. Hirshfeld surface coverage based on interactions of atoms on the **M-MST⁻** anion with all nearby atoms of neighboring molecules and Me₄N⁺ cation. Most of the interactions are from H atoms of the **M-MST⁻** anion with surrounding atoms.

	Co-MST-H₂O	Ni-MST-H₂O
H close contacts	83.9%	79.7%
C close contacts	8.6%	9.8%
O close contacts	7.5%	10.5%
N close contacts	>0.1%	>0.1%
S close contacts	>0.1%	>0.1%
M close contacts	>0.1%	>0.1%

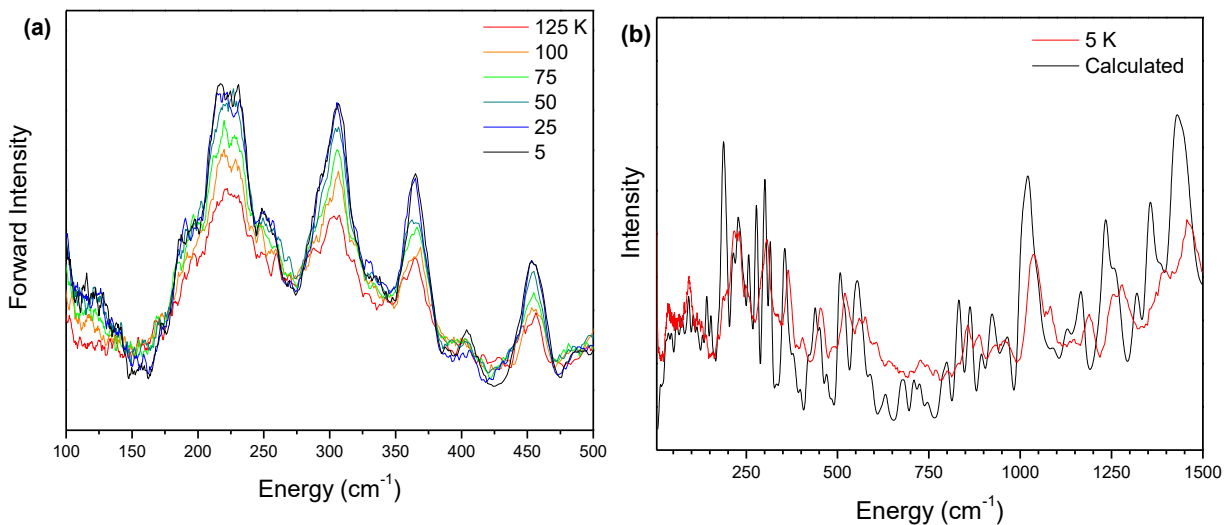


Figure 2.7. (a) Bose-corrected INS spectra of **Ni-MST-H₂O** at 100-500 cm⁻¹. There are no strong magnetic features in this region. (b) INS spectra showing calculated and experimental phonons at 5–1500 cm⁻¹ of **Ni-MST-H₂O**. Additional regions of the experimental and calculated INS are given in **Figures A2.16-A2.18**.

Earlier, Schulte, Vignesh, and Dunbar determined spin-Hamiltonian parameters of **Ni-MST-H₂O** using DC magnetic susceptibility and reduced magnetization.¹⁰⁶ The current results suggest that the magnetometry remains the only viable technique to determine spin-Hamiltonian parameters for **Ni-MST-H₂O**. We have thus focused on the phonon properties of **Ni-MST-H₂O** revealed by INS, DFT phonon calculations, and Hirshfeld surface analysis. INS spectra of **Ni-MST-H₂O** are given in **Figure 2.7**. DFT calculated INS spectrum is given in **Figure 2.7b** in comparison with the experimental INS spectrum, showing a good fit between the two spectra.

Surfaces (**Figure 2.8**) and fingerprint plots (**Figure A2.19**) for the [Ni(MST)(OH₂)]⁻ anion (named **Ni-MST-H₂O⁻**) show intense interactions between the anion and the lattice solvent H₂O (through hydrogen bonds) and the cation Me₄N⁺ through the O atoms of the sulfonyl groups, as shown by the red spots in **Figure 2.8b**. In comparison, the interactions between **Co-MST-H₂O⁻** and its cation NMe₄⁺ are not as strong, as discussed earlier and shown in **Figure 2.6b**. The interactions of the anion with the other solvent, ethyl ether (Et₂O), are present but not strong, as there are no nearby red spots around Et₂O in **Figure 2.8b**. Interactions of H atoms with other **Ni-MST-H₂O** molecules, the solvents, and the cation NMe₄⁺ take the largest share (79.7%) of close interactions with neighboring molecules, as shown in **Table 2.3**.

2.5. Conclusions

In this work, the use of advanced spectroscopies to probe magnetic transitions in **Co-MST-H₂O** has delivered spin-Hamiltonian parameters for the compound. INS studies also give phonon properties of the complex. DFT phonon calculations give calculated INS spectrum that fits well with the experimental INS spectrum. The calculations also determined phonon symmetries, their energies, and phonon movies. In addition, the DFT phonon calculations yield spin density on the Co²⁺ ion and other atoms in **Co-MST-H₂O**. Hirshfeld surface analysis

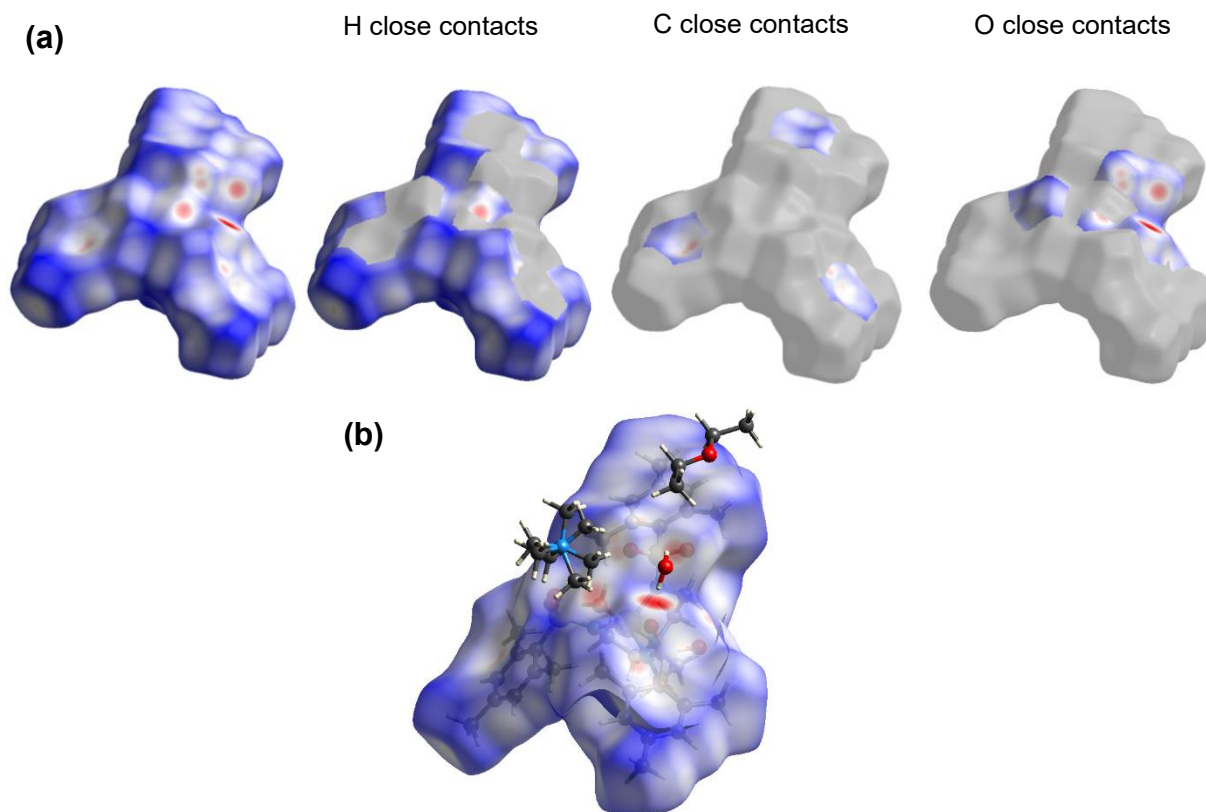


Figure 2.8. (a) Hirshfeld surfaces of the $\text{Ni-MST-H}_2\text{O}^-$ anion showing surface interactions as heat maps. Red zones indicate strong interactions with closer distances between d_e and d_i atoms, while blue zones are indicative of larger distances and less strong interactions. (b) Representations of the closest and more intense interactions of the $\text{Ni-MST-H}_2\text{O}^-$ Hirshfeld surface, showing that H_2O solvent molecule and the Me_4N^+ cation form hydrogen bonds with the O atoms in the MST^{3-} ligand. The ethyl ether (Et_2O) solvent molecule, in contrast, does not show strong interactions with the $\text{Ni-MST-H}_2\text{O}^-$ anion. The Me_4N^+ cation is disordered.

reveals how the **Co-MST-H₂O⁻** anion interacts with its cation, solvent molecules, and neighboring **Co-MST-H₂O** molecules. For **Ni-MST-H₂O**, phonon properties and intermolecular interactions have been studied by INS, DFT phonon calculations, and Hirshfeld surface analysis. FIRMS and INS studies of **Ni-MST-H₂O** did not show its magnetic transitions. Thus, the current work on **Co-MST-H₂O** offers a very good comparison (between results from magnetometry and spectroscopic techniques). For **Ni-MST-H₂O**, magnetometry is the only viable technique to determine spin-Hamiltonian parameters for the compound in the absence of magnetic resonance or INS results.

2.6. Experimental section

2.6.1. Synthesis

Synthesis of the H₃MST ligand was completed using commercial materials with no further purification following a reported procedure.²⁰³ **Co-MST-H₂O** and **Ni-MST-H₂O** were prepared following reported procedures.^{106, 127}

2.6.2. FIRMS

Far-IR magneto-spectroscopy was completed at the National High Magnetic Field Laboratory in Tallahassee, Florida 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 propagates in free space inside the optical beamline, connecting the output of the spectrometer and top of the sample probe. The radiation then passes through the brass light-pipe through a 2.5 m distance to the field center. The probe and beamline are evacuated to eliminate strong parasitic absorptions of the air. Samples were prepared by mixing with *n*-eicosane under a

heat lamp to make a slurry, making a solid layer of polycrystalline sample. Measurements were conducted at 5 K with the sample and bolometer being cooled by low pressure He gas. Spectrum transmitted through the samples was collected between 10 and 720 cm^{-1} with a resolution of 0.3 cm^{-1} .

2.6.3. HFEPR

HFEPR spectra were collected at the National High Magnetic Field Laboratory in the EMR facility using a spectrometer previously described,²⁰⁴ modified with the use of VDI sources. The spectrometer is associated with a 15/17 T warm-bore superconducting magnet. **Co-MST-H₂O** was measured both “as is” and as a pellet pressed with *n*-eicosane to prevent torquing effects of the sample in the magnetic field.

2.6.4. INS

Variable-temperature INS spectra was collected at Oak Ridge National Laboratory using VISION, an indirect-geometry vibrational spectrometer.¹⁵² About 500 mg of sample was used for data collection, sealed in a vanadium can within a helium environment. VISION has two detector banks; magnetic transitions are more intense in the forward scattering detectors for their low scattering angle dependence.

2.6.5. Phonon and INS calculations

DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP).²⁰⁵ Lattice parameters and atomic coordinates from published structures were used for the structure. Atomic force constants were calculated by VASP using finite displacement method, and vibrational eigen-frequencies and modes were calculated using Phonopy and OCLIMAX software was used to convert DFT calculated phonon results to the simulated INS spectra.²⁰⁶⁻²¹¹

2.6.6. Hirshfeld surface analysis

Surfaces were generated using Crystal Explorer.^{170, 173} Surfaces for this analysis were generated from reported structures.¹⁰⁶ Only atoms within the SMM complex were selected to allow for determination of interactions with counter ions and nearby SMM complexes within the crystal structure. Charges for the metal-containing anions in **Co-MST-H₂O** and **Ni-MST-H₂O** were set to -1 while the NMe₄⁺ counter ion was set to +1.

Chapter 3: Atomic-scale visualization of the toroidal order in a trimeric Dy(III) compound

This chapter is based on the following manuscript to be submitted for publication:

Michael J. Jenkins, Madalynn G. Marshall, Jie Xing, Xiaoping Wang, Christina M. Hoffman, Huibo Cao, Rongying Jin, Zi-Ling Xue. Atomic-scale visualization of the toroidal order in a trimeric dysprosium(III) compound

Author contributions

Michael J. Jenkins synthesized and performed preliminary characterization of **Dy₃-1** and **Dy₃-2**. He studied crystal stabilities and developed the method to grow large crystals of **Dy₃-2**. Jenkins and Zi-Ling Xue investigated the selection of **Dy₃-1** for the initial studies. Jenkins, Xiaoping Wang, and Christina Hoffmann solved the structure of **Dy₃-2** using single-crystal X-ray diffraction. Wang and Hoffmann also conducted the single-crystal neutron diffraction of **Dy₃-1** on TOPAZ at Oak Ridge National Laboratory (ORNL). Jie Xing completed magnetic susceptibility measurements and analysis. Jenkins, Madalynn Marshall, Huibo Cao, and Xue participated in the two neutron diffraction experiments. Marshall completed neutron diffraction data analyses from the two experiments. Xue, Cao, and Rongying Jin initiated and supervised the project. Jenkins and Xue wrote the manuscript with input from other authors.

3.1. Abstract

Single-molecule toroics (SMTs) offer a unique platform for next-generation quantum devices, utilizing head-to-tail spin arrangements to encode qubits and manipulate spin currents. However, there has been no direct observation of the toroidal moment in an SMT. Here, we

report synthesis and comprehensive characterization, including polarized neutron diffraction (PND), of a trinuclear Dy(III) cluster, $[\text{Dy}_3(\mu_3\text{-OH})(\text{teaH}_2)_3(\text{paa})_3]\text{Cl}(\text{OMe})\cdot\text{PhCN}\cdot 3\text{MeOH}$ [teaH_3 = triethanolamine, paaH = N-(2-pyridyl)-acetoacetamide]]. Crystallization of the highly symmetric Dy_3 cluster has yielded large single crystals ($>1\text{ mm}^3$) with stability suitable for PND and magnetometry studies. DC (direct current) magnetometry confirms pronounced anisotropic coupling of antiferromagnetic normal to the molecular plane and mixed ferromagnetic/antiferromagnetic in-plane coupling, consistent with a toroidal ground state. Most significantly, PND on a single crystal at 5 K delivers a direct, atomically resolved mapping of the local magnetic susceptibility tensor of each Dy^{3+} ion, providing unequivocal, experimental proof of the head-to-tail spin arrangement that defines the toroidal moment. Simulations based on the refined tensor reproduce the observed magnetization anisotropy without additional fitting parameters, validating the methodology. This work represents the first direct, atomic-scale determination of para-toroidic dipoles and the field-polarization of antiferro-toroidic order in an SMT and establishes a blueprint for integrating PND with magnetometry to guide the rational design of toroidal qubits and spintronic architectures.

3.2. Introduction

Single-molecule toroics (SMTs), characterized by their ring-shaped atomic arrangement, have gained considerable attention in quantum information science and spintronics.^{4, 7, 8, 10-12, 36, 37, 43, 73, 75, 76, 78, 104, 212-223} Their unique structural, magnetic, and electronic properties make them promising candidates for applications such as qubits for quantum computing.^{4, 10, 36} These applications seek to take advantage of the tunable properties of the spin systems inherent in SMTs, where the electronic and magnetic structure of these compounds can be influenced by the coordination environment of the magnetic ions.^{4, 7, 9-12, 224, 225} From the initial report of SMTs in

2008, there has been rapid growth in the field with both theoretical and experimental studies.^{21, 35, 41, 44, 46, 226-251} Most SMTs are lanthanide-based compounds, using large spins of the Ln^{3+} ions such as Dy^{3+} . There have been reports of planar rings from Dy_3 up to Dy_6 , mixed transition metal-lanthanide rings and clusters, as well as non-planar SMTs.^{22, 35, 37, 45, 220, 226, 230, 237, 238, 241-245, 248, 250-292} In addition to Dy^{3+} -containing SMTs, compounds with other Ln^{3+} ions such as Ho^{3+} and Tb^{3+} have also been reported with toroidal magnetic moments.^{37, 276, 278, 293} Typically the toroidal moments of SMTs have been probed using magnetometry, where changes to the net magnetic moment are observed at low temperatures, when the magnetic moments start to form their characteristic ring-shaped spin structures. These changes in magnetic moments can lead to non-magnetic ground states, as reported by Chibotaru, Ungur, and Socini.²⁶ However, the loss of a net magnetic moment does not necessarily point to the presence of a toroidal moment in a cluster compound.³⁵ While the magnetometry could provide the data consistent with such a magnetic toroidal moment, additional measurements with other advanced techniques, such as cantilever torque magnetometry, high-field EPR, and far-IR spectroscopy, are necessary to examine the ground state and magnetic excitations.^{42, 229, 265, 294} At the magnetic excited states, there is no longer an absence of a magnetic moment, thus allowing for perturbation of spin states within the SMT compounds through the magnetic excitations.^{35, 227, 265} These experiments, as well as the associated theory and data fitting, lead to the simulation of the direction, intensity, and coupling of magnetic moments of the SMTs. However, the above-mentioned techniques are indirect methods and cannot unambiguously determine the net toroidal moment due to the loss of local spin information relative to the lattice environment.²⁹⁵ In this work, we have investigated a new Dy_3 compound using the combination of magnetometry and polarized neutron diffraction (PND) to unambiguously determine the toroidal moment. Langley, Rajaraman, Murray and

coworkers recently reported that $[\text{Dy}_3(\mu\text{-OH})(\text{teaH}_2)_3(\text{paa})_3]\text{Cl}_2\cdot\text{MeCN}\cdot 4\text{H}_2\text{O}$ (**Dy3-1**), containing a dication $[\text{Dy}_3(\mu\text{-OH})(\text{teaH}_2)_3(\text{paa})_3]^{2+}$, showed SMT properties based on magnetometry studies of powder samples and *ab initio* calculations.²⁷⁶ This compound was initially selected for the current PND studies for its crystallographic trigonal *P*-3 (No. 147) space group. There is a crystallographic C_3 axis through the center of the molecule, making the three Dy^{3+} ions equivalent. Such a compound in a highly symmetric space group is a superior choice for PND measurements. As discussed below, we have instead prepared an analog in a different solvent mixture, using a distinct method to grow large, stable crystals of $[\text{Dy}_3(\mu_3\text{-OH})(\text{teaH}_2)_3(\text{paa})_3]\text{Cl}(\text{OMe})\cdot\text{PhCN}\cdot 3\text{MeOH}$ (**Dy3-2**), also containing a $[\text{Dy}_3(\mu_3\text{-O})(\text{teaH}_2)_3(\text{paa})_3]^{2+}$ dication, in the *P*-3c1 (No. 165) space group.

The toroidal moment in SMTs is due to head-to-tail spin arrangements (**Figure 3.1**) within the cluster molecule. Toroidal spin states can be formed from a planar arrangement of spins or from out of plane spins that couple in a helical pattern, leading to the cancellation of spins within the toroidal plane, although there may still be out of plane dipole contributions to the overall spin states.^{37, 44, 227, 296} Toroidal moments are difficult to be directly observed, because metal ions, acting as electromagnetic particles with net magnetic dipoles or electric charges, can couple to the toroidal moment or obscure their signals. Therefore, highly sensitive techniques are required to observe the toroidal moment.

In the case of SMT molecules, determining the susceptibility tensor of the magnetic ions within the molecule is an efficient way to directly examine toroidal spin arrangement. Direct experimental determination of the head-to-tail spin arrangement would allow for a better understanding of the toroidal moment. To experimentally determine this toroidal moment, we have sought the combined use of PND and magnetometry to find the arrangement of spin inside

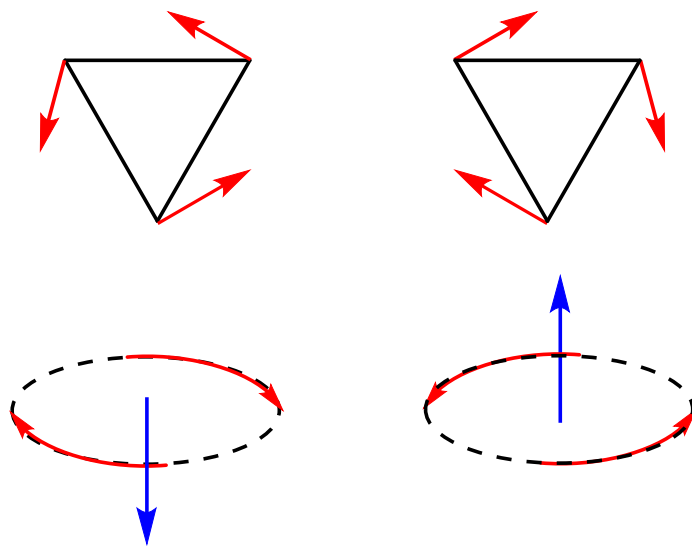


Figure 3.1. Planar spin alignment of coupled Dy^{3+} ions within an SMT.

the cluster molecule.

Magnetometry is a routine method often using powder samples to study molecular magnetic materials including SMTs, providing magnetization measurements used to determine the overall magnetic anisotropy. The magnetic anisotropy of SMTs has been used to model the direction and scale of atomic magnetic susceptibility as well as the coupling between magnetic ions.^{37, 44, 46}

Polarized neutron diffraction (PND) is a unique technique to probe molecular magnetism.^{59-63, 65-69, 297, 298} In PND, spin-up and spin-down neutrons are alternatively generated and scattered by, e.g., a single crystal of a sample inside an external magnetic field.⁵⁹ The magnetic field makes unpaired electrons in the sample to align “up” at a low temperature (e.g., 2 K). The spin-up and spin-down incident neutrons have different interactions with the “up” electron spins, leading to different diffraction intensities, even though the nuclear interactions of the atoms in the sample with the incident neutrons are the same. The difference in the diffraction intensities is used to yield spin density of the crystal and magnetization vectors of the atoms with the unpaired electrons. In PND, Bragg peak intensities of spin-up and spin-down neutrons are measured. These intensity ratios of spin-up and spin-down neutron diffraction peaks, called the flipping ratios, are described by the formula in Eq. 3.1:

$$R(k) = R(hkl) = \frac{I^+}{I^-} = \frac{F_N^2 + 2pq^2F_NF_M + q^2F_M^2}{F_N^2 - 2epq^2F_NF_M + q^2F_M^2} \quad (3.1)$$

where I^+ and I^- are the diffracted intensities at a fixed Bragg position k by spin-up and spin-down incident neutrons, respectively, q is the sine of the angle between the scattering vector and the magnetic field direction, p is the polarization of the incident beam, and e is the flipping efficiency.

By fitting the measured flipping ratios, the magnetic susceptibility tensor can be determined.^{69,}

PND has been effective to determine spin arrangements for both *d* and *f* block compounds. It has been used to determine spin arrangements for clusters and compounds with one metal ion.^{59-69, 297, 298} Magnetic anisotropy of a Dy³⁺-based single-molecule magnet (SMM) has been studied using PND to analytically determine the atomic magnetic susceptibility tensor as reported by Klahn and coworkers.⁶¹ Similarly, PND has been used to compare similarities and differences of Dy³⁺ and Ho³⁺ SMMs [Ln(H₂O)₅(HMPA)₂]₃ (HMPA = hexamethylphosphoramide), showing that the transverse elements of the atomic susceptibility are significantly different, with the Dy³⁺ SMM being nearly axial and the Ho³⁺-analog showing significant transverse anisotropy.²⁹⁷ Temperature evolution of atomic susceptibility has also been studied using PND, showing reorientation of anisotropy axis within a spin ice compound.⁶⁷ PND has also been used to determine spin density in an Fe₈ cluster, [Fe₈O₂(OH)₁₂(tacn)₆]₃Br_{4.3}(ClO₄)_{3.7}·6H₂O (Fe₈pcl; tacn = 1,4,7-triazacyclononane), as well as which of the eight Fe³⁺ ions (*S* = 5/2) have up spins and which have down spins, leading to antiferromagnetic interactions in the cluster compound with a total *S* = 10.²⁹⁸ PND shows that two opposite Fe³⁺ ions on the edges of the molecule carry down spins, and the other six Fe³⁺ atoms carry up spins. To our knowledge, PND has not been used to probe an SMT. The current work demonstrates that PND reveals directly the head-to-tail spin arrangement in an SMT. The magnetic susceptibility tensor of magnetic ions in the SMT is used to examine the atomic-scale spin structure and directly determine the toroidal spin arrangement. In this work, we demonstrate, for the first time, the direct experimental visualization of toroidal spin ordering at the atomic level in a Dy₃-based SMT using a combined approach of magnetometry and polarized neutron diffraction. This integrated strategy overcomes the limitations of prior indirect methods

and sets a new standard for probing molecular-scale magnetism.

3.3. Results and discussion

3.3.1. Selection of the compound and its synthesis

For PND experiments, high-quality data acquisition requires a large single crystal (>1 mm³) with well-defined morphology and high symmetry. Large crystals with a highly symmetric space group are particularly advantageous, as they enhance the interpretability and resolution of magnetic susceptibility tensors. Following the published procedure by Langley and coworkers,^{261, 276} we were able to prepare the reported compound [Dy₃(μ -OH)(teaH₂)₃(paa)₃]Cl₂ in mixed methanol-acetonitrile (MeOH-MeCN) solution, and grow its crystals, **Dy₃-1**, by layering the solution with diethyl ether (Et₂O). We then attempted to grow larger crystals of the reported compound for the PND experiment by using slow solvent vapor diffusion (**Figure A3.1**), which did succeed in giving crystals of improved size. However, crystals of **Dy₃-1** quickly (in ~ 1 min) degraded when exposed to air, likely due to solvent loss in the crystals. As a result, single-crystal neutron diffraction using a single crystal of **Dy₃-1** at TOPAZ (Single-Crystal Diffractometer),³⁰⁰ Oak Ridge National Laboratory (ORNL) was unsuccessful. The diffraction data indicated pronounced smearing of Bragg peaks consistent with decomposition during the experiment.

To resolve this issue, we have used a different solvent mixture (PhCN and MeOH) in the synthesis and growth of crystals. In addition, rather than layering the solution of the product with diethylether,^{261, 276} slow vapor diffusion of diethyl ether to the solution was utilized, as detailed in the Chapter 3 addenda (**Figure A3.1**). The new approach led to the synthesis of **Dy₃-2**, [Dy₃(μ_3 -OH)(teaH₂)₃(paa)₃]Cl(OMe)·PhCN·3MeOH, which gave large crystals ($1.1 \times 1.0 \times 1.5$ mm³) for the PND experiment. The reported **Dy₃-1**,

$[\text{Dy}_3(\mu\text{-OH})(\text{teaH}_2)_3(\text{paa})_3]\text{Cl}_2\cdot\text{MeCN}\cdot 4\text{H}_2\text{O}$, has two Cl^- anions, one MeCN and four H_2O solvent molecules in the lattice. In contrast, **Dy₃-2** has one Cl^- anion and one OMe^- anion in addition to one PhCN and three MeOH solvent molecules in the lattice. The crystals of **Dy₃-2** are semi-transparent with a yellow hue in the hexagonal shape. A photo of the large crystal used in the PND experiment is given in **Figure A3.2** in the addenda for Chapter 3. No degradation of **Dy₃-2** crystals was observed in the process (about 3-4 min) of crystal selection and mounting for either polarized neutron diffraction or single-crystal susceptibility measurement. When a **Dy₃-2** crystal was covered with a thin layer of fluorinated grease, it maintained structural integrity throughout the PND experiment or the neutron diffraction experiment under variable magnetic fields. Two different crystals of **Dy₃-2** were used for the PND and variable-field single-crystal neutron diffraction.

The single-crystal structure of **Dy₃-2**, $[\text{Dy}_3(\mu_3\text{-OH})(\text{teaH}_2)_3(\text{paa})_3]\text{Cl}(\text{OMe})\cdot\text{PhCN}\cdot 3\text{MeOH}$, determined by X-ray diffraction, is in trigonal $P\text{-}3c1$ (No. 165) space group with D_{3d} crystallographic point group symmetry (**Figure 3.2**). The crystal structure of **Dy₃-2** is summarized in Chapter 3 addenda.

3.3.2. Magnetic properties

Since **Dy₃-2** is a new compound with significant differences from **Dy₃-1**, it is imperative to study the magnetic susceptibility of **Dy₃-2**. DC magnetic susceptibility data was collected for **Dy₃-2** using both a polycrystalline sample and a single crystal. For the polycrystalline sample (**Dy₃-2_{poly}**) between 2 and 300 K, the data were collected with an applied DC field of 0.1 T as well as field dependent magnetization with the sample held at 1.9 K and the applied field varied from 0.0 to 7.0 T. These measurements were then also conducted with a single crystal oriented with the hexagonal face both parallel (**Dy₃-2_{||}**) and perpendicular (**Dy₃-2_⊥**) to the magnetic field,

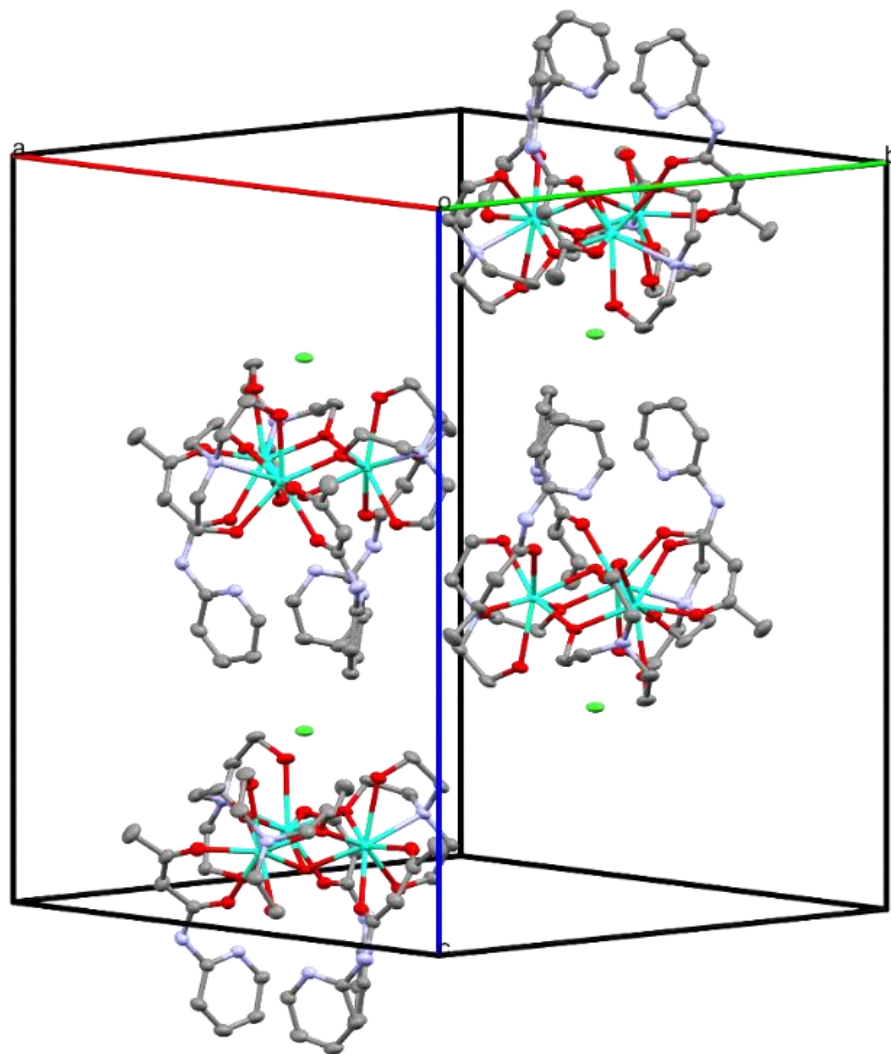


Figure 3.2. Crystallographic unit cell of **Dy₃-2** containing four molecules. Solvent molecules and H atoms are omitted for clarity. Dy³⁺ trimers show opposing stacking within the unit cell.

as depicted in **Figure 3.3**. This data was plotted as $\chi_M T$ vs T , χ vs T , and $1/\chi$ vs T to allow for comparison (**Figure 3.4**). The $\chi_M T$ value at 300 K for the powdered sample of **Dy₃-2_{poly}** is 39.06 cm³ K mol⁻¹, while the single-crystal values are 23.3 and 43.8 cm³ K mol⁻¹ for the **Dy₃-2_⊥** and **Dy₃-2_∥** measurements, respectively (**Figure 3.4**). The **Dy₃-2_{poly}** and **Dy₃-2_∥** measurements are consistent with the expected value of 42.5 cm³ K mol⁻¹ for 3 non-interacting Dy³⁺ ions, as well as comparable to **Dy₃-1** which has a reported value of 41.63.²⁶¹ However, the **Dy₃-2_⊥** measurement is significantly lower. This is likely due to the antiferromagnetic coupling of spins along the normal direction, leading to a small saturated magnetic moment. From the $\chi_M T$ vs temperature (**Figure 3.4a**), there is an inflection point at 16 K and a broad maximum at 84 K. The χ vs T plot (**Figure 3.4d**) shows similar sharp changes at 16 K for **Dy₃-2_∥** though the changes for **Dy₃-2_{poly}** and **Dy₃-2_⊥** are not as sharp and are around 7 K. At 2 K the $\chi_M T$ values reach 42.36, 29.84, and 10.68 cm³ K mol⁻¹ for **Dy₃-2_∥**, **Dy₃-2_{poly}**, and **Dy₃-2_⊥**, respectively, showing anisotropic magnetism at both low and room temperatures. Further examination of the magnetization in relation to temperature shows that there is a loss of typical SMT behavior in the data collected for the **Dy₃-2_⊥** sample between 10 and 20 K (**Figure 3.4b**). This may explain the changes in ordering in the $\chi_M T$ versus T around 16 K.

Curie-Weiss paramagnetic behavior has been examined using the $1/\chi$ vs T data, showing that the Curie-Weiss temperatures are -151 K, -15.8 K, and 25.45 K for the **Dy₃-2_⊥**, **Dy₃-2_{poly}**, and **Dy₃-2_∥** samples, respectively (**Figure 3.4c**). Negative and positive Curie-Weiss temperatures are indicative of antiferromagnetic (AFM) and ferromagnetic (FM) couplings, respectively. Thus, FM coupling dominates the in-plane direction and AFM coupling prevails in the interplane

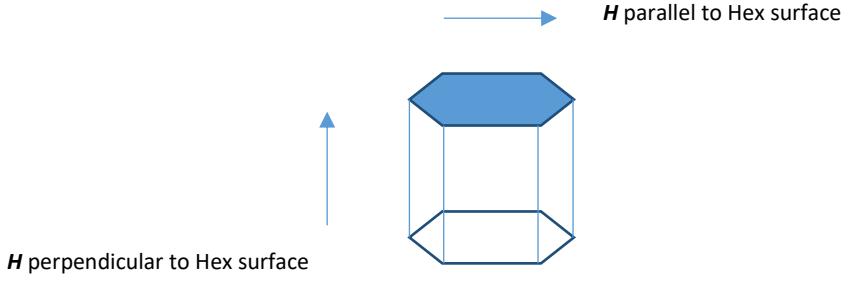


Figure 3.3. Depiction of single-crystal orientation vs external field H for magnetic measurements.

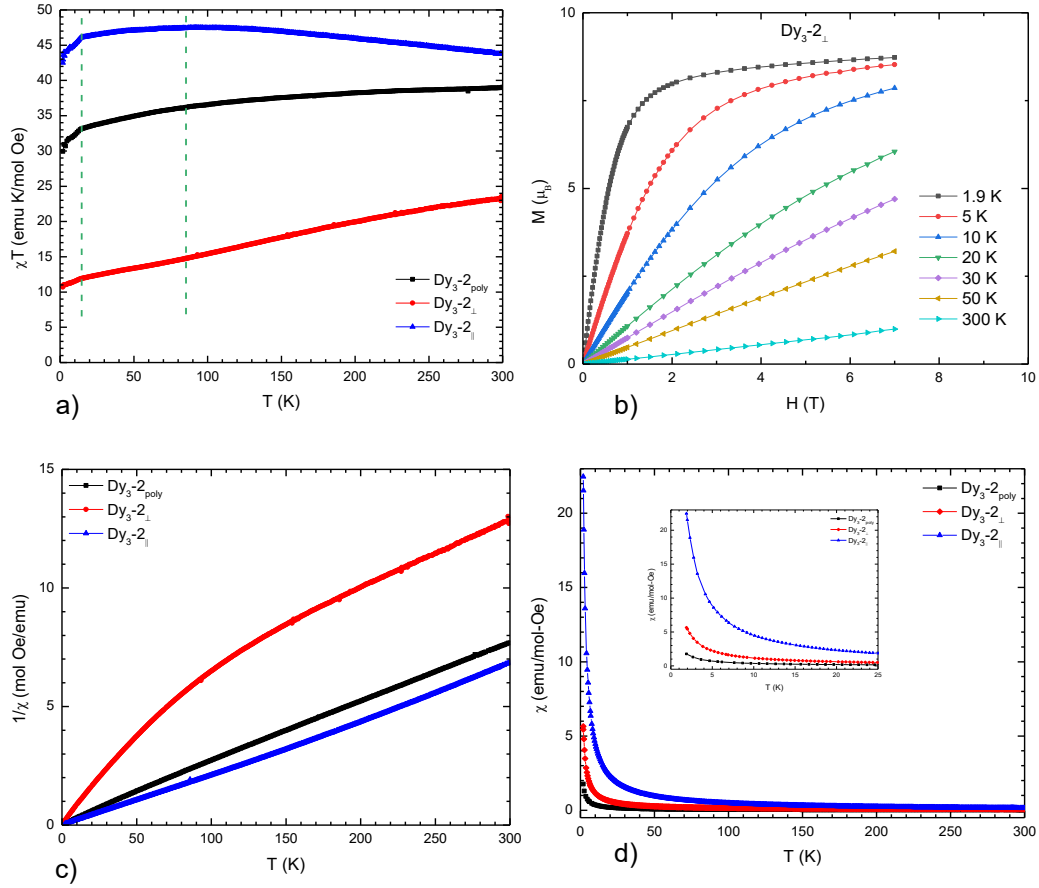


Figure 3.4: Magnetic susceptibility data for **Dy₃-2** showing the powder and single-crystal sample. (a) χT vs T ; (b) Variable-temperature M vs H of **Dy₃-2_⊥** (M and H are lengths of magnetization $\mathbf{M}$ and external field $\mathbf{H}$); (c) $1/\chi$ vs T ; (d) χ vs T .

direction from the single-crystal magnetization results. Determining how these Curie-Weiss temperatures are related to the coupling of magnetic moments, toroidal moments, and single-ion anisotropy is complicated, requiring multiple models to be applied to examine the AFM and FM couplings in SMTs. The Curie constant for each Dy^{3+} ion was also determined showing μ_{eff} values of $9.63 \mu_{\text{B}}$, $10.42 \mu_{\text{B}}$ and $10.30 \mu_{\text{B}}$ for the **Dy₃-2_⊥**, **Dy₃-2_{poly}**, and **Dy₃-2_{||}** samples, respectively, which is consistent with the moment of a Dy^{3+} ion.

Magnetization of all samples shows the stereotypical shape of an SMT.^{35, 37, 44, 46} In the M vs H plots in **Figure 3.5**, hysteresis is only observed in the powdered sample. This may be expected when examining the crystal structure of **Dy₃-2**, which appears to have an alternating stacking structure that could lead to the cancellation of net toroidal moments within the single crystal. Differences between **Dy₃-2_{||}** and **Dy₃-2_⊥** show significant magnetic anisotropy, suggesting that the coupling among the Dy^{3+} ions within this molecule is retained regardless of direction of the external magnetic field. Interestingly, the magnetization obtained from a polycrystalline sample shows difference in the increasing and decreasing field conditions (**Figure 3.5a**). As M in the decreasing field condition is larger than that in the increasing condition, there is likely trapped flux due to impurities existing in the powder sample. Nevertheless, with magnetic anisotropy in single crystals, spin configuration may be detected by PND.

3.3.3. Polarized neutron diffraction

To understand the magnetic anisotropy of the Dy^{3+} spins in **Dy₃-2**, we have measured the local magnetic susceptibility tensor from spin of the Dy^{3+} ion by polarized neutron diffraction. The reflections were measured in the spin-up and spin-down neutron diffraction with an applied

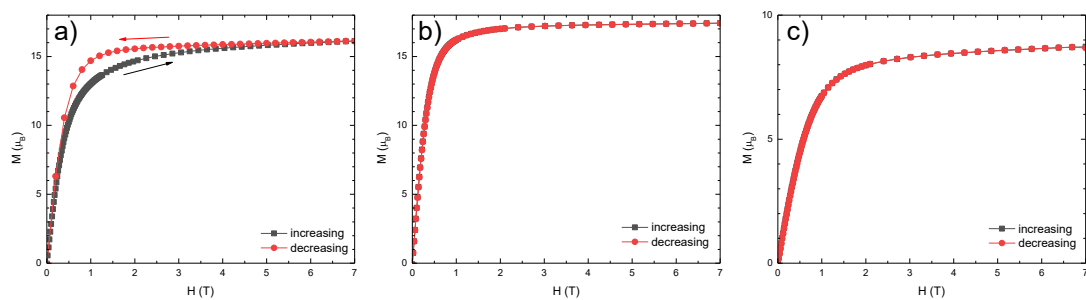


Figure 3.5. Magnetization vs field collected at 1.9 K: (a) **Dy₃-2_{poly}**; (b) **Dy₃-2_{||}**; (c) **Dy₃-2_⊥**.

magnetic field along the *ab* plane where 27 good-quality flipping ratios were obtained. The susceptibility tensor parameters χ_{33} and χ_{13} were fixed to be consistent with the bulk magnetization measurements. A plot of the experimental versus calculated flipping ratios in **Figure 3.6** indicates that a suitable refinement of the flipping ratios was achieved.

The resulting refined magnetization tensor was found to be equal to

$$\vec{\chi}_{Dy} = \frac{mi}{B} = \begin{bmatrix} 1.27(22) & -1.39(31) & -1(2) \\ -1.39(31) & 2.74(30) & 1.00 \\ -1(2) & 1.00 & 1.80 \end{bmatrix}$$

Due to the crystallographic symmetry of the compound, this tensor is symmetric among all three Dy^{3+} ions in the molecule. The magnetization ellipsoids are shown in **Figure 3.6b**, revealing that the overall spin arrangement gives the head-to-tail antiferromagnetic (AFM) coupling required of an SMT compound.

To improve the refinement parameters, the nuclear structure of **Dy₃-2** determined by single-crystal X-ray diffraction (SCXRD) was used for the refinement of the flipping ratios. However, since the SCXRD structure data and the PND data were collected at 100 K and 5 K, respectively, the thermal differences may affect the tensor determination. From PND, one can also see the stacking of the toroidal magnetic moments within the crystal structure with the applied field, leading to an overall cancellation of moments. This is because, among the four Dy_3 molecules in a unit cell, there are two rotating clockwise and two counterclockwise Dy_3 molecules, as shown in **Figure 3.8**. Without the applied field, there is less ordering of the toroidal moment, showing a paramagnet state that would also lack hysteresis.

The susceptibility tensor for Dy^{3+} ions determined from PND also allows for simulation of magnetization data (**Figure 3.7**) and a comparison to our experimental data. The simulation

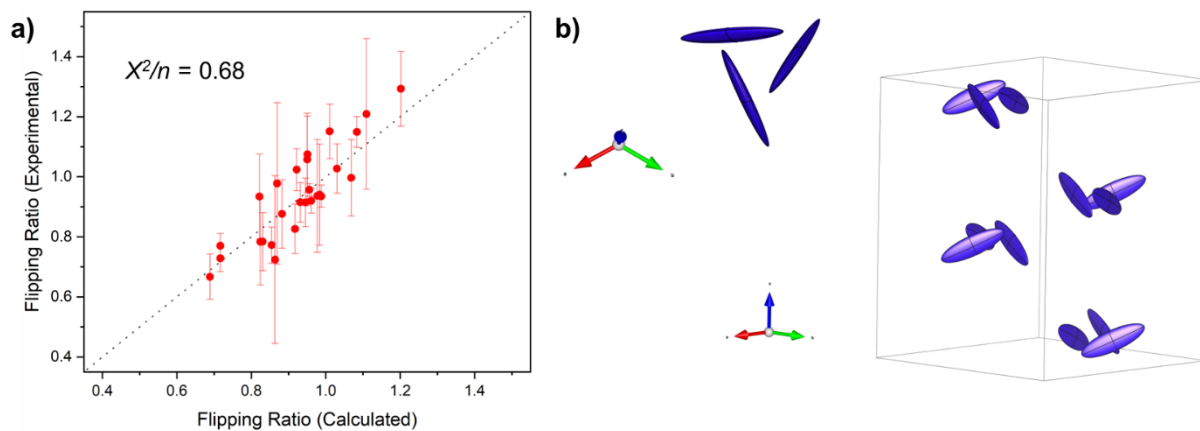


Figure 3.6. (a) Flipping ratios for **Dy₃-2**. (b) The refined susceptibility tensor for **Dy₃-2** in the crystallographic unit cell. The head-to-tail spin arrangement is observed in the *ab* plane, while the toroidal moment would be pointed along the *c* axis.

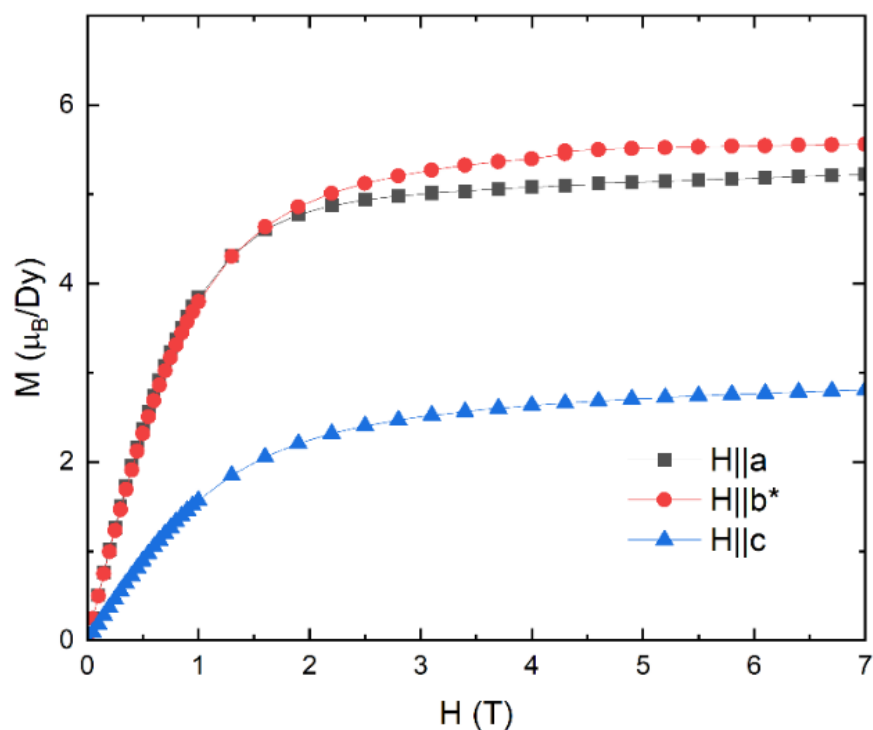


Figure 3.7. Simulation of magnetization based on one Dy^{3+} ion within the **Dy₃-2** compound based on PND refinement of the susceptibility tensor.

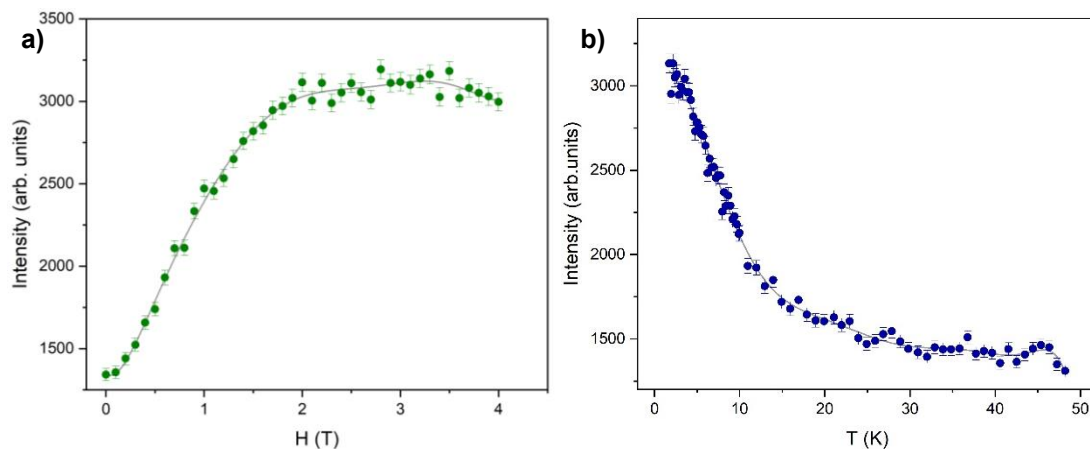


Figure 3.8. (a) Field-dependent order parameter with data collected at 5.0 K with 0.1 T/step. (b) Temperature-dependent order parameters for the magnetic form factor of **Dy₃-2** at 4.0 T. Field induced magnetic order emerges at 0.2 T. Magnetic order appears at ~10 K with an applied magnetic field of 4.0 T.

shows that there should be a large difference in the magnetization of a crystal between the ab plane and the c axis. This is also observed in the magnetization data in **Figure 3.5**. The simulation from PND, when scaled to three Dy^{3+} ions, gives the magnetization of 16.2 when $H \parallel a$. In comparison, the experimentally determined magnetization constant is 17.4 for **Dy₃-2_{||}**. Similarly, the simulation gives magnetization of 8.2 when $H \parallel c$, which is close to 8.4, the experimentally determined magnetization for **Dy₃-2_⊥**. These simulations matching the experimental results show that the susceptibility tensor is accurate with the thermal effects between the single-crystal structure and the PND data.

3.3.4. Variable-magnetic-field single-crystal neutron diffraction

Single-crystal neutron diffraction has been used to examine the field-induced magnetic order and the toroidic order in solid-state materials. For **Dy₃-2**, there are two main phenomena to examine. The first is the direction of the magnetic moment within each toroidal dipole and the second is the field-induced antiferro-toroidic order due to the canted spins out-of-plane. Single-crystal neutron diffraction experiments were performed at different applied magnetic fields parallel to the c axis at 5.0 K. The magnetic fields varied between 0.0 T and 4.0 T with 0.1 T change each time, and magnetic scattering at (2 0 0) was measured. As shown in **Figure 3.8a**, field-induced magnetic order along the c axis begins to emerge at ~ 0.2 T and maximizes at ~ 2 T. Temperature-dependent magnetic scattering at (2 0 0) was also measured between 1.5 K and 50.0 K with an applied magnetic field of 4.0 T. Below 10 K, the temperature was changed 0.25 K per step to collect the magnetic scattering intensity. Above 10 K, the data were collected with 1 K a step. As shown in **Figure 3.8b**, field-induced magnetic-ordering appears at ~ 10 K.

3.4. Conclusions

We have presented a new SMT candidate, $[\text{Dy}_3(\mu_3\text{-OH})(\text{teaH}_2)_3(\text{paa})_3]\text{Cl}(\text{OMe})\cdot\text{PhCN}\cdot 3\text{MeOH}$ (**Dy₃-2**) and demonstrated that it fulfills key structural and magnetic criteria of an SMT compound. Through the combined use of magnetometry and neutron diffraction, we have unambiguously determined the head-to-tail spin arrangement for this Dy₃ SMT, confirming the toroidal moment. **Dy₃-2** shows typical SMT characteristics in DC susceptibility studies, both for polycrystalline and single crystal samples. The use of PND allows for mapping the atomic susceptibility tensor of Dy³⁺ ions within the compound and confirms the toroidal spin arrangement. This is, to our knowledge, the first direct experimental determination of the toroidal spin arrangement in an SMT compound.

3.5. Experimental section

Syntheses of **Dy₃-1**, **Dy₃-2**, and **paaH** and the structure determination by single-crystal X-ray diffraction are given in Chapter 3 addenda.

3.5.1 Magnetic susceptibility measurements

DC Magnetic Susceptibility measurements were completed using a Quantum Design MPMS-7 T at the SmartState Center for Experimental Nanoscale Physics, University of South Carolina. Magnetization by variable temperature and variable magnetic field was collected. Measurements were taken of a powdered sample as well as single crystals oriented in multiple directions. Single crystals were coated with a thin layer of silicon grease to protect the crystal from degradation.

3.5.2. Polarized neutron diffraction (PND)

The HB-3A DEMAND³⁰¹ at the High Flux Isotope Reactor (HFIR), Oak Ridge National Laboratory (ORNL) was used to perform the polarized single crystal neutron diffraction

measurements with a polarized neutron beam of 1.542 Å from a bent Si-220 monochromator³⁰² and a calibrated neutron polarization of 76%. The sample was measured at 5 K with $\mathbf{H} // ab$ and a permanent magnetic set was used to fix the field to 0.6 T. The CrysPy software⁶⁹ was used to analyze the measured flipping ratios.

3.5.3. Neutron diffraction under variable-magnetic fields

The HB-3A DEMAND³⁰¹ at the High Flux Isotope Reactor (HFIR), Oak Ridge National Laboratory (ORNL) was used to perform the single crystal neutron diffraction measurements. The sample was measured at 1.5 K with a variable magnetic field ranging from 0 to 4 T. Data subtraction and integration was completed using FulProf.^{303, 304}

Chapter 4: Ni(II)-based Haldane topological spin-1 chains within 2-dimensional metal-organic frameworks

This chapter is based on the following manuscript to be submitted for publication:

Michael J. Jenkins, Brandon Watson-Sanders, Daniel Duong, Silu Huang, Pagnareach Tin, Cheng Li, Qiang Zhang, Thomas Proffen, Luke L. Daemn, Rongying Jin, Zi-Ling Xue. Ni(II)-based Haldane topological spin-1 chains within metal-organic frameworks.

Author Contributions

Michael J. Jenkins and Pagnareach Tin synthesized compounds and prepared them for experimentation. Brandon Watson-Sanders collected DC magnetization data and performed gap fitting. Daniel Duong and Silu Huang collected preliminary specific heat measurements up to 14 T. Cheng Li, Qiang Zhang, and Thomas Proffen collected POWGEN data or helped interpret the data. Luke Daemen assisted in collection and interpretation of INS results. Jurek Krzystek collected HFESR spectra and helped interpret the results. Ziling Xue initiated the project and supervised the research. Jenkins and Xue wrote the manuscript with input from other authors.

4.1. Abstract

Haldane topological materials have been studied for their potential applications in spintronics and quantum computing, due to their symmetry-protected energy gaps from the spin chains. Here, we discuss the Haldane properties of two Ni(II)-based metal-organic frameworks $[\text{Ni}(\mu\text{-bpa})(\mu\text{-ox})]$ [**NiBaO**; bpa = 1,2-di(pyridin-4-yl)ethane); ox^{2-} = oxalate] and $[\text{Ni}(\mu\text{-bpe})(\mu\text{-ox})]$ [**NiBeO**, bpe = 1,2-di(pyridin-4-yl)ethene] that form two-dimensional sheets

of $\text{Ni}^{2+}\text{-ox}^{2-}$ spin-1 chains with nitrogen-based organic linkers between the chains. These spin chains are probed by variable-temperature powder neutron diffraction, variable temperature inelastic neutron scattering (INS), DC susceptibility, specific heat measurements, and high-field and -frequency electron spin resonance (HFESR). Vibrational properties have been probed by INS and far-IR spectroscopy. The results suggest that interactions between Ni(ox) chains in **NiBaO** and **NiBeO** are weaker than in $[\text{Ni}(\mu\text{-4,4'-bpy})(\mu\text{-ox})]$ (**NiBO**).

4.2. Introduction

In 1983, Haldane proposed that one-dimensional (1-D) antiferromagnetic Heisenberg spin chains show two distinct classes depending on whether the quantum spin number is an integer or half-integer.^{47, 48} For integer spin chains, the Haldane phase or ground state demonstrates a finite excitation gap and short-range antiferromagnetic order. The half-integer spin chain does not show a finite excitation gap but instead is in a gapless state.⁴⁷⁻⁵¹ Further research and modelling by Affleck, Kennedy, Lieb, and Tasaki (AKLT) later explain the gapped state in integer spins is due to a ground state with spin-1/2 edge states at the end of finite spin chains, which form singlet or triplet ground states depending on the configuration of boundary conditions (**Figures 4.1 and 4.2**).^{49, 50, 52-55} The nonzero energy gap is preserved under perturbation, showing the topological nature of the Haldane phase and that protected symmetries such as time-reversal are maintained.³⁰⁵ This behavior is significantly different from conventional antiferromagnetic materials such as nickel(II) oxide (**NiO**), in which long-range magnetic order emerges.⁵⁷ In **NiO**, the formation of a magnetic unit cell distinct from the crystallographic unit cell gives rise to additional magnetic Bragg reflections in diffraction

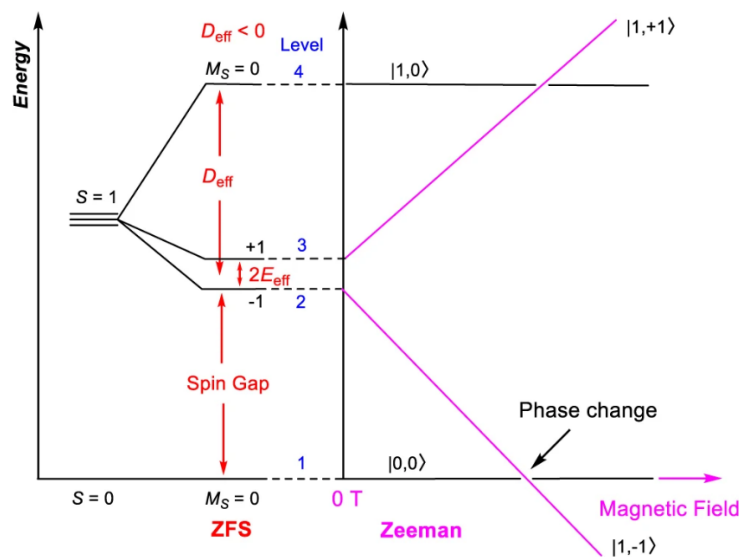


Figure 4.1. Energy diagram of the Haldane phase, showing perturbations of anisotropy leading to ZFS and the effects of magnetic field on Zeeman splitting. Adapted from P. Tin, M. J. Jenkins et. al.⁵⁶

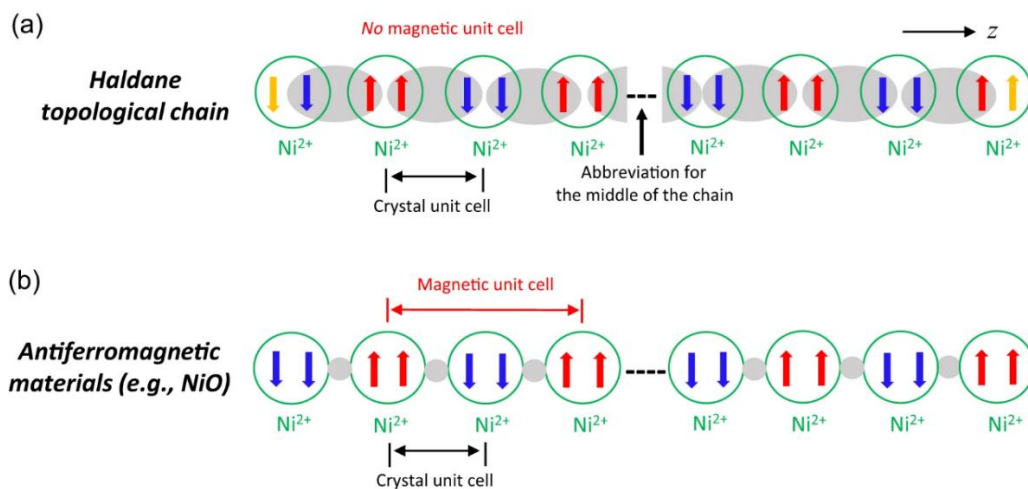


Figure 4.2. a) Scheme of the AKLT model representation of the spin-1 Haldane chain showing the coupling between two electrons of two neighboring $\text{Ni}(\text{II})$ ions within the chain, leaving one unpaired electron at each end of the chain. Green circles show individual Ni^{2+} ions, coupling is shown in the gray oval, quantum coupled electrons are shown as red and blue arrows, and unpaired electrons are shown in orange arrows at the end of the chain. b) Scheme showing typical antiferromagnetic structure in NiO below the Neel temperature. O^{2-} ions are shown as gray circles. Antiferromagnetic coupling gives a magnetic structure at twice the d-spacing of the crystal unit cell. Adapted from P. Tin, M. J. Jenkins et al.⁵⁶

patterns, indicative of the classical magnetic ordering absent in the quantum-disordered Haldane phase. There have been multiple Haldane spin-1 materials studied using Ni^{2+} as the metal ion, from cationic 1-D chains such as NENP $[\text{Ni}(\text{en})_2(\mu\text{-NO}_2)](\text{ClO}_4)$ (en = ethylenediamine),³⁰⁶⁻³¹² NENB $[\text{Ni}(\text{en})_2(\mu\text{-NO}_2)](\text{BF}_4)$,³¹³ NINO $[\text{Ni}(1,3\text{-propanediamine})_2(\mu\text{-NO}_2)](\text{ClO}_4)$,^{307, 314} NDMAZ $[\text{Ni}(\text{dmpn})_2(\mu\text{-N}_3)](\text{ClO}_4)$ (dmpn = 1,3-diamino-2,2-dimethylpropane),³¹⁵ or neutral MOF systems such as NiBO $[\text{Ni}(\mu\text{-4,4'-bpy})(\mu\text{-ox})]$ (ox^{2-} = oxalate) which we reported recently,^{56, 316} **NiBaO** $[\text{Ni}(\mu\text{-bpa})(\mu\text{-ox})]$ (bpa = 1,2-di(pyridin-4-yl)ethane),³¹⁷ and **NiBeO** $[\text{Ni}(\mu\text{-bpe})(\mu\text{-ox})]$ (bpe = 1,2-di(pyridin-4-yl)ethene).³¹⁷ In the case of cationic chains, there must be a non-coordinating anion such as ClO_4^- or BF_4^- in the structures. In the case of the neutral MOF systems with Ni^{2+} ions, oxalate²⁻ ligand is used in addition to a neutral bridging N-based ligand. The use of a neutral MOF to form the Haldane spin-1 chain allows for, e.g., exfoliation of sufficiently large crystals giving 2-D nanosheets that should exhibit their low-dimensional topological properties. There is also the ability to compare the effect of interchain-ligands on the energy gap and perturbation stability of otherwise similar chains.

Syntheses of **NiBaO** and **NiBeO** were reported by Garcia-Couceiro, Castillo, Luqu, and coworkers.³¹⁷ Results of DC magnetic magnetometry suggest that **NiBaO** and **NiBeO** are Haldane materials.³¹⁷ Herein, we report detailed studies of these two MOF-based Haldane spin-1 chains. **NiBaO**, **NiBeO**, and NiBO are similar in the $\text{Ni}^{2+}\text{-ox}^{2-}$ spin-chains but different in the interchain ligands, 4,4'-bipyridine for NiBO, 1,2-di(pyridin-4-yl)ethane (bpa) for **NiBaO**, and 1,2-di(pyridin-4-yl)ethene (bpe) for **NiBeO** (**Figure 4.3**). We are interested in **NiBaO** and **NiBeO** for the following: (a) Confirming that **NiBaO** and **NiBeO** are Haldane by advanced techniques; (b) Effects of bpa and bpe on inter-chain magnetic interactions. The bpa and bpe bidentate ligands are longer than 4,4'-bpy. Also, the two pyridine ligands in bpe are potentially

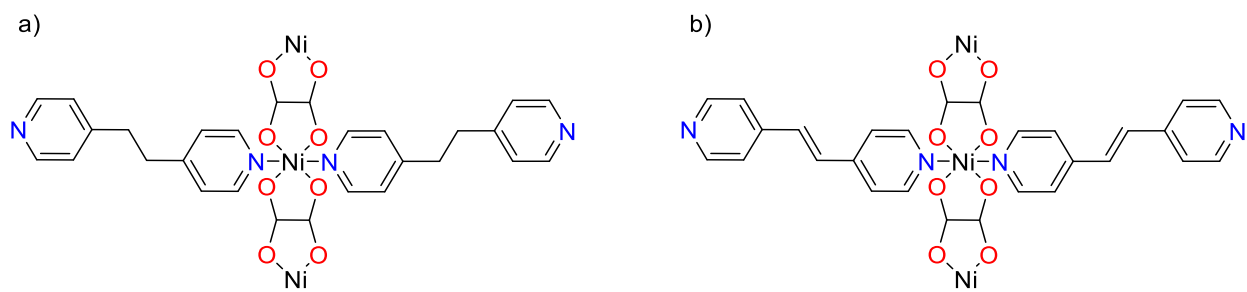


Figure 4.3. a) Simplified structure of **NiBaO** and b) **NiBeO**, showing a small portion of the polymeric 2-D MOF structure.

conjugated, while they are not in bpa. The $\text{Ni}^{2+}\text{-ox}^{2-}$ spin-1 chains are assumed to be essentially identical, with any differences in properties being derived from the difference in the bpa vs bpe ligand.

The increased conjugation of the bpe ligand may be expected to increase coupling between spin-1 chains, though the difference is expected to be small due to the large distance between the chains. **NiBaO** and **NiBeO** have been probed in the current work by a variety of techniques, including temperature-dependent powder neutron diffraction, DC magnetometry, high-field and -frequency electron spin resonance (HFESR), inelastic neutron scattering (INS), and specific-heat measurements. Temperature-dependent powder neutron diffraction results show no long-range antiferromagnetic ordering in **NiBaO** or **NiBeO** within the Haldane phase determined by magnetometry. DC magnetometry allows for antiferromagnetic phase determination, spin-gap fitting, and magnetic perturbation, showing that these materials are robust up to 7 T from the collapse of the Haldane phase. Similarly, specific heat measurements up to 14 T show no collapse of the Haldane phase. INS shows weak magnetic transitions that may be correlated to a spin gap, but further work is required to confirm the INS results.

4.3. Results and discussion

4.3.1 Synthesis

The synthesis of **NiBaO** and **NiBeO** were reported earlier,³¹⁷ and the conditions of the reactions were kept the same except changes discussed in the experimental section.

In attempts to decrease the incoherent scattering caused by H atoms in **NiBaO** and **NiBeO** and thus increase the S/N ratio in neutron scattering experiments, there were attempts to deuterate the interchain ligands bpa and bpe. The most effective method from our testing was based on base-mediated deuteration using $\text{DMSO-}d_6$ as the D source in a procedure inspired by

the work of Kopf et al.³¹⁸ Details of the reactions and other attempted deuteration reactions are given in the experimental section.

The deuteration of the interchain ligands proceeds from the deprotonation of the pyridine-based rings by the dimsyl anion, following a typical anionic pathway for H/D exchange as documented for several classes of compounds.³¹⁸⁻³²¹ It was expected from Kopf's work that there would be high levels of deuteration on the pyridine ring, specifically the ortho position, with a small amount of the alkyl- or alkene-chain deuteration. From mass spectrometry data, the base-mediated H/D exchange gave a dispersion from bpa-*d*₃ to bpa-*d*₈, and bpe-*d*₃ to bpe-*d*₆ as shown in **Figure A4.1** and **Figure A4.2**. The average deuteration of the ligands was approximately 50%. The use of ¹H NMR on both the deuterated ligand and a reference non-deuterated sample allows for comparison and determination of which sites are deuterated (**Figure A4.3**).

4.3.2. Variable-temperature powder neutron diffraction

Variable-temperature powder neutron diffraction was conducted at 1.8, 10, 20, 100, and 200 K for **NiBaO**. For **NiBeO** data was collected at 10, 20, 50, 75, 100, 150, and 200 K. Variable-temperature powder neutron diffraction was chosen to study these compounds to examine potential phase transitions that might lead to long-range magnetic ordering. As discussed earlier, if the spin-1 chain is in the Haldane phase there should be no long-range magnetic ordering leading to new magnetic Bragg reflections at low temperatures. Instead, there should only be peaks associated with nuclear diffraction from the crystal unit cell. As shown in **Figure 4.4** and **Figure 4.5**, there were no new peaks in the Variable-temperature powder neutron diffraction for either **NiBaO** or **NiBeO** associated with new magnetic Bragg reflections, thus showing that there is no long-range antiferromagnetic ordering. Combining this

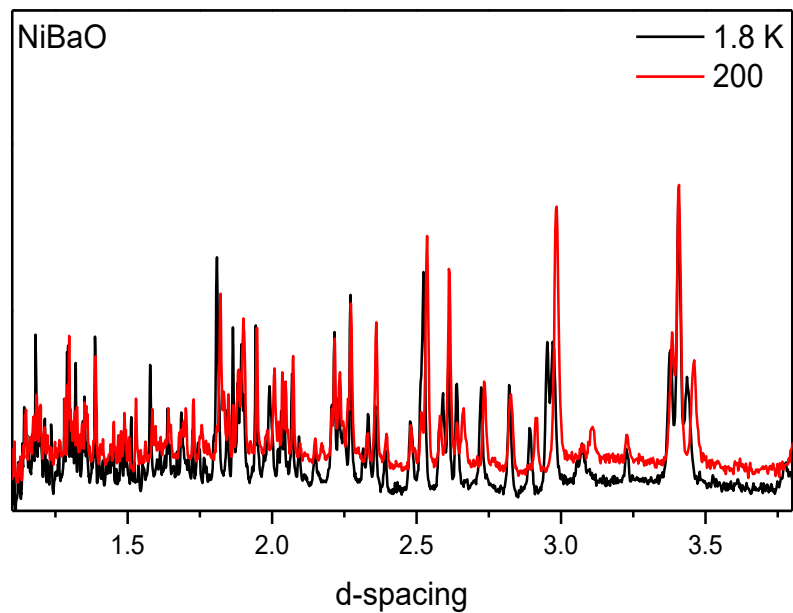


Figure 4.4. Patterns of powder neutron diffraction for **NiBaO** at 1.8 and 200 K.

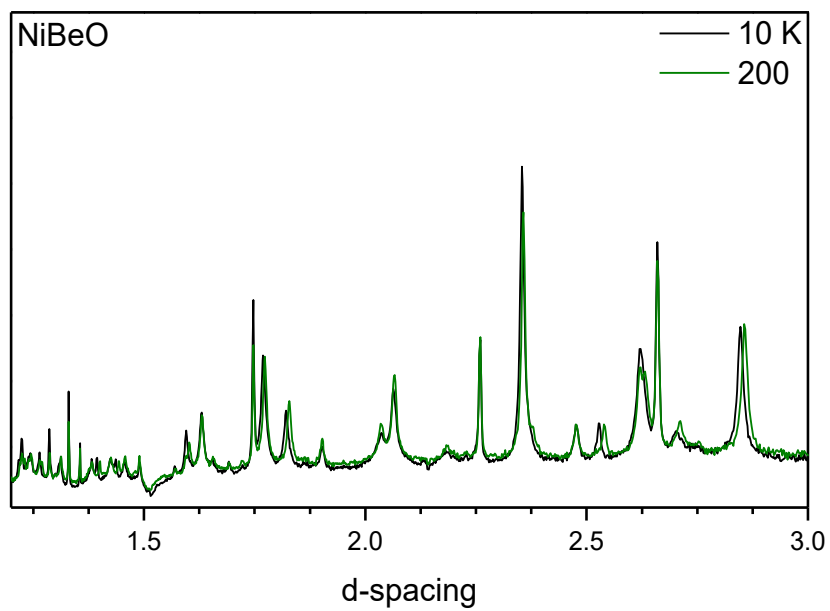


Figure 4.5. Patterns of powder neutron diffraction for **NiBeO** at 10 and 200 K.

result with DC magnetometry, showing antiferromagnetic ordering in **NiBaO** and **NiBeO**, the antiferromagnetic order in both **NiBaO** and **NiBeO** is consistent with that of a Haldane phase.

4.3.3. DC magnetic susceptibility

Figure 4.6 and **Figure 4.7** show temperature dependence of the DC magnetic susceptibility of **NiBaO** and **NiBeO**, respectively, using a powder sample at 0.1 T applied magnetic field. Lowering the temperature from 300 K to 1.8 K shows a broad maximum near 50 K for both samples and a sharp decrease afterward toward zero magnetic susceptibility around 5 K, after which there is a plateauing in the case of **NiBaO** and a sharp uptick in the case of **NiBeO**. This can be observed in the inset spectra of the low temperature data for **NiBeO** in **Figure 4.7**, where after 4 K there is a sharp increase in magnetic susceptibility, which would be indicative of a phase change from the quantumly entangled Haldane phase to a ferrimagnetic or ferromagnetic phase. The broad maxima, or Neel point, is indicative of short-range interchain correlations or suppression of long-range ordering due to weak interchain coupling. This is typical of Haldane materials as there is a slow thermal crossover from a quantum disordered Haldane phase to a classical paramagnetic material due to the breakdown of the topological protection to perturbation.^{322, 323}

The high temperature data can be fitted to the Curie-Weiss law:

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

Giving Curie-Weiss temperatures of -130 K and -207 K for **NiBaO** and **NiBeO**, respectively, indicating net antiferromagnetic interactions in the high temperature region. From fitting to the Curie-Weiss equation we can also determine the Curie constants, which are 1.72 and 1.94 $\text{cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for **NiBaO** and **NiBeO**, respectively, as shown in **Figure 4.8**.

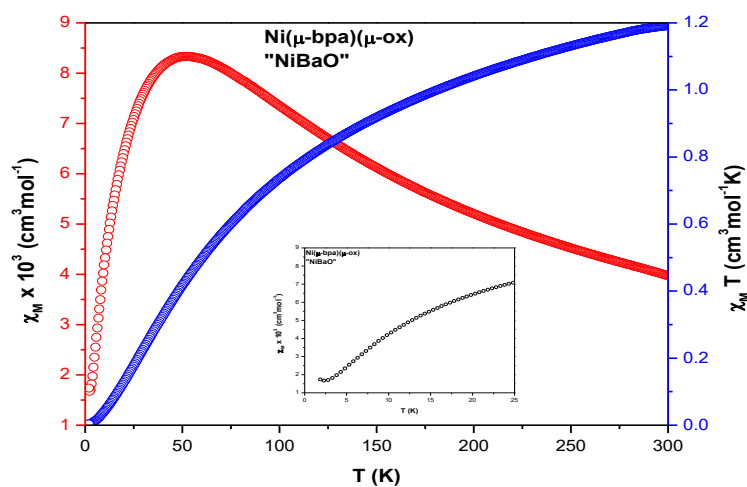


Figure 4.6. DC magnetic susceptibility of **NiBaO** showing χ vs T (red) and χT vs T (blue) plots at 1.8–300 K. The inserted figure is a focus on the low temperature region (1.8–25 K) of the χ vs T plot.

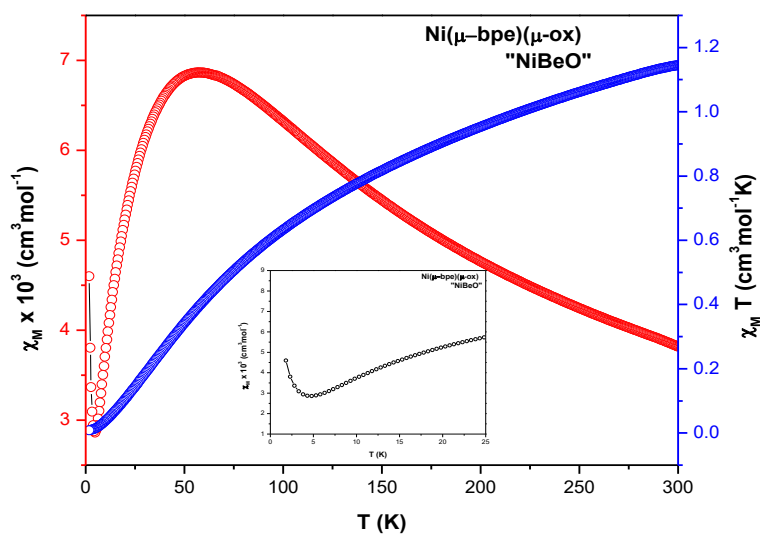


Figure 4.7. DC magnetic susceptibility of **NiBeO** showing χ vs T (red) and χT vs T (blue) plots at 0.8–300 K. The inserted figure is a focus on the low temperature region (1.8–25 K) of the χ vs T plot.

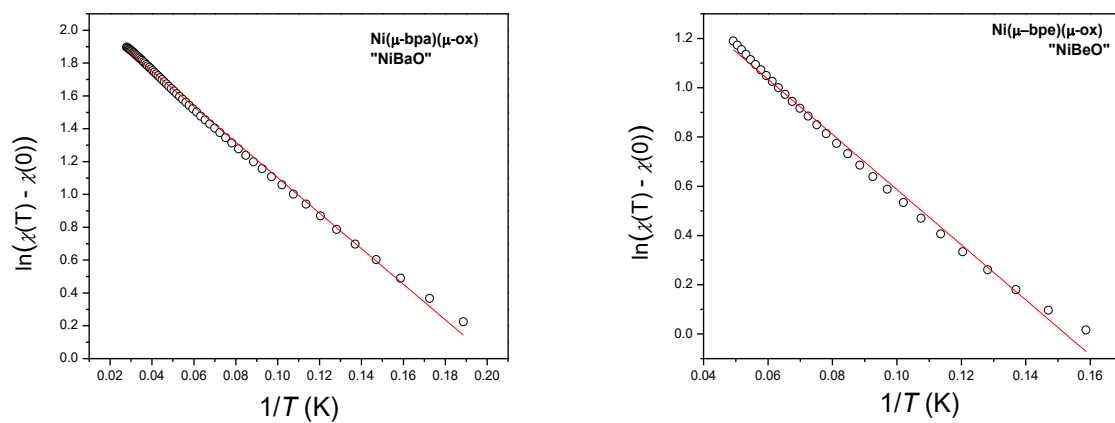


Figure 4.8. a) Plot of $\ln[\chi(T) - \chi(0)]$ vs $1/T$ for data between 20 K and 4 K for **NiBaO** and b) **NiBeO**. The red line shows the fit used for extracting the spin gap.

The Curie constant can then be used to extract the effective magnetic moment for Ni^{2+} ions in the spin chains, giving μ_{eff} values of 3.70 and 3.94 μ_{B} for **NiBaO** and **NiBeO**, respectively. These values are higher than the spin-only magnetic moment of 2.83 μ_{B} . The results show that there are contributions to μ_{eff} from spin-orbit coupling or zero-field splitting, which would be expected in an octahedral Ni^{2+} system such as **NiBaO** and **NiBeO**.

The decrease in DC magnetic susceptibility at low temperature is indicative of antiferromagnetic coupling and of a magnetic excitation gap as seen in other spin-1 chain systems. Spin gap data fitting of the low-temperature DC magnetic susceptibility using the Eq. 4.2 gives a value of $E_g = 7.5$ and 7.8 cm^{-1} for **NiBaO** and **NiBeO**, respectively.

$$\chi(T) = \chi(0) + C e^{\frac{-E_g}{k_B T}} \quad (\text{Eq. 4.2})$$

where E_g is the spin gap and $\chi(0)$ is an offset to account for low temperature diamagnetic interactions.

Collecting magnetization isotherms for the low temperature region allows us to probe the stability of the gapped magnetic phase, which is expected to be somewhat stable to external perturbation (**Figures 4.9** and **4.10**). If there is a sharp change in the characteristics of the magnetic isotherm, the change should indicate a critical field has been reached, closing the Haldane gap and allowing the triplet excited state to populate. There is also the ability to see thermal excitation population differences within the material, giving different magnetic moments for each temperature shown.

For **NiBeO**, isotherms at 1.8-3.7 K show features, at low fields, more like a ferro- or ferri-magnetic material. Then, at higher fields, the isotherms show features that are expected of a

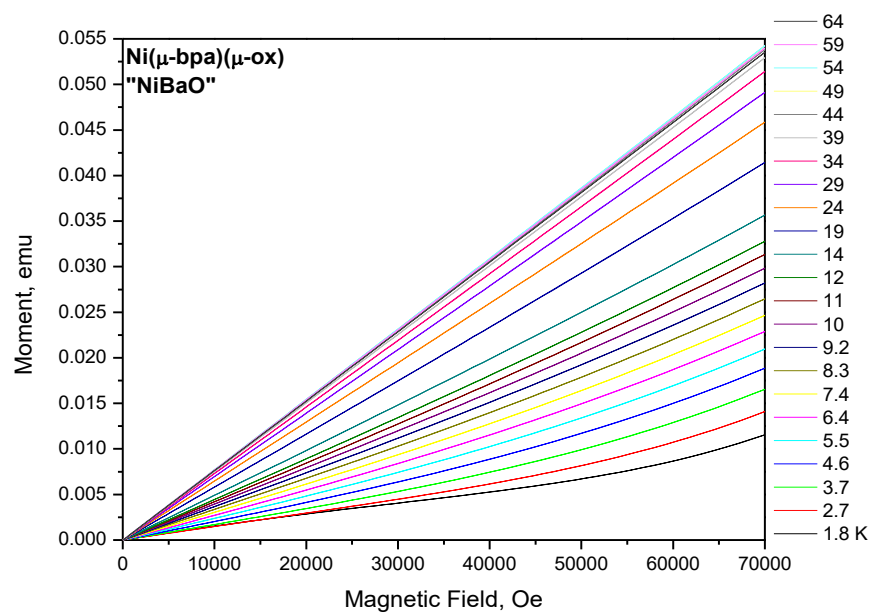


Figure 4.9. Magnetic isotherm of **NiBaO**.

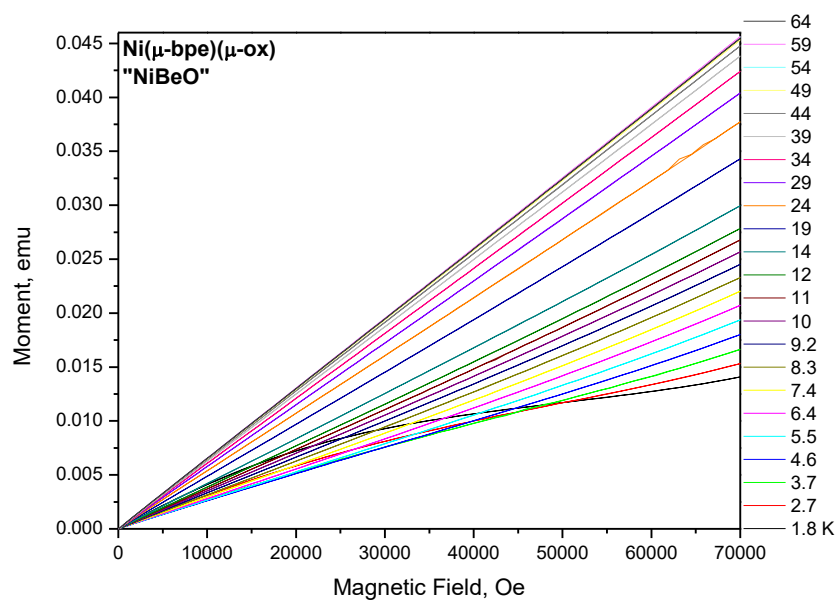


Figure 4.10. Magnetic isotherm of **NiBeO**.

Haldane phase, as shown in **Figure 4.10**. These changes are consistent with a field induced collapse of one magnetic phase into another, such as one might expect from a ferrimagnetic phase to the quantum order of a Haldane phase within this material. This phase difference at low temperatures is also observable in the DC susceptibility plot insert, with an uptick below 4 K that corresponds to a different magnetic ordering than the expected Haldane phase.

To further probe the stability of the Haldane phase, we measured specific heat up to 14 T. Neither **NiBaO** nor **NiBeO** showed the collapse of the Haldane phase with scans from 5 to 15 K (**Figure A4.10** and **Figure A4.11**). This is significantly different from previous results of the similar Haldane material NiBO, showing a pronounced phase change around 9 T.⁵⁶ This comparison to NiBO shows that, although NiBaO, NiBeO, and NiBO are all spin-1 chains, there is less interchain coupling leading to non-Haldane magnetic ordering NiBaO and NiBeO

4.3.4. High-field electron spin resonance

HFESR measurements were performed on powder samples of **NiBaO** and **NiBeO** (118 and 113 mg, respectively) at 4.5 K to probe transitions within the triplet excited state. The samples produce virtually identical spectra, showing two resonances, labeled as A and B in **Figure 4.11**. Resonance A is partly obscured by an oxygen signal but is real and can be followed over a range of frequencies, showing a linear correlation with frequency and with a *g*-factor of about 2.3. Its frequency dependence suggests that it is an equivalent of a “double quantum transition”³²⁴ in paramagnetic complexes of Ni(II) and as such is probably of little or no interest. Resonance B, however, shows a different dependence and indicates a finite energy gap at zero field, on the order of 180 GHz = 6 cm⁻¹. This estimate was made with an assumption that the frequency dependence is linear, which does not have to be the case. In fact, spectra recorded in the 235–275 GHz range (**Figure 4.12**) do not show Resonance B which could mean two things:

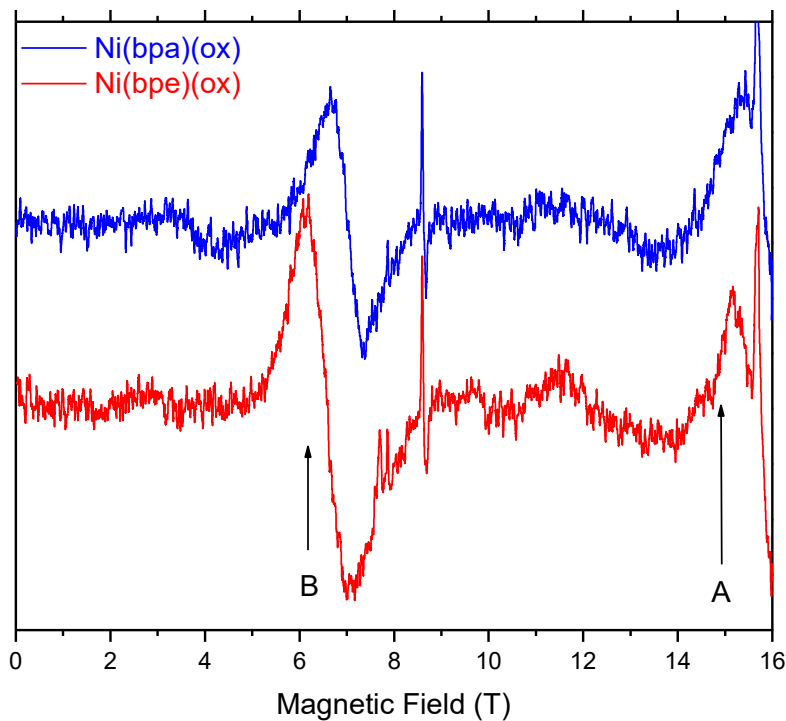


Figure 4.11. HFESR spectrum of **NiBaO** and **NiBeO** at 4.5 K and 498 GHz. Letters A and B indicate resonances originating from the sample. The narrow signals at 8.6 and 15.9 T come from molecular dioxygen.

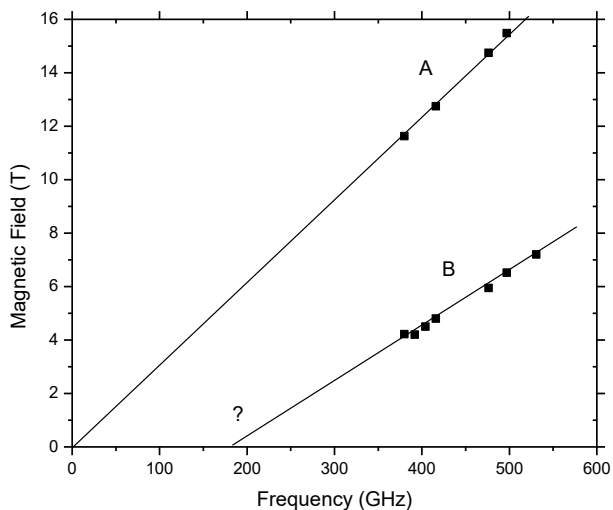


Figure 4.12. A field vs. frequency dependence of HFESR resonances of **NiBeO** at 4.5 K. Letters A and B indicate resonances originating from the sample shown in **Figure 4.11**.

(a) the frequency dependence is not linear, and branch B goes to zero field at frequency higher than 275 GHz, which would mean that the gap is larger than 9 cm^{-1} , or (b) the resonance gets broadened at low frequencies beyond recognition.

4.3.5. Inelastic neutron scattering

INS was completed at VISION to study the spin gaps in **NiBaO** and **NiBeO**. The measurements were conducted from 5-40 K (**NiBaO**) or 5-100 K (**NiBeO**) to examine the magnetic excitations from the ground state to triplet excited state, shown in **Figures 4.13** and **4.14**. The data collected was Bose-Einstein corrected to reduce phonon characteristics, giving temperature dependent magnetic peaks within the spectrum. The data collected did not give sufficient differences in temperature spectra to define magnetic transitions from the ground to excited states within the spectra.

4.3.6. Phonon characteristics from INS and far-IR magneto-spectroscopy (FIRMS)

The phonons described in these studies are both inter- and intra-molecular vibrations. Phonons from INS are based on the kinetic energy transfer by neutrons to the sample which removes symmetry-based selection rules required for optical spectroscopies such as IR or Raman. **Figure 4.15** gives the INS spectra of **NiBaO** and **NiBeO**, showing major phonon features below 1700 cm^{-1} with another distinct feature around 3200 cm^{-1} . We also attempted to study the phonon features and magnetic transitions of these 2-D MOFs using far-IR magneto-spectroscopy (FIRMS), but it was ineffective in elucidating any magnetic transitions (**Figure A4.12**). FIRMS has not successfully shown magnetic excitations of Haldane materials, possibly due to the low energy of such magnetic transitions or that they may not be the correct symmetry to view in IR spectroscopies.

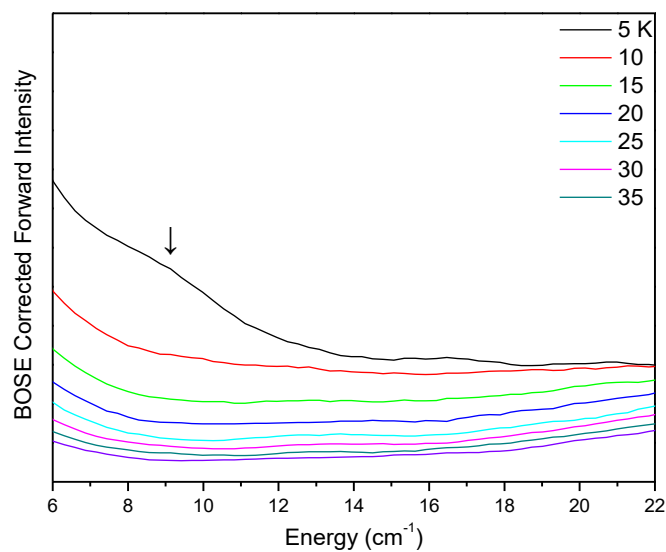


Figure 4.13. INS data for **NiBaO** collected at 5, 10, 15, 20, 25, 30, and 35 K. There is a minor peak that may be related to magnetic transitions at 9 cm⁻¹.

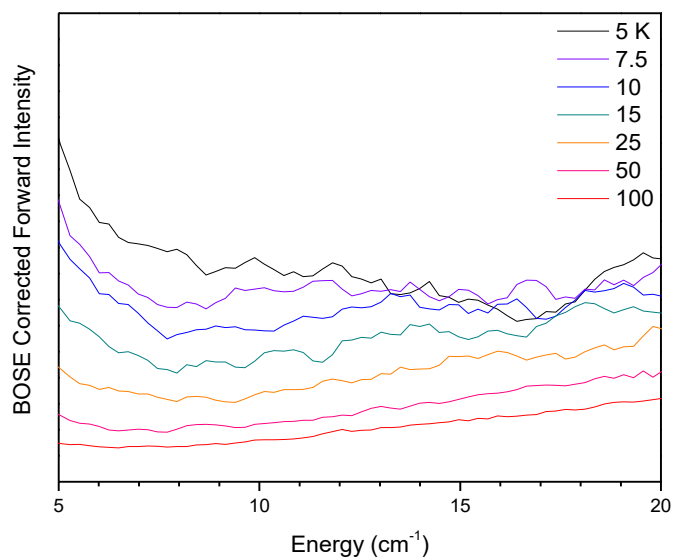


Figure 4.14. INS Data for **NiBeO** collected at 5, 7.5, 10, 15, 25, 50, and 100 K. There are no peaks strong enough to claim they are related to magnetic transitions.

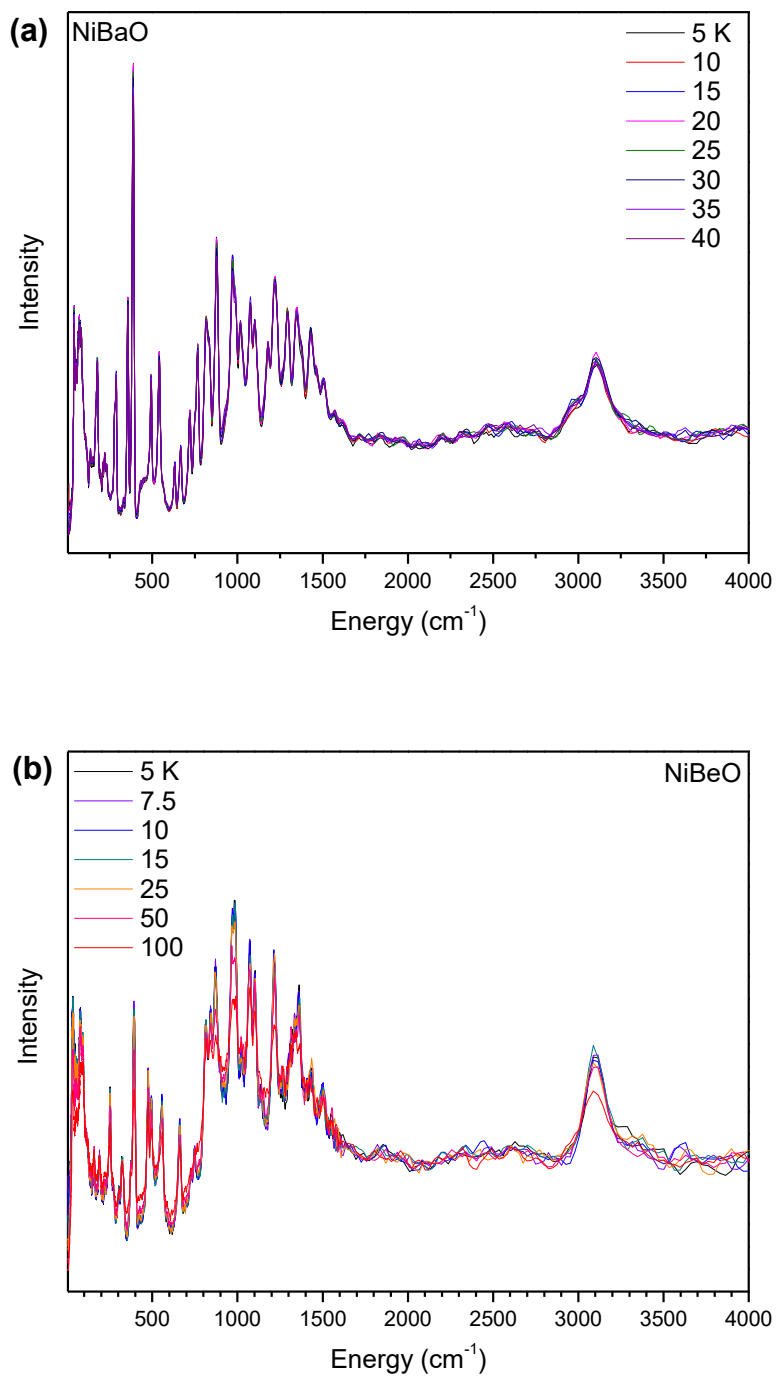


Figure 4.15. Bose-corrected INS spectra for a) **NiBaO** and b) **NiBeO**. Average of the forward- and back-scattering data are used here. The main phonon features are observed below 1700 cm^{-1} , except for a strong peak at $\sim 3200 \text{ cm}^{-1}$.

4.4. Conclusions

Herein we have provided characterization and analysis of two 2D-MOFs showing Haldane spin-1 chain character. From a combined analysis of variable-temperature powder neutron diffraction, DC magnetometry, and HFESR we have characterized the magnetism of these MOFs. INS and far-IR spectroscopy have been used to characterize the low energy phonons of these compounds. We have shown that the Haldane phases of these compounds are stable to perturbation up to 14 T.

4.5. Experimental section

4.5.1. Synthesis

NiBaO was prepared by hydrothermal reactions of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (1.0 mmol), $\text{H}_2\text{ox} \cdot 2\text{H}_2\text{O}$ (1.0 mmol), and bpa (1.0 mmol) in 7 mL of water in a 1:1:1 molar ratio. Reactions were completed in a 23-mL digestion bomb for 144 h at 170 °C. The product was washed with cold water and diethyl ether and dried in air, giving a blue polycrystalline or powder product.

NiBeO was prepared by hydrothermal reactions of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (1.0 mmol), $\text{H}_2\text{ox} \cdot 2\text{H}_2\text{O}$ (1.0 mmol), and bpe (1.5 mmol) in 7 mL of water in a 2:2:3 molar ratio. Reactions were completed in a 23-mL digestion bomb for 144 h at 170 °C. The product was washed with cold water and diethyl ether and dried in air, giving a blue-grey polycrystalline or powder.

In attempts to grow crystals for these compounds suitable for single-crystal X-ray diffraction (SCXRD) multiple variations were made to the synthetic parameters, as discussed in the addenda for Chapter 4. The only modifications that give acceptable crystals used a 4:3 water/ethanol solvent mix, with the same heating and slow cooling as typically used. Although crystals from this procedure did diffract in SCXRD, their quality was still not high enough to give a publishable structure.

Deuteration of ligands was completed using a method inspired by the work of Kopf et al.³¹⁸ Here, the protio ligand of choice (bpa or bpe, 0.5 mmol, 92 mg) was loaded into a Schlenk flask with KO^t-Bu (0.5 mmol) and a stir bar which was then evacuated and refilled with N₂, which was repeated 3 times. To the flask was then added DMSO-*d*₆ (17 eq., 600 μL) and deionized water (1.1 eq., 10 μL) under a slow nitrogen purge. The flask was then sealed and heated to 120 °C for 16 h with gentle stirring. The resulting thick brown mixture was then diluted with dichloromethane (DCM, 10 mL), washed with a saturated sodium chloride brine (20 mL), and extracted with DCM (2 × 20 mL). The organic layers were dried over sodium sulfate for 12 hours and then concentrated. The resulting product was dissolved in acetonitrile and passed through a silica plug. After removing the excess solvent, the dried ligand was recovered (~70% recovery). This process was also completed at a double scale, with identical results. Using MS and ¹H NMR it was determined that about 50% deuteration was achieved, as shown in Chapter 4 addenda. When sequential reactions were attempted to further deuteration, the compound seemed to decompose and there was a complete loss of product.

Other H/D exchange reactions were conducted, including the use of Pd/C in D₂O and the use of WCl₆ with C₆D₆ based on the literature methods.³²⁵⁻³²⁷ These trials were not as successful as the use of base-mediated methods and were therefore not used. Further discussion of these trials is given in Section A4.1.2 in the addenda for Chapter 4.

4.5.2. Magnetometry

DC magnetic susceptibility measurements at 0.1 T were conducted at the Center for Nanophase Materials Sciences (CNMS), Oak Ridge National Laboratory (ORNL) using the superconducting quantum interference device (SQUID) magnetometer by Quantum Design.

Variable-temperature and variable-field DC magnetic susceptibility measurements were also collected.

Specific heat data was collected on a PPMS-SQUID magnetometer made by Quantum Design at the SmartState Center for Experimental Nanoscale Physics, University of South Carolina. Data was collected at 0 T and 14 T and showed essentially no difference besides what would be expected from magnetic field effects.

4.5.3. Inelastic neutron scattering

VT-INS data were collected by placing a powder sample (approximately 0.5 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.

4.5.4. Powder neutron diffraction

Neutron diffraction data were collected at the POWGEN diffractometer, Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL) between 1.8 K and 200 K using an Orange Cryostat (for **NiBaO**) or 10 K and 200 K and the standard sample environment (for **NiBeO**). A powder sample 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.

4.5.6. High-frequency electron spin resonance

HFESR experiments were performed at the National High Magnetic Field Laboratory using a bespoke ESR spectrometer with a 17 T superconducting magnet that has been described previously.²⁰⁴

Chapter 5: Solvatochromism of cupric chloride and its conversion to copper oxide

This chapter is based on the following paper:

Michael J. Jenkins, Miranda A. Phillips, Zi-Ling Xue, Solvatochromism of Cupric Chloride and Its Conversion to Copper Oxide. *J. Chem. Educ.* **2023**, *100*, 12, 4772–4779.

<https://doi.org/10.1021/acs.jchemed.3c00493>

M. J. Jenkins and M. Phillips conducted the synthesis and characterization of CuO. Jenkins conducted the UV-vis, IR and X-ray studies. Jenkins and Z.-L. Xue wrote the manuscript.

5.1. Abstract

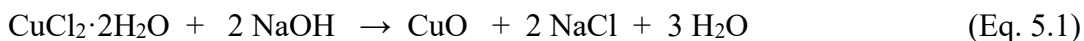
This experiment demonstrates that copper(II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) in different solvents (acetone, isopropyl alcohol or water) displays divergent colors and visible-near IR spectra. Both the reactions of these solutions with two equiv. of sodium hydroxide (NaOH) and the direct solid-state reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with 2NaOH using a mortar and pestle give copper(II) oxide (CuO). Undergraduate students learn the following: (1) *d-d* electronic transitions in a transition metal complex; (2) Effects of solvent polarity changes on the electronic ground and excited state of Cu^{2+} ions as well as color differences; (3) Direct solid-state reaction as a green synthetic method; (4) Gradual formation of CuO from solution reactions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with 2 equiv. of NaOH; (5) Characterization of chemical compounds in solutions by visible-near IR spectroscopy and solid products by IR and powder X-ray diffraction (PXRD). This experiment is suitable as a junior-level inorganic chemistry experiment.

5.2. Introduction

Solvent is often important in a chemical reaction and properties of solvents, such as polarity, acidity-basicity, and the ability to hydrogen-bond, can impact the reaction process including reaction kinetics. The choice of solvent can also impact the color and absorption spectrum of a solution. Solvatochromism refers to the phenomenon when the color of a solution changes based on the polarity of the solvent that the solute is dissolved in.^{328, 329} These changes in solvent polarity lead to a difference in the electronic ground and excited state of the solute and thus, the energy gap between them changes. As a result, the absorption spectrum of the solute changes in position, intensity, and band shape, most frequently viewed as an energy shift in the local maximum of the absorbance. In the visible spectrum, solvatochromism is observed as color change. When a metal complex is dissolved in different solvents, coordination of the solvents as ligands to the metal ion may yield different complexes with various colors. Thus, the color differences among solutions of a metal complex in different solvents may not fit the definition of solvatochromism originally developed for organic compounds.^{328, 329} However, the colors of the solutions are a result of dissolving a compound in different solvents. In the current work, solvatochromism is used broadly referring to the case of a metal complex dissolved in different solvents.

Certain reactions may be carried out in the solid state without the use of a solvent. Such reactions may be classified as mechanochemistry.³³⁰ In some cases, the reaction products are unique, *i.e.*, different from those obtained from solution reactions.^{330, 331} For example, Xin and coworkers have demonstrated that solid–solid reactions between 4-methylbenzenamine and $MCl_2 \cdot nH_2O$ ($M = Cu^{2+}$, $n = 2$; Co^{2+} or Ni^{2+} , $n = 6$) yield $M(NH_2C_6H_4Me)_2Cl_2$, while these reactions attempted in solution yield no product.³³¹

The current experiment is designed to provide students an opportunity to observe the solvatochromic properties of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in water, acetone, and isopropyl alcohol, by measuring the visible spectra of the solutions. In addition, students will conduct the reaction in Eq. 5.1 in three different solvents as well as in the solid state, allowing them to test principles of green chemistry. Green chemistry has been a highly active research area in recent years.³³²⁻³³⁶ This relatively new chemistry area deals with the design of chemical products and processes that reduce or eliminate the generation of hazardous substances.³³² “Less Hazardous Chemical Syntheses” and “Safer Solvents and Auxiliaries” are two principles of green chemistry that can be explored in this experiment.³³³ After the reactions are completed, students will use IR and PXRD spectra to characterize the products and determine if the synthesis of CuO is successful.



5.2.1. Learning objectives

- (1) Observe how solvents affect absorption spectra of the dissolved $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ complex;
- (2) Study how solvents impact the reactions in solutions, including the gradual formation of CuO ;
- (3) Conduct the reaction in the solid state and compare it with those in solutions.

Submitted reports by the students were used to determine if the goals of the experiment were successful.

5.2.2. Hazards

All experimental procedures should be carried out in fume hoods. Students should wear gloves and safety goggles at all times during the experiment. Copper(II) chloride dihydrate is harmful if swallowed. It causes eye, skin, and respiratory tract irritation. Target organs include respiratory system, eyes, and skin. Copper(II) chloride dihydrate is also toxic to aquatic

organisms, and it may cause long-term adverse effects in the aquatic environment. Sodium hydroxide is corrosive. It can cause severe burns to the skin. Acetone and isopropyl alcohol are flammable solvents. Students should be reminded to keep these solvents away from flames. Acetone causes irritation once in contact with skin and eyes. Isopropyl alcohol causes serious eye irritation. Breathing vapors of both organic compounds cause drowsiness or dizziness. For specific safety instructions, please refer to the students' handouts and Safety Data Sheets (SDSs) available for free from chemical companies.

5.3. Experimental section

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Analytical reagent, Mallinckrodt), acetone ($\text{Me}_2\text{C}=\text{O}$, Certified ACS, Fisher Scientific), isopropanol (*i*-PrOH, Certified ACS, Fisher Scientific), and NaOH (Certified ACS, Fisher Scientific) were used as received. Deionized water was prepared in house and used for the experiments below.

IR spectra were obtained on a Bruker Alpha II Compact FT-IR Spectrometer in the ATR (attenuated total reflectance) mode. UV-visible-near IR spectra were recorded on an Agilent 8453 UV-visible spectroscopy system or an Agilent Cary 100 UV-visible spectrophotometer. Powder X-ray diffraction (PXRD) was conducted on a Panalytical Empyrean diffractometer with a $\text{Cu } K_\alpha$ source.

5.3.1. UV-visible spectroscopic characterization of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in acetone, isopropanol, and water

Three samples of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (170 mg, 1.00 mmol) were each added to three vials along with 10 mL of acetone, isopropanol, and water, respectively. Spectra were taken for each solution at 380-900 nm as well as 300-1100 nm. A serial dilution using volumetric glassware was required to obtain a spectrum within the optimum absorbance range of the instruments, with

concentrations of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ at 0.020 M, 0.002 M, and 0.0015 M in solutions of water, isopropanol, and acetone, respectively, showing the best spectra.

5.3.2. Formation of CuO in acetone, isopropanol, and water and from the solid-state reaction

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (170 mg, 1.0 mmol) was dissolved in three vials containing 10 mL of acetone, isopropanol, and deionized water, respectively. NaOH pellets (80 mg, 2.0 mmol) were ground in a mortar and pestle, and then added to each solution. These solutions were kept stirring for 2 days. Supernatants were removed by filtration and the products were washed with their respective solvents and then washed with 15 mL of water. Products were further dried using a heat gun at 100(10) °C, leaving dark brown or black powders of CuO. Yield was determined to be 86.4%, 90.1%, and 89.1% for the reactions done in acetone, isopropanol and water reactions respectively.

For the solid-state reaction, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (340 mg, 2.0 mmol) and NaOH (160 mg, 4.0 mmol) were added to a clean and dry mortar and pestle. The solid mixture was ground together until a color change to brown or black was observed. The color change typically occurs within a few minutes. The black powder product was then dried with a heat gun. After collection, washing with water to remove NaCl, and re-drying, the yield of the isolated product 52.2%. There were solids left on both mortar and pestle that could not be removed by spatula, likely reducing the yield.

The four solid products from the reactions were characterized by IR spectra at 400-4000 cm^{-1} . In addition, the products were characterized by powder X-ray diffraction in the 2θ range of 5-70 degree (°) to confirm that they were CuO.

The use of an oven or a hot plate at about 100 °C instead of the use of a heat gun to dry the products has been shown to yield similar results.

5.4. Results and discussion

5.4.1. Visible spectra of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in different solvents

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in water, isopropanol, and acetone gives solutions visibly blue, green, and yellow-green, respectively, as shown in **Figure 5.1**. Boéré has recently published the single-crystal structure of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.³³⁷

Visible spectra of each solution in the range of 380-750 nm^{338, 339} were obtained (**Figure 5.2a**).

For the visible spectra of all three solutions, there is a broad absorption peak >780 nm in the near-IR range, as shown in **Figure 5.2b**. These absorptions have maximums at 815 nm, 855 nm, and 927 nm for the water, isopropanol, and acetone solutions, respectively. The near-IR peaks extend into the right side of the visible spectra. For the water solution in **Figure 5.2a** the extended near-IR peak leads to the absorption in red wavelengths. According to the color circle/wheel,³⁴⁰⁻³⁴² absorption in one color leads to the observation of the complementary color.

Thus, the absorption in red wavelengths gives the solution blue color, as seen in **Figure 5.1a**. For the isopropanol solution, there is a strong UV absorption at 346 nm extending to the left side of the visible spectrum (**Figure 5.2a**). The extension of this UV peak leads to the absorption of the violet-blue wavelengths of the solution. Using the color circle/wheel^{340, 341} or more simply the RGB (red, green and blue) model,³⁴³ absorptions of both red and blue colors for the isopropanol solution leaves green color to the solution, which is observed (**Figure 5.1b**). For the acetone solution, there are absorptions of both red (from the extension of the near-IR peak at 927 nm) and purple-blue color wavelengths (from the extension of the UV peak at 347 nm) as the isopropanol solution. In addition, there is a peak at 472 nm extending to about 550 nm in the blue-green range, making the isopropanol solution much darker (**Figure 5.1c**).

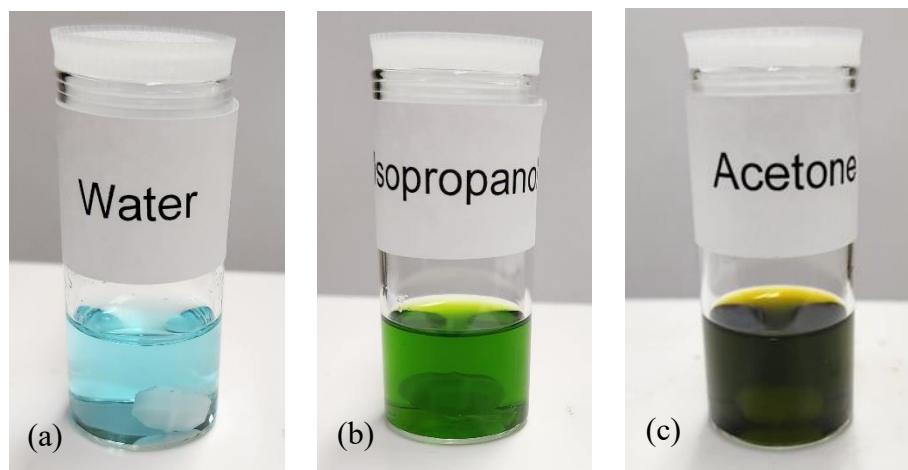


Figure 5.1. Solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in three different solvents: (a) Water; (b) Isopropanol; (c) Acetone.

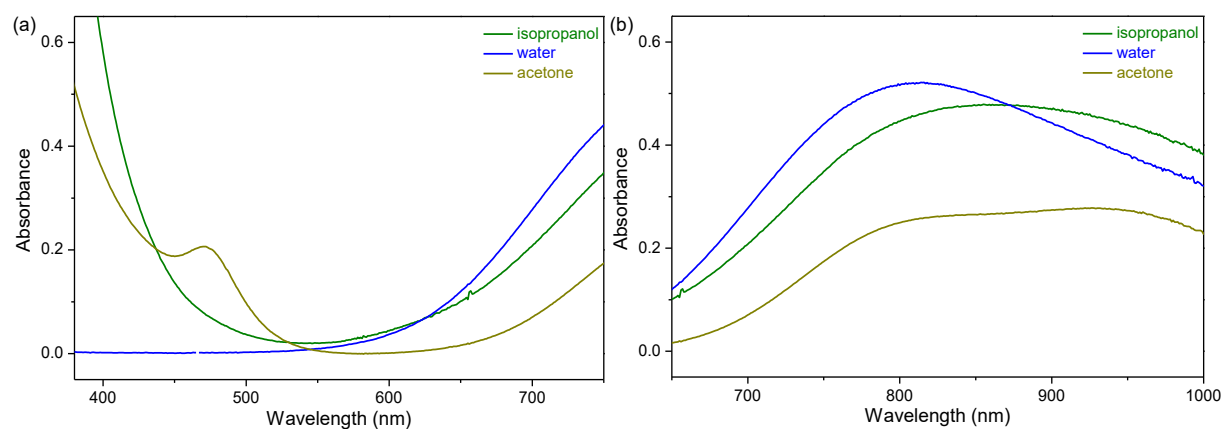


Figure 5.2. (a) Visible spectra of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in acetone, isopropanol, and water at 380-750 nm; (b) Spectra at 650-1000 nm focusing on the low energy visible and near-IR range. Pure solvents were used as references for the spectra. Full spectra at 300-1100 nm are given in **Figure A5.3**.

The near-IR peaks of the copper chloride solutions in the three solutions (**Figure 5.2b**) show the solvatochromic effect,^{339, 344} as shown in **Figure 5.3** and **Table A5.4**. In acetone, the least polar of the three solvents, the near-IR peak is at 927 nm, the longest wavelength (and lowest energy) of the three absorption peaks. In water, the most polar of the three solvents, the near-IR peak is at 815 nm, the shortest wavelength (and highest energy) of the three absorption peaks. In isopropanol with polarity between acetone and water, its near-IR peak is 855 nm between those of acetone and water.

This solvatochromic property matches that described as negative solvatochromism,^{328, 329} when the transition energy increases as the solvent polarity increases, as shown in **Figure 5.4**.³⁴⁵ For the solute molecule with a dipole moment, the increase in solvent polarity leads to a larger dipole moment in the ground state than that in the excited state of the solute molecule.

It should be pointed out that $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in isopropanol and acetone may lead to the coordination of the organic molecules as ligands to Cu^{2+} ions, affording in essence different complexes than $\text{Cu}(\text{H}_2\text{O})_n^{2+}$ ($n = 4, 5, 6$), the Cu^{2+} complex in water.³⁴⁶⁻³⁵⁵ In fact, the spectrum in acetone (**Figure 5.2**) show a peak at 472 nm. The nature of this transition is not clear but it is likely from the interaction of acetone with, or its binding to, the Cu^{2+} ion.³⁵⁵⁻³⁵⁸ Thus, strictly speaking, the color differences among solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in water, isopropanol, and acetone discussed here may not fit the definition of solvatochromism originally developed for organic compounds dissolved in solvents with different polarities.^{328, 329} However, broadly speaking, the colors of the three solutions in **Figure 5.1** and spectra in **Figure 5.2** are a result of dissolving the compound $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in different solvents. Another note is that, even for the Cu^{2+} -water complex, $\text{Cu}(\text{H}_2\text{O})_n^{2+}$, its aqueous structure, including the number of water ligands, n , is the subject of earlier^{355, 359} and recent experimental and theoretical studies.^{346-354, 359} Thus,

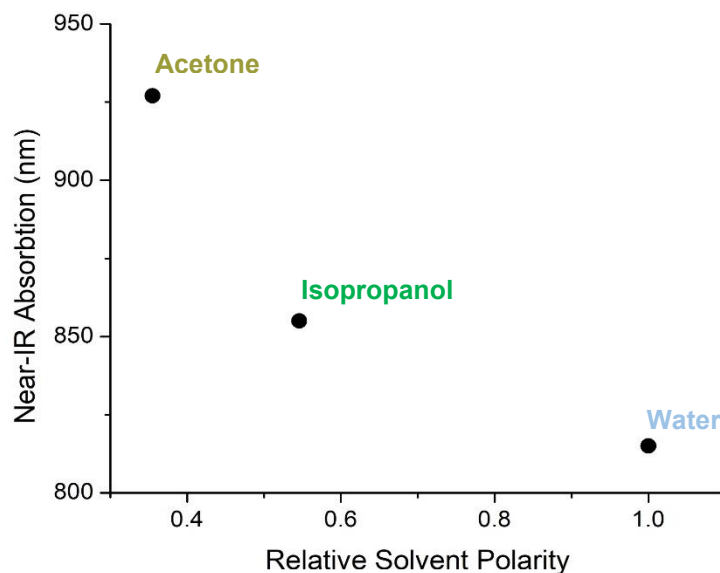


Figure 5.3. Plot of near-IR peaks in water, isopropanol, and acetone vs. relative solvent polarities. The relative polarities are normalized from measurements of the transition energy at 25 °C of the long-wavelength visible absorption of a standard pyridinium N-phenolate betaine dye in Ref. 344.

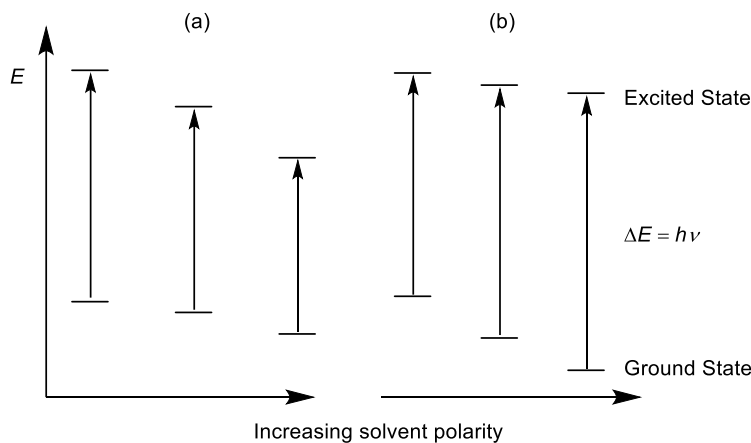


Figure 5.4. Representation of solvent effects of polar solutes in polar solvents.^{329, 345} (a) Positive solvatochromism (bathochromic or red shift): Absorption energy decreases, or moves to longer wavelengths, as the solvent polarity increases. (b) Negative solvatochromism (hypsochromic or blue shift): Absorption energy increases, or moves to shorter wavelengths, as the solvent polarity increases. This figure is adapted with permission from Refs. 329, 345. Copyright 1988 John Wiley and Sons.

there are research opportunities to study the Cu^{2+} complexes in different solvents, including water, isopropanol, and acetone. For the current work, the discussions are limited to those at the undergraduate level, including solvatochromism that may include the same metal complex dissolved in different solvents.

In an octahedral transition metal complex with six ligands, five d orbitals of the metal ions are split into t_{2g} and e_g levels (**Figure 5.5**). For d^9 complexes such as $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, the nine electrons leave one hole in the d orbitals. For $d_{x^2-y^2}$ and d_{z^2} orbitals in the e_g level, one orbital contains two electrons and the other has just one electron. In order to lower the energy, $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ undergoes the so-called Jahn-Teller distortion. The two H_2O ligands along the z axis are elongated, making the Cu-O bond lengths in the z direction longer than those in the x,y plane, as observed in the crystal structures of $[\text{Cu}(\text{H}_2\text{O})_6]\text{SiF}_6$ and $[\text{Cu}(\text{H}_2\text{O})_6](\text{BrO}_3)_2$.^{346, 349} One orbital in the e_g level, d_{z^2} with two electrons in the case of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, is lower in energy than $d_{x^2-y^2}$ with one electron. Electrons in the filled orbitals d_{z^2} , d_{xz} , d_{yz} or d_{xy} in **Figure 5.5** may be excited to the partially filled $d_{x^2-y^2}$, giving spectra in the UV, visible or near-IR range.³⁵⁸

5.4.2. Formation and characterization of CuO from solution and solid-state reactions

The synthesis of CuO from the reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with 2 equiv of NaOH in water, isopropanol, and acetone was completed within 72 hours. The reaction in the acetone solution finished the most quickly, with no further changes in color after 4 hours. The reaction in the isopropanol solution finished in around 8 hours with no further changes in color or increase in the amount of the product. Photos of the solutions before adding NaOH and at different times after NaOH addition are given in **Table A5.1** in the addenda for Chapter 5. Throughout the

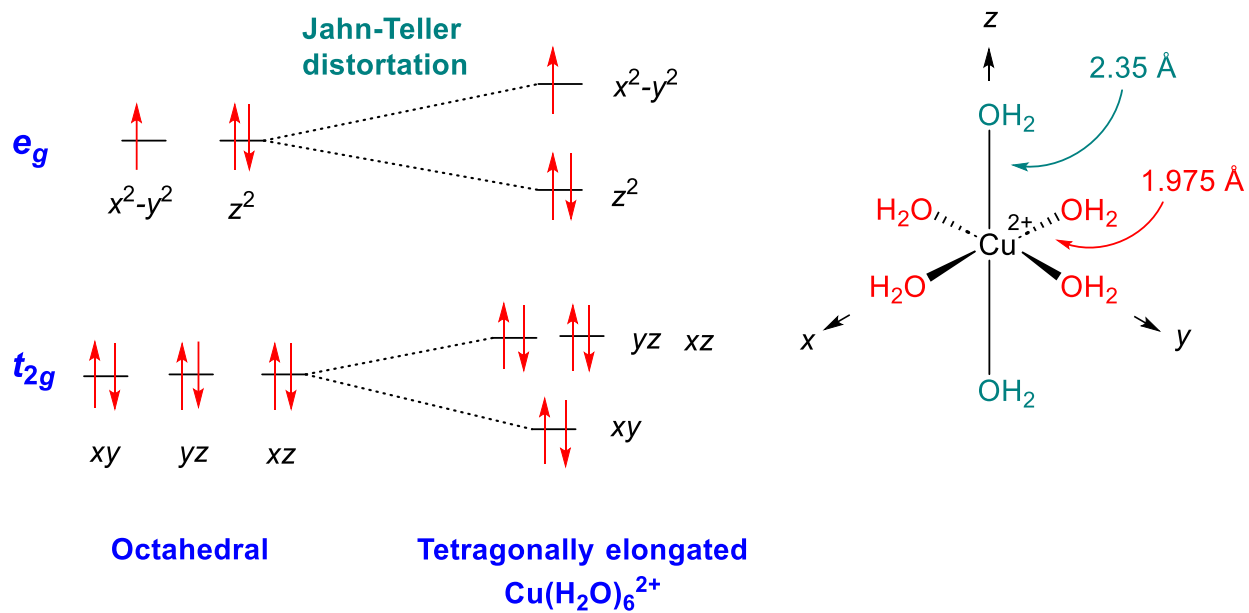


Figure 5.5. Splitting of the five d orbitals in a d^9 octahedral complex into t_{2g} and e_g levels and Jahn-Teller distortion in $\text{Cu}(\text{H}_2\text{O})_6^{2+}$, giving a tetragonal-elongated structure.

reaction, the isopropanol solution yielded green flecks inside the solution. They are most likely those of CuO nanoparticles, which tend to have green, green/brown, or brown/black coloring, though it could be $\text{Cu}_2(\text{OH})_3\text{Cl}$ which has a similar color.^{360, 361} Nanoparticles of the same material such as GaAs³⁶² and gold³⁶³ have been known to show different colors. After drying/heating the product solids in the current reactions, the green color disappeared, and all products were a dark brown/black color. Determination of nanoparticle synthesis, size, distribution, or other properties is outside of the scope of this experiment. The water solution took the longest to finish, with a lot of sol-gel-like materials in solution after 12 hours. This is most likely due to the large solubilities of both $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and NaOH in water, requiring longer time to complete the reaction.

The formation of CuO from the reaction in water *may* proceed through the so-called sol-gel process.³⁶⁴⁻³⁶⁹ In such a reaction, molecules are first converted into colloids (or *sol*) which act as precursors to form integrated networks (or *gel*) of either discrete particles or a network of coordinated ions, leading to the eventual formation of solids. Sol-gel processes typically refer to the hydrolysis of metal alkoxides or silicon alkoxides such as $\text{Ti}(\text{O}-n\text{-Bu})_4$ or $\text{Si}(\text{OEt})_4$, forming TiO_2 or SiO_2 .^{364, 365} Such reactions have been used to make unique porous materials with different applications.^{364, 365, 367-373} Our speculation of the sol-gel process in the formation of CuO in the reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with NaOH is based in part on our observation of the reaction shown in **Table A5.1**. Henry and coworkers have synthesized Cu(II) hydroxide gels from the reaction of $\text{Cu}(\text{acetate})_2$ with NH_3 in the presence of a small amount of K_2SO_4 .³⁶⁶ The gels are a mixture of $\text{Cu}_4(\text{OH})_6(\text{SO}_4) \cdot \text{H}_2\text{O}$ and acetate-based organic/inorganic polymers. Powder X-ray diffraction (PXRD) of powdered xerogels, which are formed from drying after water refluxing, show also the presence of CuO.³⁶⁶ Similar processes have been used to make CuO or mixed

metal oxides containing CuO.³⁶⁷⁻³⁶⁹ If indeed the sol-gel process occurs in the current reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with NaOH, it may go through the steps in **Figure 5.6**.

CuO has also been formed directly by the reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solid with 2 equiv of NaOH solid in a mortar and pestle.^{331, 374} The two solids were first each ground into powders using different mortars and pestles. The first powder was then added to the second and grinding the mixture of powders quickly led to the formation of black CuO powder. No addition of a solvent is needed for the solid-state reaction.

Since NaCl is also a product of the reaction between CuCl_2 and 2 equiv. of NaOH, the solids from the reaction were washed by water to remove NaCl. Afterwards, the solids were each dried at about 100 °C before IR and PXRD analyses.

The products were analyzed via IR spectroscopy (**Figure 5.7**), indicating that four products are the same, showing the peaks at 475, 508, 588, 847, 895, and 987 cm^{-1} , although with different intensities. Two noticeable broad O-H stretching absorptions at about 3,300-3,500 cm^{-1} were also observed, indicating that the solids may still retain some water from the reactions. From the data published by Ghosh and Naskar,³⁷⁵ the bands around 480, 530, and 596 cm^{-1} are Cu-O stretching vibrations in CuO.

Powder X-ray diffraction (PXRD) is a non-destructive technique to determine crystal phase of a solid.³⁷⁶ The CuO products from the reaction in the three solutions and solid state were analyzed, giving the diffraction patterns in **Figure 5.8** showing similar crystalline phases. The most prominent peaks are at $2\theta = 16.3^\circ, 27.4^\circ, 31.8^\circ, 35.4^\circ, 38.9^\circ, 45.5^\circ, 56.5^\circ, 66.3^\circ$, and 68.1° . The CuO solid formed in water also shows peaks at $2\theta = 53^\circ$, and 58° . From JCPDS-05-0661, the diffraction lines for the CuO monoclinic structure are $2\theta = 32.47, 35.49, 38.68, 48.65, 53.36, 58.25$ and 61.45 . For CuO nanoparticles, Das et al. reported peaks at $2\theta = 33.3^\circ, 35.7^\circ, 38.9^\circ$,

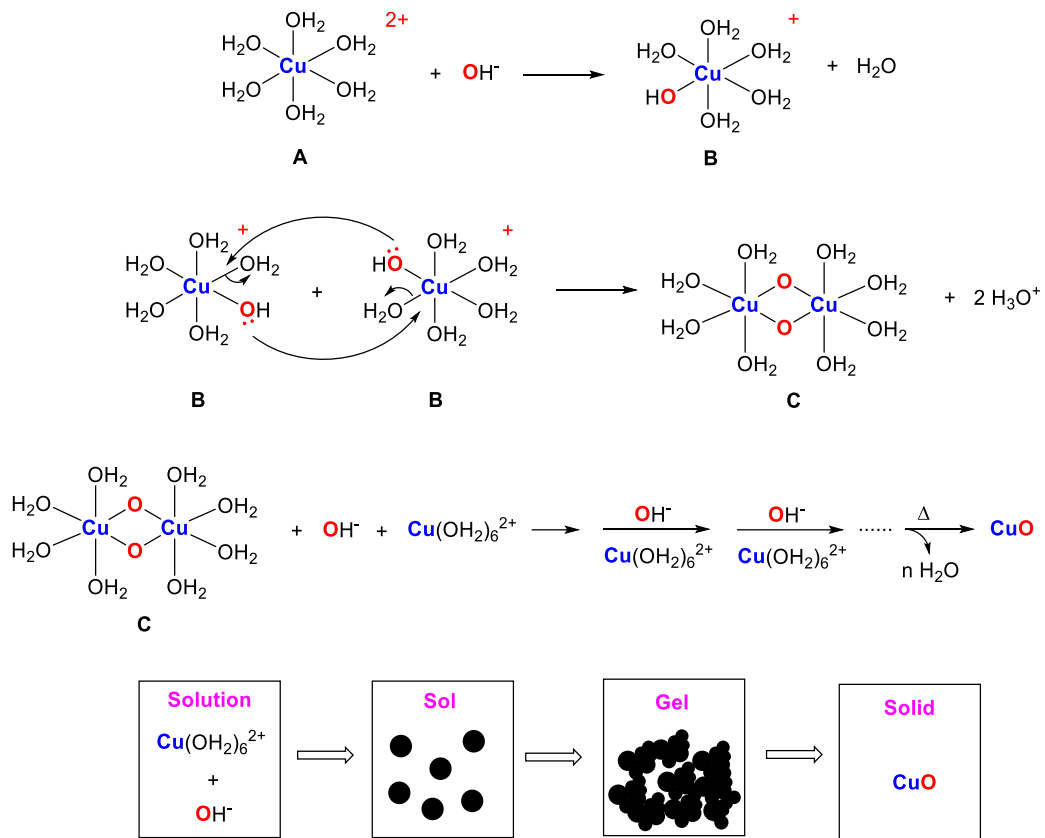


Figure 5.6. Schematic depiction of the sol-gel process in the formation of CuO in water.

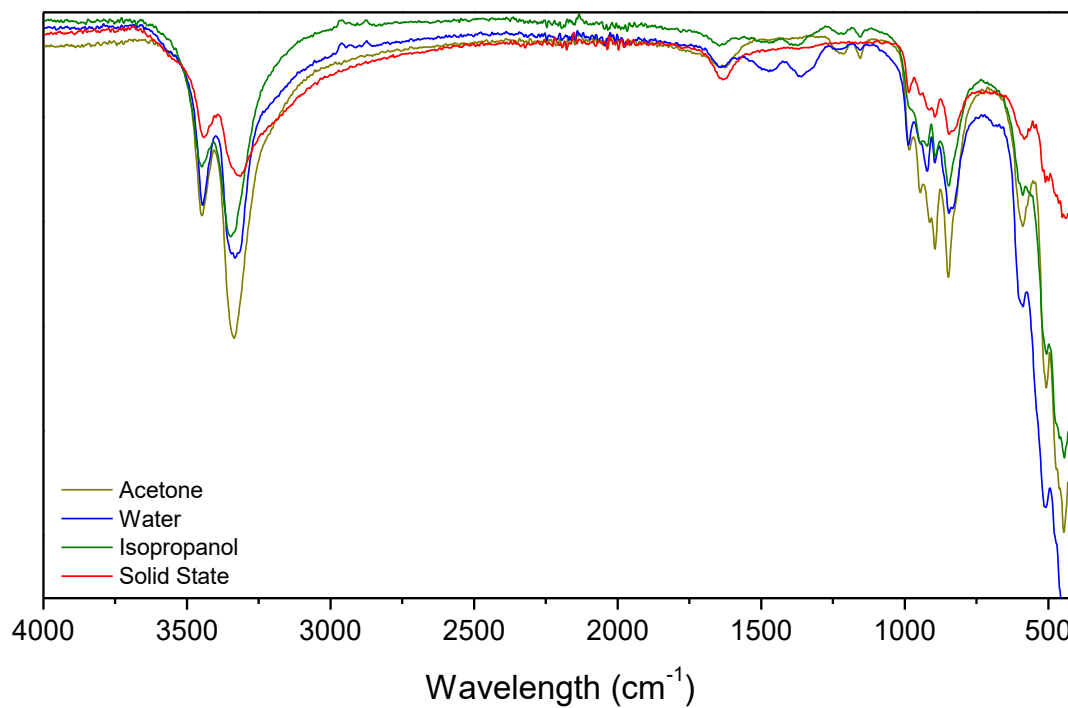


Figure 5.7. IR spectra of CuO products after drying. Individual spectrum is given in the addendum.

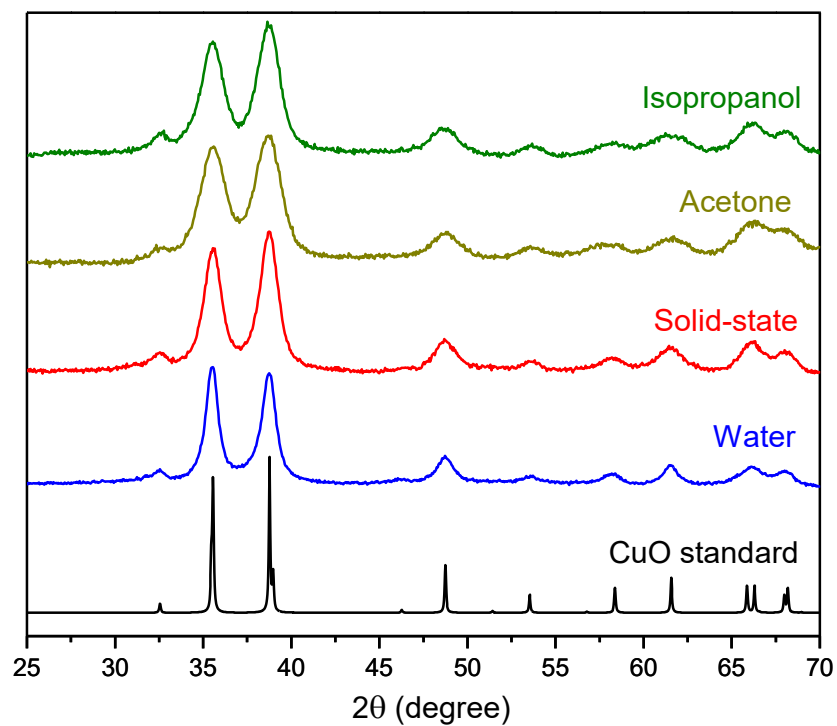


Figure 5.8. PXRD of CuO products from different processes. Products were dried in a furnace at 200 °C for 1 hour.

48.9°, 53.4°, and 58.2°. ³⁷⁷ The PXRD patterns of the three solid products from the reactions here match those of the standard and published work. The broadness of the PXRD peaks in **Figure 5.8** may indicate the CuO particles are not as crystalline as the standard. PXRD patterns of the products *without* washing by water are given in **Figure A5.4**, which show the presence of NaCl in the solids.

Comparison of the products from the reaction in three solutions and the solid-state shows that they all give CuO, as PXRD patterns show. The solid-state reaction is completed in a few minutes after grinding the mixture of the solids, while those in solutions take hours to show the formation of the products. One other advantage of the solid-state process is that no solvent is needed for the reaction, showing that it is greener than those conducted in solutions, especially those involving organic solvents of acetone and isopropanol. However, the isolated yield of CuO at 52.2% from the solid-state reaction is significantly lower than 86.4%-90.1% from the reactions in solution. As indicated earlier, solids on the mortar and pestle lead to at least some of the lost product.

5.5. Assessment outcome

This experiment was performed in Chem 449 (*Advanced Synthesis Laboratory*, 2 credits) at the University of Tennessee-Knoxville. This senior lab course seeks to teach modern techniques of synthesis and characterization of organic and inorganic compounds and materials, as well as handling air-sensitive materials, chromatographic purification, spectroscopic characterization, and X-ray structure determination. Students conduct two 3 hr-labs per week and work with a partner(s). In Fall 2022, 15 students in Chem 449 conducted the experiment, including collecting visible-near IR spectra of the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solutions as well as IR spectra and powder X-ray diffraction (PXRD) of the CuO products. The students had completed a

junior-level inorganic chemistry course, in which metal complexes and d orbital splittings were discussed. A short prelab presentation (about 10 minutes) was given by the lecturer, introducing solvatochromism and X-ray diffraction. Students were then asked to submit a prelab report, providing their understanding of the chemistry, procedures, and hazards in the experiment. They easily completed the experiment in two lab periods. Each student was required to submit a laboratory report with the following sections: Introduction, Experimental Section, Results and Discussion, Conclusions, and References. While most understood well the chemistry in the experiment and characterization of the products, several students did not fully explain the results of the experiment. There was some confusion over how to correctly interpret the UV-visible spectra. Some students made correlations between the width of the peaks and solvatochromic effects, as the width of the absorption band in acetone at about 350 nm in **Figure A5.3** was larger than those in water or isopropanol. That is, they did not focus on the shift of the local maxima, but the overall width of a whole absorption peak. Other students focused on the beginnings of peaks in the visible region rather than the absorption maxima and used the shifts in the beginnings in discussing the solvatochromic shift. To remedy these shortcomings, we suggest that, in the prelab, a more detailed discussion be made by the lecturer about how to interpret and compare absorption spectra. Although this experiment was used in a senior synthetic laboratory course, we think it is suitable for junior or sophomore course, as some students also noted.

5.6. Conclusion

This experiment provides students an opportunity to investigate the effects of solvents on synthetic reactions as well as examining solvatochromic effects. Negative solvatochromism was observed with solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in water, isopropanol, and acetone, in which the Cu^{2+} complex(es) absorbs the light of lower energy as solvent polarity decreases. Solvatochromism

here is demonstrated qualitatively and quantitatively in the colors of the three solutions and their visible spectra. In the reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with 2 equiv. of NaOH in the solid state or in the three solutions, the final products were CuO, as identified by IR spectra and powder X-ray diffraction (PXRD). This experiment offers students opportunities to observe how solvents affect absorption spectra of a metal complex and study the formation CuO in different solutions and from a solid-state reaction. In addition, students will learn about the research opportunities in the area. Possible research topics may consist of the following: Structure of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and other complexes in aqueous solution; Roles of organic solvents in the mixed aqueous-organic solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$; Effects of other solvents such as methanol, ethanol, and butanol on the UV-visible absorption of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$; Kinetics and the mechanistic pathway in the process forming CuO, including confirming that the reaction indeed proceeds through the sol-gel procedure; Use of scanning electron microscopy (SEM) to characterize the transient flecks in the reaction in isopropanol.

Chapter 6: Concluding remarks and recommendations

This dissertation primarily focuses on the use of optical and neutron spectroscopies to study the magnetic properties of molecular compounds and the effects of structure and vibration on the magnetic excitations of these compounds. To accomplish this the use of inelastic neutron scattering (INS), far-IR magneto-spectroscopy (FIRMS), and high-field, and -frequency electron spin resonance (HFESR) has been employed. There has also been the inclusion of diffraction techniques such as powder neutron diffraction, polarized neutron diffraction (PND), single-crystal neutron diffraction, and powder X-ray diffraction to study structure of these materials. The combinations of these techniques, along with data fitting and calculation, lead to a better understanding of the fundamental correlations between structure and magnetism.

The work in this dissertation has the following overall contributions: (1) Better understanding of fundamental properties of SMMs, an SMT, and Haldane topological materials; (2) Demonstration that PND is an advanced technique to directly observe a toroidal moment in SMT molecules. The studies of **Co-MST-H₂O** in Chapter 2 show that the local molecular symmetry may dominate, even though the crystallographic symmetry is lower. Results of **Dy₃-2** in Chapter 3 demonstrate that PND directly reveals a toroidal moment, confirming its presence in the SMT molecule. The use of the longer interchain ligands (than 4-4'-bpy), bpa and bpe, reduces interactions and coupling between Haldane spin-1 chains in **NiBaO** and **NiBeO** when compared to NiBO as shown in Chapter 4, making **NiBaO** and **NiBeO** potentially better topological materials.

Chapter 2 focuses on the use of advanced spectroscopies to study the magnetic properties of **Co-MST-H₂O** and **Ni-MST-H₂O** compounds and the effects of structure and vibration on their magnetic excitations. To accomplish this, the use of INS, FIRMS, and density functional

theory (DFT) calculations have been employed. There has also been the inclusion of Hirshfeld surface analysis to study intermolecular interactions in these materials. For **Co-MST-H₂O**, INS studies have delivered spin-Hamiltonian parameters and phonon properties of the complex, with DFT phonon calculations providing calculated spectra that fit well with experimental results. The calculations have also determined phonon symmetries, energies, and spin density distributions on the Co²⁺ ion and other atoms. For **Ni-MST-H₂O**, phonon properties and intermolecular interactions have been characterized, though magnetic transitions were not observed through spectroscopic techniques. The combination of these techniques, along with data fitting and theoretical calculations, allows one to better understand the fundamental correlations between structure, vibration, and magnetism in these molecular systems, with magnetometry serving as the primary technique for determining spin-Hamiltonian parameters when spectroscopic methods prove insufficient.

Opportunities to examine the M-MST family of complexes remain, such as observing further ligand interactions, replacing the bound water with a positively charged ligand such as 1-methylpyrazin-1-ium, shown in **Figure 6.1**. This will lead to large changes in intermolecular interactions due to a removal of the counterions within the crystal lattice, potentially leading to changes in relaxation mechanisms. Changes to the ligand environment might also lead to complexes that are less air sensitive, leading to broader applications. Additionally, the study of other SMMs with C_{3v} symmetry might elucidate further understanding of the lack of spin-phonon coupling within our studies, so that one might better understand the correlation between structure, magnetism, and the causes of spin-phonon coupling.

The work of Chapter 3 presents a new SMT candidate, **Dy₃-2**, and demonstrates that it fulfills key structural and magnetic criteria of an SMT compound. The use of magnetometry and

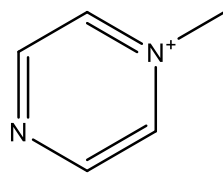


Figure 6.1. Structure of 1-methylpyrazin-1-ium.

neutron diffraction has been employed to unambiguously determine the head-to-tail spin arrangement for this Dy₃ SMT and confirm the toroidal moment. Included also is polarized neutron diffraction and variable-field neutron diffraction techniques, examining the magnetic structure of this material. **Dy₃-2** shows typical SMT characteristics in DC susceptibility studies for both polycrystalline and single crystal samples. The use of PND allows for mapping the atomic susceptibility tensor of Dy³⁺ ions within the compound and confirms the toroidal spin arrangement, while variable-field neutron diffraction enables modeling of the magnetic structure and demonstrates the AFM ordering of the Dy³⁺ ions within the crystal structure. The combination of these techniques allows one to better understand the fundamental correlations between structure and magnetism in SMT compounds, providing what is, to our knowledge, the first direct experimental determination of the toroidal spin arrangement in a SMT compound.

One of the characteristics of SMTs important to understand for applications within devices is their electromagnetic properties. There are not clear ways to study the effects of an electric field on the toroidal moment, especially not in a manner that allows one to directly determine those changes. This area is ripe for development of characterization techniques, as well as for studying potential application of SMTs for device integration.

Chapter 4 shows results from experiments to determine the effects of interchain ligands on Ni(II)-based spin-1 Haldane chain 2-D MOFs. This work primarily focuses on the use of neutron scattering and magnetic spectroscopies to study the Haldane spin-1 chain character of **NiBaO** and **NiBeO**, which differ in structure by their interchain ligands. To accomplish this, the use of variable-temperature powder neutron diffraction, DC magnetometry, and high-field electron spin resonance has been employed to thoroughly characterize the magnetism of these compounds. There has also been the inclusion of inelastic neutron scattering and far-IR

spectroscopy to characterize the low energy phonons of these materials. The Haldane phase of these compounds has been shown to be stable to perturbation up to 14 T through high-field studies. The combination of these techniques allows one to better understand the fundamental correlations between structure and low-dimensional magnetism in MOF systems. Future research opportunities include the use of specific heat studies at magnetic fields higher than 14 T to further probe the Haldane phase behavior and stability to perturbation, exfoliation of the MOFs to investigate low-dimensional magnetic properties in reduced dimensions, and theoretical calculations to examine the differences between the two MOFs' magnetic properties at the molecular level.

Chapter 5 concentrates on the use of solvatochromic studies and synthetic methods to investigate the effects of solvents on Cu^{2+} complexes and the formation of CuO in different reaction media. The use of UV-visible spectroscopy, infrared spectroscopy, and powder X-ray diffraction has been employed to characterize the solvatochromic behavior and reaction products. There has also been the inclusion of solid-state synthetic methods to study the formation of CuO from different reaction conditions. Negative solvatochromism has been observed with solutions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in water, isopropanol, and acetone, where the Cu^{2+} complex(es) absorbs light of lower energy as solvent polarity decreases. The solvatochromic effects are demonstrated both qualitatively through solution colors and quantitatively through visible spectra. In reactions of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with 2 equiv. of NaOH in solid state or in the three solutions, CuO has been identified as the final product through IR spectroscopy and PXRD analysis. The combination of these techniques allows one to better understand the fundamental correlations between solvent effects, spectroscopic properties, and synthetic outcomes in Cu^{2+} systems. Future research opportunities include structural studies of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ complexes in solution, investigation of

organic solvent roles in mixed aqueous-organic systems, kinetic and mechanistic studies of CuO formation pathways, and characterization of reaction intermediates using scanning electron microscopy.

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Appendix

Addenda for Chapter 2

A2.1. Additional results for **Co-MST-H₂O**

A2.1.1. PXRD of **Co-MST-H₂O**

There are no significant differences between the samples used for INS and FIRMS/HFEPR (**Figure A2.1**). The dehydration of **Co-MST-H₂O** may be due to the experimental conditions used for the FIRMS experiment. In FIRMS, there is a significant low pressure ($\sim 1.5 \times 10^{-4}$ mbar) while spectra are collected. There may have been cracks in the eicosane, leading to the exposure of the sample to low pressure and dehydration of **Co-MST-H₂O** to **Co-MST**.

In INS, the **Co-MST-H₂O** sample was sealed at ambient pressure in a metal sample can. Thus, dehydration is not likely.

A2.1.2. Additional FIRMS results

Shown in **Figures A2.2-3**.

A2.1.3. Additional HFEPR results

Shown in **Figures A2.4-5**.

A2.1.4. Additional INS results

Shown in **Figures A2.6-10**.

A2.2. DFT calculations for **Co-MST-H₂O**

A2.2.1. Calculated phonons with symmetry

Shown in **Table A2.1**.

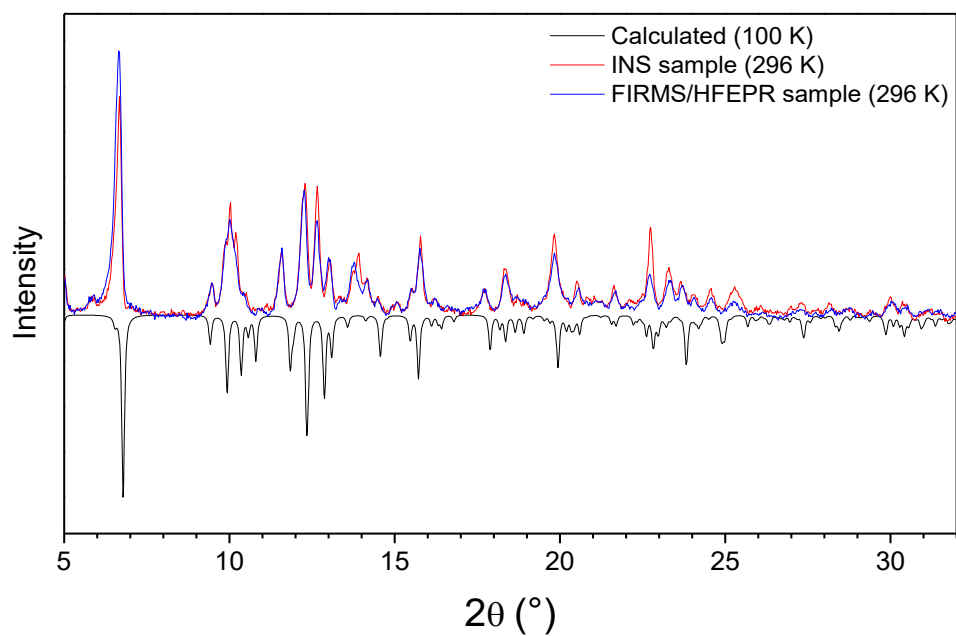


Figure A2.1. PXRD patterns at 296 K of **Co-MST-H₂O** samples for INS and FIRMS/HFEPR compared to the calculated pattern from the reported single-crystal structure at 100 K.¹⁰⁶

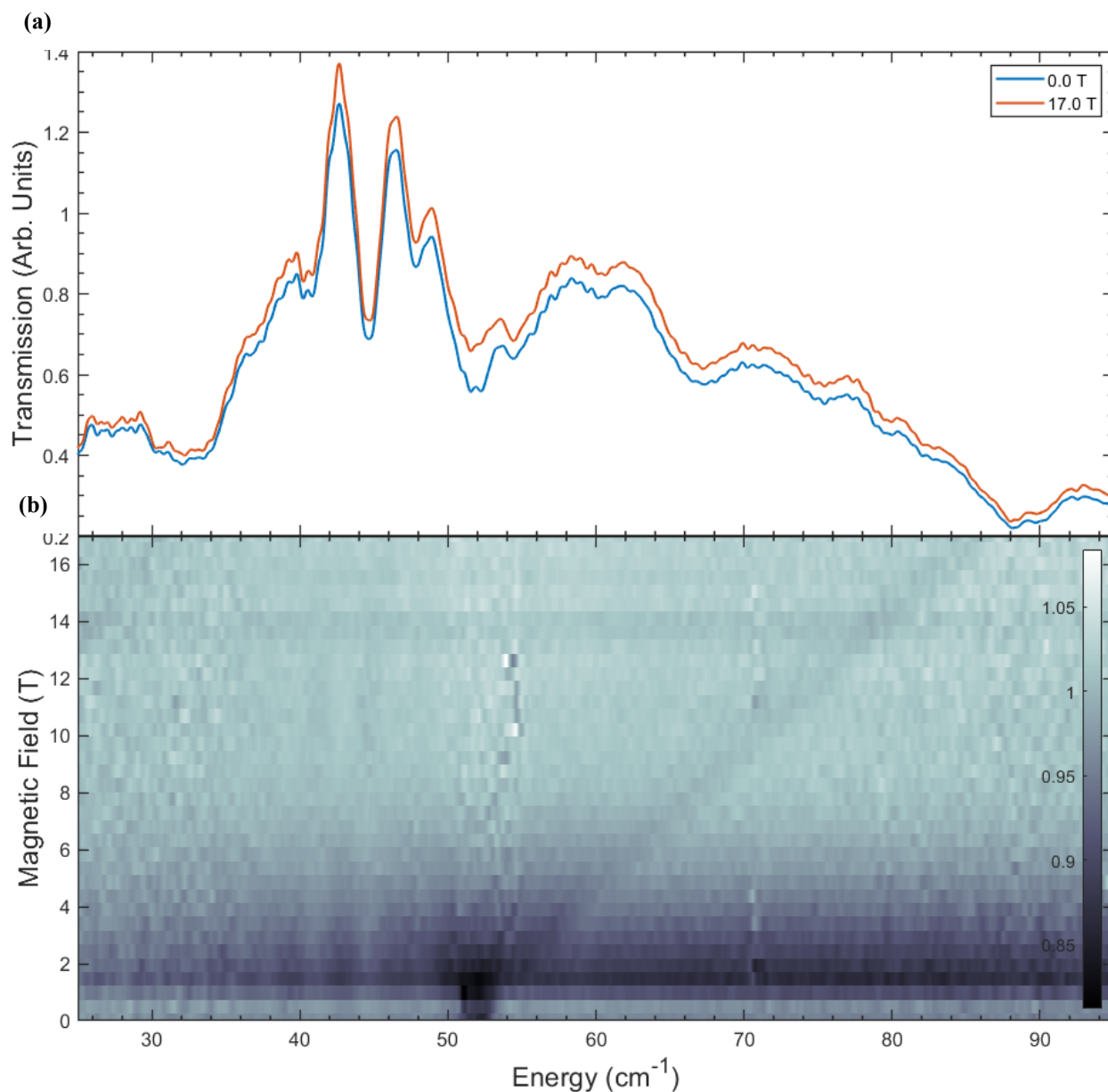


Figure A2.2. (a) FIRMS transmission spectra for a **Co-MST-H₂O** sample placed in the Voigt configuration.³⁷⁸ (b) 2D plot of the normalized (by average) transmission. **Figure 2.3** shows the FIRMS transmission spectra for a sample in the Faraday configuration.³⁷⁸ There is a greater field dependence of data collected by Voigt transmission.

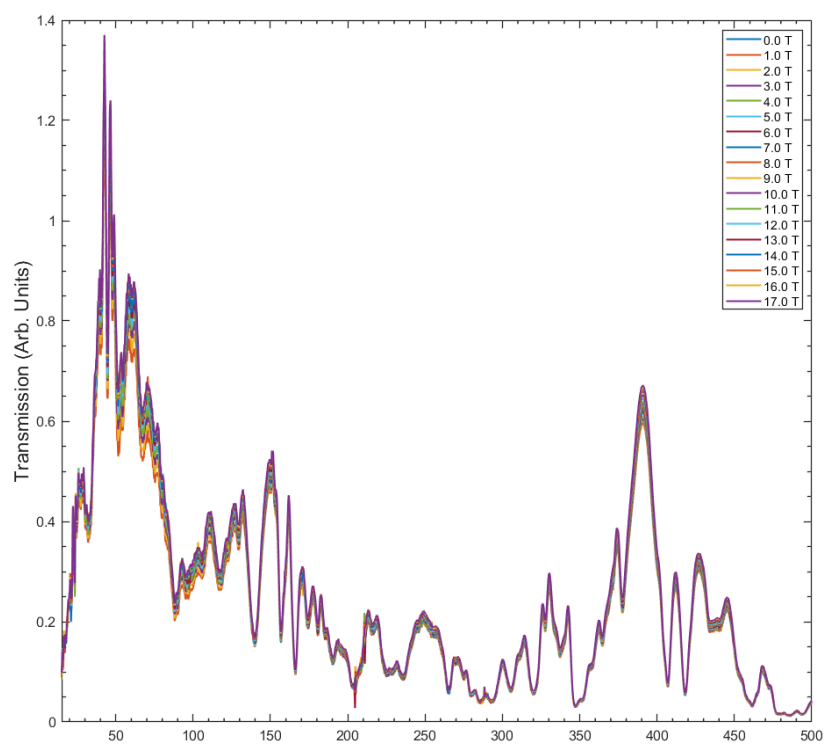


Figure A2.3. Averaged data of **Co-MST-H₂O** with all T-value scans, showing phonon features at 10-500 cm⁻¹.

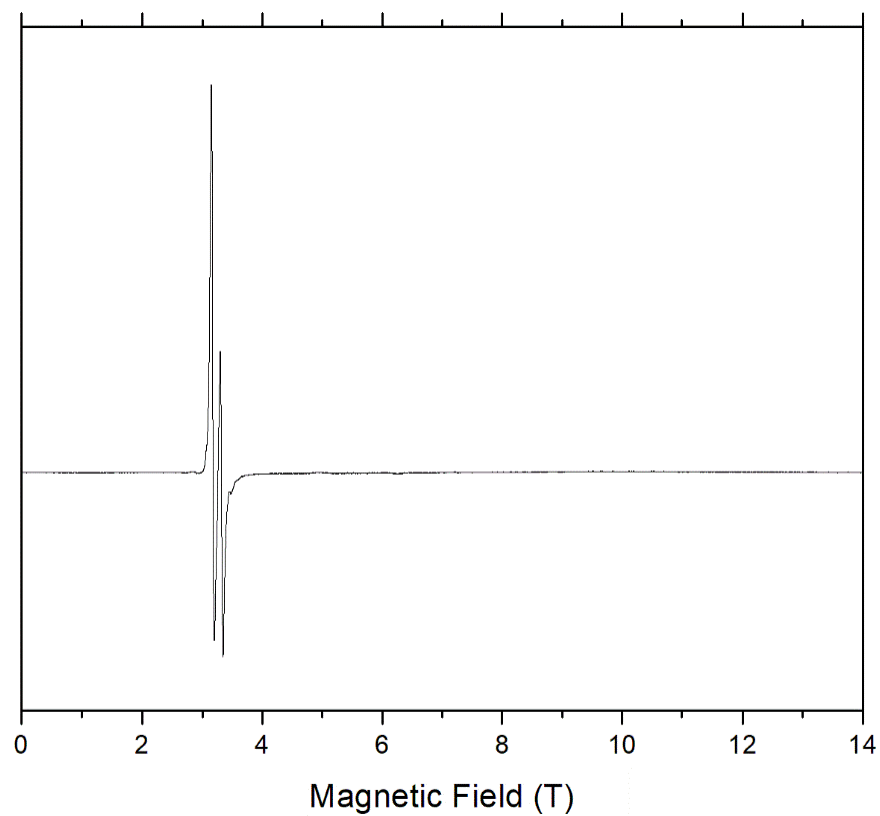


Figure A2.4. HFEPR spectrum of an unconstrained (loose) sample of **Co-MST-H₂O** at 10 K and 203 GHz. The two resonances with different intensities correspond to different spin species A and B, with the lower intensity being that of B. Species A can be identified as compound **Co-MST-H₂O**, and species B as the dehydrated compound **Co-MST**.

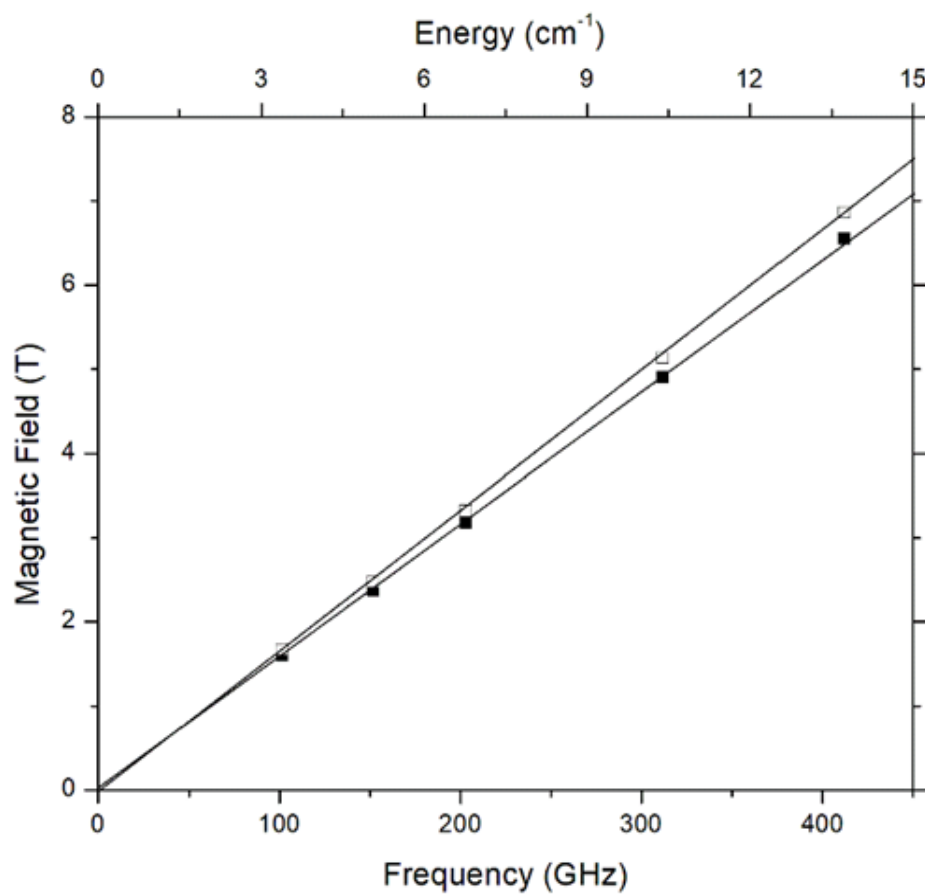


Figure A2.5. Frequency dependence of the EPR resonances observed in the unconstrained (loose) sample of **Co-MST-H₂O** at 10 K and 203 GHz. The lines correspond to *g*-values of 2.20 and 2.30 for the high-intensity (A) and low-intensity (B) resonances respectively.

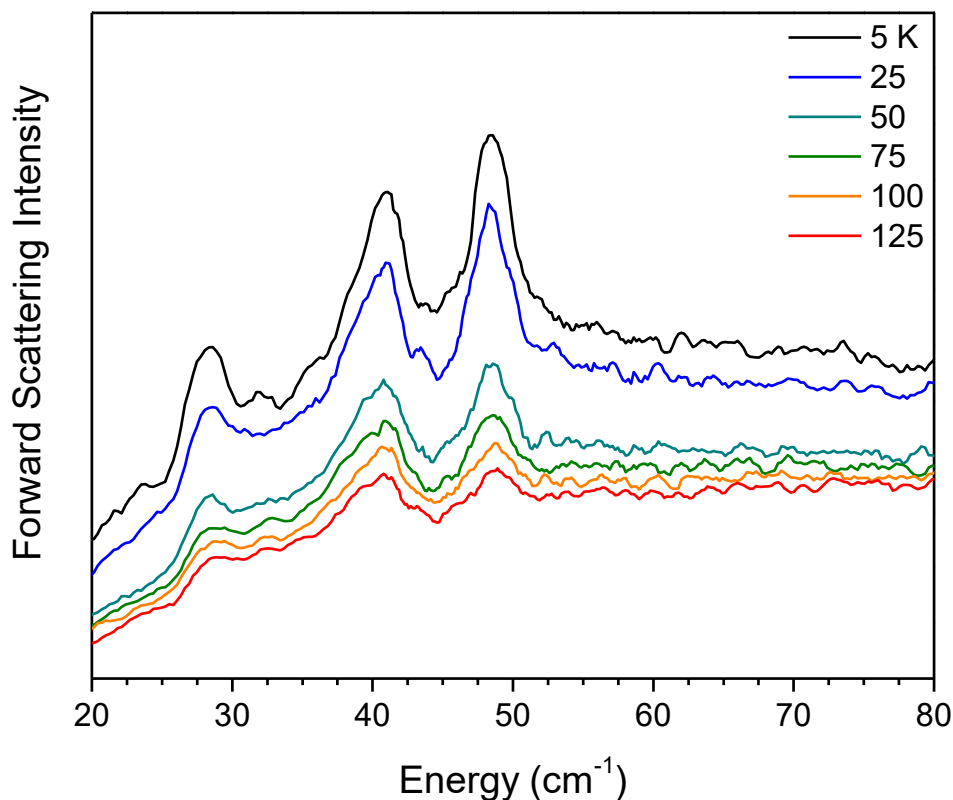


Figure A2.6. Forward scattering spectra of **Co-MST-H₂O** at 20-80 cm⁻¹. There are two temperature-dependent peaks at 28.5 and 40.2 cm⁻¹ that are not in the backward scattering spectra in Figure 2.5. These peaks show both temperature and Q dependence. ($Q = k_i - k_f$ is the momentum transfer and Q is the magnitude of Q , where k_i refers to the momentum of the incoming neutron and k_f of the outgoing neutron.)¹⁵² The observations suggest the peaks are magnetic. The sources giving these peaks are not clear. Impurities from degradation of **Co-MST-H₂O** or starting materials may contribute to these peaks, though they were not observed in PXRD (**Figure A2.1**).

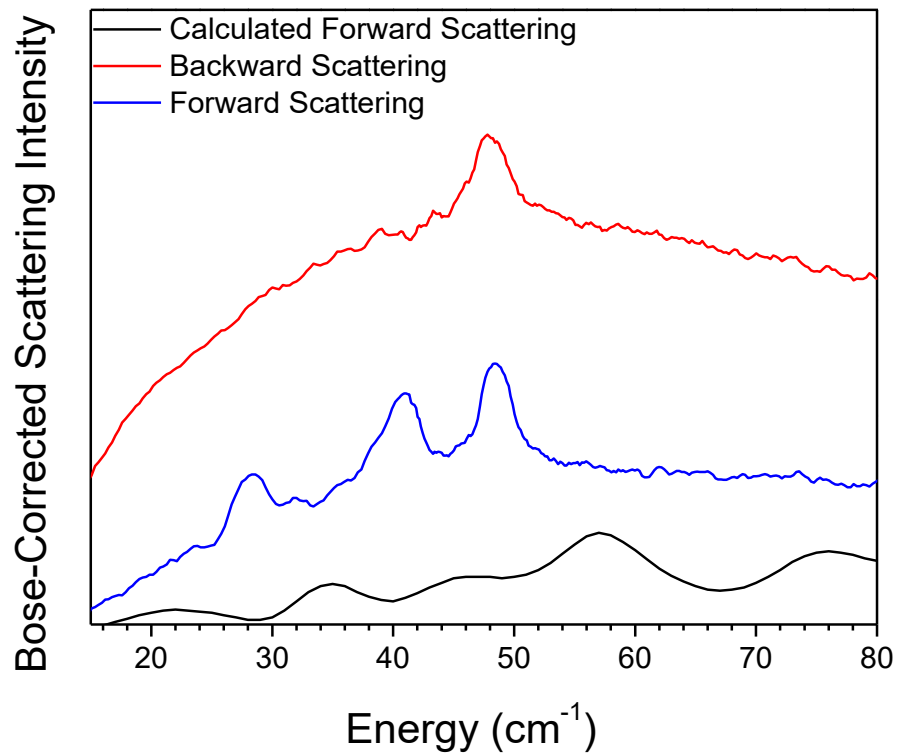


Figure A2.7. INS spectra of **Co-MST-H₂O** at 5 K in comparison with the calculated phonon spectrum in the low energy (15-80 cm^{-1}) region with both forward- and back-scattering spectra.

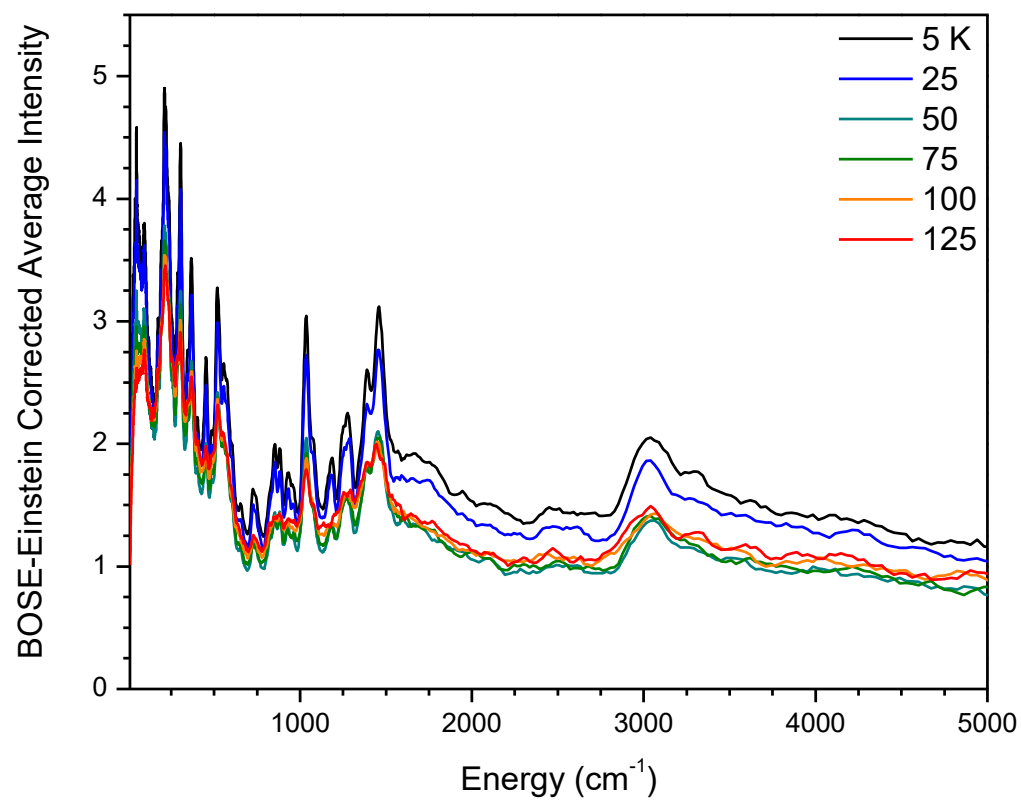


Figure A2.8. INS spectra of **Co-MST-H₂O** at 10-5000 cm⁻¹.

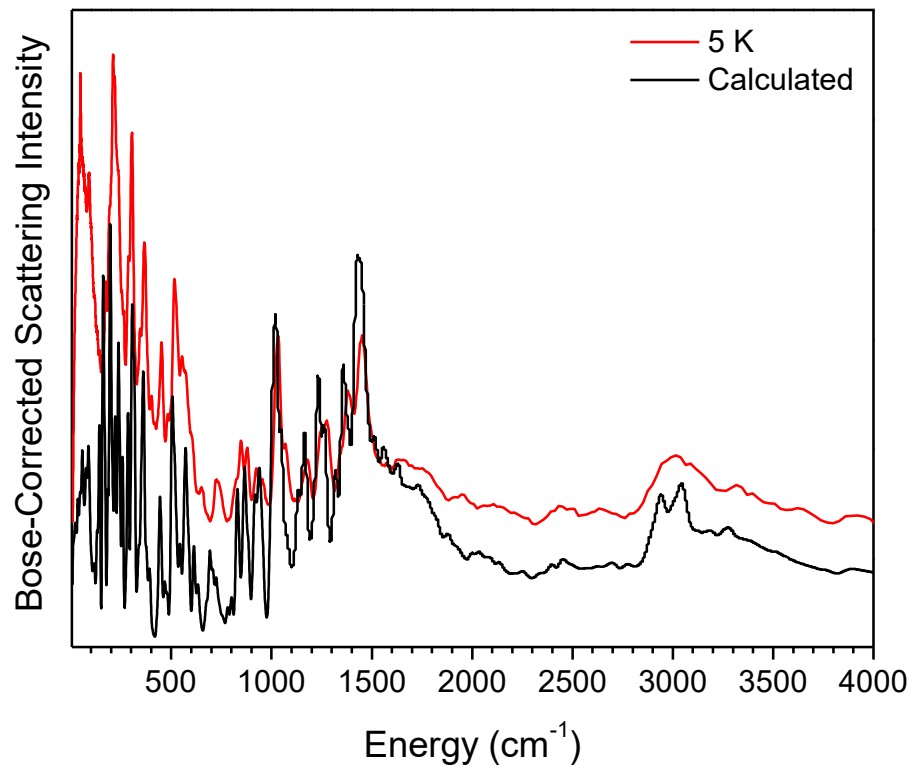


Figure A2.9. Calculated vs experimental spectra of **Co-MST-H₂O** at 5-4000 cm⁻¹. Differences between the calculated and 5 K spectra are not sufficient to determine magnetic excitations clearly.

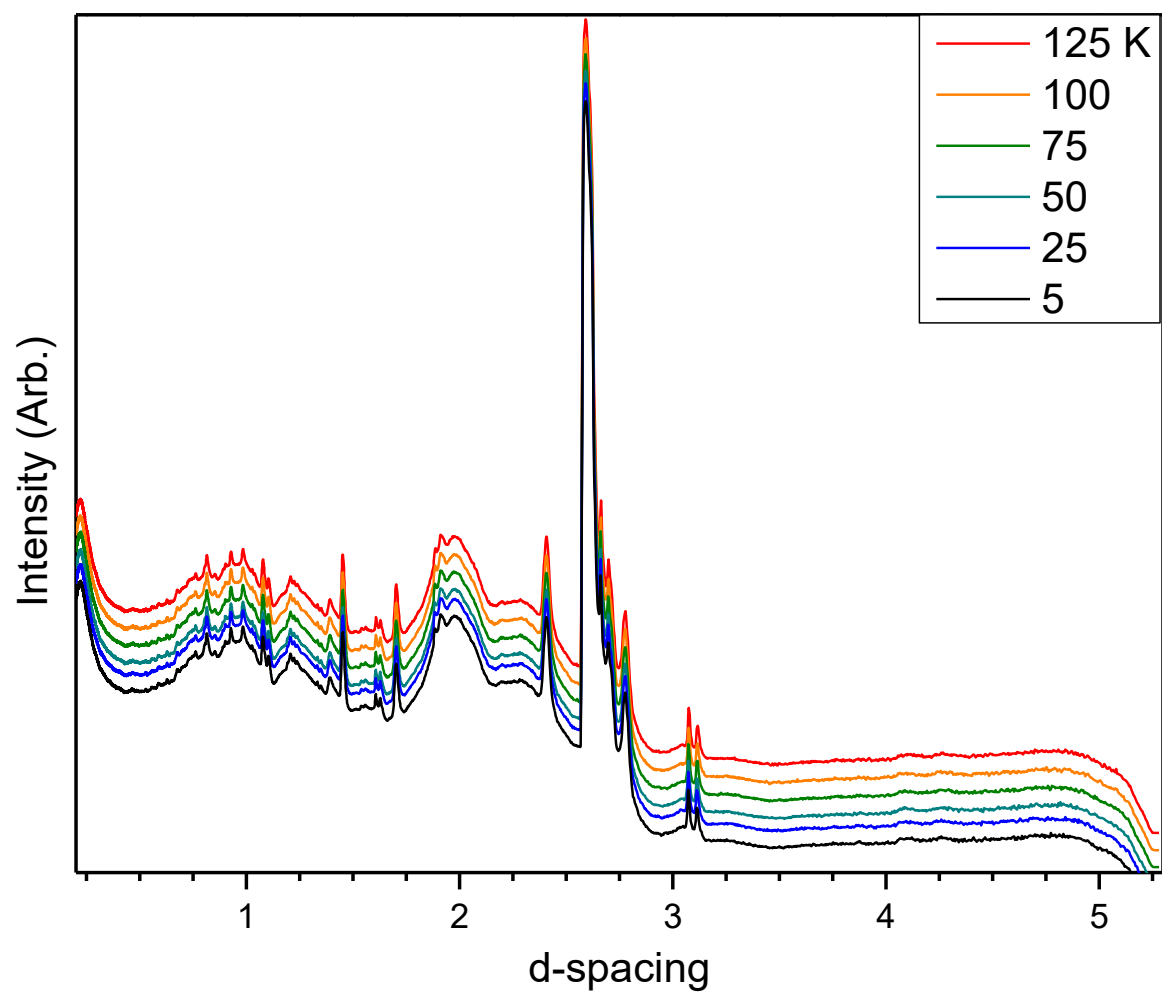


Figure A2.10. Waterfall powder neutron diffraction from VISION for **Co-MST-H₂O**. Lack of changes to peak shape and location indicates a lack of phase change from high to low temperature.

Table A2.1. Calculated phonons from VASP calculations for **Co-MST-H₂O** with symmetry

Phonon No.	Frequency (cm ⁻¹)	Symmetry	Phonon No.	Frequency (cm ⁻¹)	Symmetry
1	5.28	A_u	34	68.05	A_g
2	6.54	A_g	35	68.71	A_u
3	13.57	A_u	36	70.51	A_g
4	18.02	A_g	37	70.54	A_u
5	19.61	A_u	38	73.93	A_u
6	25.18	A_g	39	75.65	A_g
7	27.86	A_g	40	76.73	A_g
8	28.58	A_u	41	77.25	A_u
9	29.88	A_u	42	80.22	A_g
10	30.21	A_g	43	80.95	A_u
11	32.51	A_g	44	83.72	A_g
12	35.06	A_g	45	84.85	A_u
13	35.27	A_u	46	85.95	A_g
14	37.90	A_g	47	87.16	A_u
15	37.94	A_g	48	89.18	A_g
16	38.69	A_u	49	90.55	A_u
17	42.08	A_u	50	92.02	A_g
18	44.37	A_g	51	92.40	A_g

Table A2.1 Continued

19	45.11	A_u	52	93.08	A_u
20	45.69	A_u	53	96.56	A_g
21	45.98	A_u	54	96.63	A_u
22	46.76	A_g	55	100.42	A_u
23	47.65	A_g	56	101.22	A_g
24	50.62	A_g	57	102.21	A_g
25	53.95	A_g	58	107.21	A_u
26	54.59	A_u	59	107.65	A_g
27	56.59	A_g	60	109.69	A_u
28	56.95	A_u	61	115.81	A_g
29	58.28	A_u	62	116.33	A_u
30	60.62	A_g	63	117.90	A_g
31	60.83	A_u	64	122.31	A_u
32	65.85	A_u	65	122.64	A_g
33	66.44	A_g	66	127.63	A_u
67	130.80	A_g	103	211.43	A_u
68	131.07	A_u	104	211.68	A_g
69	133.40	A_u	105	216.35	A_g
70	135.09	A_g	106	216.95	A_u
71	138.77	A_g	107	218.45	A_g
72	139.50	A_u	108	218.86	A_u

Table A2.1 Continued

73	145.17	A_u	109	220.10	A_u
74	145.86	A_g	110	220.61	A_g
75	156.06	A_u	111	222.35	A_u
76	156.78	A_g	112	223.88	A_g
77	159.28	A_g	113	224.99	A_u
78	159.95	A_u	114	227.96	A_g
79	162.57	A_g	115	233.18	A_g
80	164.09	A_g	116	233.76	A_u
81	164.25	A_u	117	235.68	A_g
82	166.05	A_u	118	236.14	A_u
83	168.56	A_u	119	237.87	A_g
84	169.94	A_g	120	239.85	A_u
85	171.87	A_u	121	240.53	A_g
86	172.98	A_g	122	240.95	A_u
87	182.18	A_g	123	245.00	A_u
88	182.81	A_u	124	247.39	A_g
89	186.80	A_u	125	256.11	A_g
90	187.24	A_g	126	257.90	A_u
91	193.20	A_g	127	259.59	A_g
92	193.39	A_u	128	260.55	A_u
93	193.70	A_u	129	271.80	A_g

Table A2.1 Continued

94	195.54	A_g	130	272.32	A_u
95	197.95	A_u	131	275.44	A_u
96	198.63	A_g	132	275.93	A_g
97	199.05	A_u	133	277.26	A_u
98	205.10	A_g	134	278.57	A_g
99	205.44	A_g	135	281.31	A_u
100	205.86	A_u	136	281.62	A_g
101	207.26	A_u	137	284.11	A_g
102	208.16	A_g	138	286.56	A_g
139	287.01	A_u	175	363.30	A_u
140	288.11	A_u	176	363.85	A_g
141	297.50	A_u	177	365.84	A_u
142	298.59	A_g	178	366.43	A_g
143	298.99	A_u	179	376.66	A_g
144	300.43	A_g	180	376.96	A_u
145	303.76	A_g	181	387.47	A_g
146	303.96	A_u	182	387.57	A_u
147	304.45	A_g	183	394.11	A_u
148	307.06	A_u	184	394.60	A_g
149	307.42	A_g	185	432.00	A_u
150	308.13	A_u	186	432.07	A_g

Table A2.1 Continued

151	310.30	A_u	187	441.70	A_u
152	311.24	A_g	188	442.84	A_g
153	315.05	A_g	189	444.14	A_g
154	317.06	A_u	190	445.79	A_u
155	317.10	A_g	191	451.01	A_g
156	318.03	A_u	192	453.18	A_u
157	331.81	A_g	193	467.02	A_u
158	332.52	A_u	194	467.44	A_g
159	338.58	A_u	195	471.72	A_u
160	340.71	A_g	196	472.43	A_g
161	341.06	A_u	197	480.83	A_u
162	341.78	A_g	198	481.37	A_g
163	347.96	A_g	199	498.82	A_u
164	348.97	A_u	200	500.01	A_g
165	351.53	A_g	201	504.35	A_u
166	352.32	A_u	202	504.86	A_g
167	353.65	A_g	203	505.13	A_u
168	354.22	A_u	204	505.14	A_g
169	358.84	A_u	205	505.63	A_u
170	359.02	A_g	206	506.94	A_g
171	360.09	A_g	207	508.01	A_u

Table A2.1 Continued

172	360.71	A_g	208	508.39	A_g
173	360.78	A_u	209	512.95	A_u
174	360.98	A_u	210	513.48	A_g
211	515.49	A_g	247	585.91	A_g
212	515.97	A_u	248	586.80	A_g
213	517.29	A_g	249	589.28	A_g
214	517.30	A_u	250	591.27	A_u
215	518.51	A_u	251	612.89	A_g
216	518.58	A_g	252	613.21	A_u
217	520.23	A_g	253	621.57	A_g
218	520.30	A_u	254	621.66	A_u
219	522.45	A_g	255	628.93	A_u
220	524.07	A_u	256	629.88	A_g
221	527.38	A_u	257	634.94	A_g
222	527.82	A_g	258	635.69	A_u
223	528.82	A_g	259	675.29	A_u
224	529.49	A_u	260	676.83	A_u
225	538.39	A_u	261	676.99	A_g
226	538.77	A_g	262	681.78	A_g
227	544.75	A_u	263	691.93	A_u
228	545.03	A_g	264	693.76	A_g

Table A2.1 Continued

229	545.05	A_u	265	706.29	A_u
230	545.62	A_g	266	706.52	A_g
231	549.94	A_g	267	707.97	A_u
232	550.71	A_u	268	709.09	A_g
233	559.47	A_u	269	711.29	A_g
234	560.77	A_g	270	711.31	A_u
235	565.91	A_g	271	723.49	A_g
236	566.10	A_u	272	723.71	A_u
237	567.55	A_g	273	737.90	A_u
238	567.94	A_u	274	738.29	A_g
239	568.70	A_g	275	781.20	A_u
240	570.92	A_u	276	782.05	A_g
241	572.15	A_u	277	800.10	A_u
242	573.25	A_g	278	800.47	A_g
243	574.66	A_u	279	824.72	A_u
244	576.79	A_g	280	825.25	A_g
245	584.39	A_u	281	828.33	A_u
246	585.89	A_u	282	830.43	A_g
283	833.11	A_u	319	947.48	A_g
284	836.82	A_g	320	947.97	A_u
285	843.75	A_g	321	952.14	A_u

Table A2.1 Continued

286	843.87	A_u	322	952.28	A_g
287	855.87	A_u	323	955.68	A_u
288	860.35	A_g	324	956.07	A_g
289	865.80	A_g	325	958.85	A_g
290	865.82	A_u	326	959.04	A_u
291	867.80	A_u	327	994.19	A_g
292	869.53	A_g	328	994.23	A_u
293	869.83	A_g	329	996.29	A_u
294	870.01	A_u	330	996.39	A_g
295	883.57	A_u	331	997.67	A_u
296	885.66	A_g	332	997.69	A_g
297	908.69	A_g	333	1001.29	A_g
298	909.17	A_u	334	1001.87	A_u
299	914.40	A_u	335	1002.09	A_g
300	914.72	A_g	336	1002.71	A_u
301	917.87	A_g	337	1004.07	A_g
302	917.89	A_u	338	1004.68	A_u
303	918.29	A_g	339	1007.86	A_g
304	919.02	A_u	340	1008.07	A_u
305	919.68	A_g	341	1009.73	A_u
306	920.23	A_u	342	1009.76	A_g

Table A2.1 Continued

307	920.63	A_g	343	1010.84	A_u
308	921.96	A_u	344	1011.63	A_g
309	930.93	A_g	345	1012.70	A_u
310	931.10	A_u	346	1013.24	A_g
311	932.48	A_u	347	1013.32	A_u
312	933.03	A_g	348	1014.23	A_g
313	935.14	A_g	349	1015.55	A_u
314	935.51	A_u	350	1015.97	A_u
315	939.29	A_g	351	1016.13	A_g
316	939.94	A_u	352	1016.44	A_g
317	941.63	A_u	353	1017.24	A_g
318	942.12	A_g	354	1017.31	A_u
355	1019.27	A_g	391	1073.87	A_u
356	1019.52	A_u	392	1075.46	A_g
357	1020.52	A_g	393	1077.94	A_u
358	1020.80	A_u	394	1082.16	A_g
359	1022.17	A_u	395	1127.84	A_u
360	1022.30	A_g	396	1128.88	A_g
361	1023.42	A_g	397	1132.39	A_u
362	1023.71	A_u	398	1133.54	A_g
363	1024.17	A_u	399	1134.71	A_u

Table A2.1 Continued

364	1024.32	A_g	400	1134.98	A_g
365	1026.07	A_u	401	1145.51	A_u
366	1026.43	A_g	402	1146.13	A_g
367	1027.05	A_u	403	1150.09	A_g
368	1027.06	A_g	404	1152.89	A_u
369	1028.26	A_g	405	1154.28	A_g
370	1028.94	A_u	406	1154.33	A_u
371	1031.26	A_u	407	1161.55	A_u
372	1031.75	A_u	408	1162.93	A_g
373	1033.70	A_u	409	1165.87	A_u
374	1034.11	A_g	410	1165.92	A_g
375	1041.91	A_g	411	1167.04	A_u
376	1044.88	A_u	412	1167.11	A_g
377	1046.44	A_g	413	1169.61	A_g
378	1047.43	A_u	414	1169.66	A_u
379	1048.88	A_g	415	1183.92	A_u
380	1048.91	A_u	416	1187.04	A_g
381	1049.91	A_g	417	1212.63	A_g
382	1050.07	A_u	418	1213.84	A_u
383	1050.83	A_u	419	1226.74	A_g
384	1051.01	A_g	420	1228.11	A_u

Table A2.1 Continued

385	1051.93	A_u	421	1230.27	A_g
386	1052.69	A_g	422	1230.45	A_u
387	1059.61	A_u	423	1230.49	A_g
388	1059.91	A_g	424	1230.74	A_u
389	1063.15	A_u	425	1234.53	A_u
390	1067.97	A_g	426	1234.55	A_g
427	1236.93	A_u	463	1350.40	A_u
428	1236.99	A_g	464	1350.57	A_g
429	1242.99	A_g	465	1351.99	A_g
430	1244.58	A_u	466	1352.21	A_u
431	1254.53	A_g	467	1353.00	A_u
432	1256.19	A_u	468	1353.35	A_g
433	1257.80	A_g	469	1354.91	A_g
434	1258.74	A_u	470	1355.40	A_u
435	1261.19	A_u	471	1356.22	A_u
436	1261.23	A_g	472	1356.23	A_g
437	1263.63	A_g	473	1359.59	A_g
438	1265.09	A_u	474	1360.00	A_u
439	1268.05	A_g	475	1360.81	A_g
440	1268.44	A_u	476	1360.86	A_u
441	1268.74	A_g	477	1362.41	A_u

Table A2.1 Continued

442	1271.25	A_u	478	1362.52	A_g
443	1276.65	A_g	479	1367.25	A_g
444	1276.66	A_u	480	1367.27	A_u
445	1277.63	A_u	481	1369.21	A_g
446	1277.86	A_g	482	1370.20	A_u
447	1278.85	A_g	483	1371.06	A_g
448	1278.88	A_u	484	1371.66	A_u
449	1304.56	A_u	485	1381.23	A_u
450	1304.63	A_g	486	1381.34	A_g
451	1306.40	A_g	487	1382.45	A_g
452	1306.61	A_u	488	1382.78	A_u
453	1307.25	A_g	489	1382.89	A_g
454	1307.26	A_u	490	1383.28	A_u
455	1314.41	A_g	491	1385.25	A_g
456	1314.99	A_u	492	1385.55	A_u
457	1317.87	A_g	493	1386.11	A_u
458	1318.21	A_u	494	1386.77	A_g
459	1322.14	A_g	495	1387.41	A_g
460	1324.19	A_u	496	1388.21	A_u
461	1347.16	A_g	497	1388.31	A_g
462	1347.30	A_u	498	1389.47	A_u

Table A2.1 Continued

499	1392.82	A_g	535	1431.86	A_u
500	1395.25	A_u	536	1433.13	A_g
501	1404.45	A_u	537	1434.90	A_g
502	1405.31	A_g	538	1434.91	A_u
503	1408.53	A_u	539	1436.51	A_g
504	1408.71	A_g	540	1436.92	A_u
505	1411.99	A_g	541	1439.95	A_u
506	1412.10	A_u	542	1440.18	A_g
507	1412.39	A_g	543	1440.32	A_g
508	1412.73	A_g	544	1441.80	A_u
509	1412.83	A_u	545	1442.79	A_u
510	1413.33	A_u	546	1443.39	A_g
511	1415.74	A_u	547	1444.37	A_u
512	1415.80	A_g	548	1444.53	A_g
513	1418.14	A_g	549	1445.42	A_u
514	1418.50	A_u	550	1445.83	A_g
515	1419.37	A_g	551	1446.66	A_g
516	1419.61	A_u	552	1447.13	A_u
517	1420.25	A_g	553	1448.11	A_g
518	1420.93	A_u	554	1449.92	A_u
519	1421.53	A_g	555	1451.65	A_g

Table A2.1 Continued

520	1421.75	A_u	556	1451.67	A_u
521	1422.20	A_u	557	1452.60	A_u
522	1422.78	A_g	558	1452.70	A_g
523	1424.29	A_g	559	1455.60	A_u
524	1424.30	A_u	560	1455.78	A_g
525	1425.30	A_u	561	1456.63	A_u
526	1425.53	A_g	562	1457.70	A_g
527	1425.82	A_g	563	1459.48	A_u
528	1426.67	A_u	564	1460.09	A_g
529	1428.38	A_u	565	1466.93	A_u
530	1428.96	A_g	566	1471.04	A_u
531	1429.67	A_u	567	1471.08	A_g
532	1430.40	A_u	568	1477.37	A_g
533	1430.48	A_g	569	1477.46	A_u
534	1430.61	A_g	570	1482.57	A_g
571	1546.53	A_g	607	2935.92	A_g
572	1546.94	A_u	608	2935.92	A_u
573	1548.60	A_u	609	2936.20	A_u
574	1548.72	A_g	610	2936.71	A_g
575	1550.27	A_u	611	2938.22	A_u
576	1550.31	A_g	612	2938.29	A_g

Table A2.1 Continued

577	1558.35	A_g	613	2938.50	A_g
578	1558.46	A_u	614	2938.61	A_u
579	1579.58	A_g	615	2939.34	A_g
580	1579.85	A_u	616	2939.47	A_u
581	1580.53	A_g	617	2941.53	A_g
582	1580.90	A_u	618	2941.58	A_u
583	1582.50	A_g	619	2942.41	A_g
584	1582.72	A_u	620	2942.45	A_u
585	1632.72	A_u	621	2946.28	A_g
586	1633.23	A_g	622	2946.54	A_u
587	2879.21	A_u	623	2950.72	A_g
588	2879.48	A_g	624	2950.83	A_u
589	2885.38	A_u	625	2950.99	A_u
590	2885.70	A_g	626	2951.35	A_g
591	2901.20	A_u	627	2953.75	A_u
592	2901.24	A_g	628	2954.10	A_g
593	2908.11	A_u	629	2961.56	A_u
594	2908.22	A_g	630	2962.23	A_g
595	2909.57	A_g	631	2964.35	A_g
596	2909.69	A_u	632	2964.48	A_u
597	2915.07	A_u	633	2966.21	A_u

Table A2.1 Continued

598	2916.27	A_g	634	2967.51	A_g
599	2918.13	A_u	635	2971.85	A_u
600	2918.80	A_g	636	2972.66	A_g
601	2924.83	A_u	637	2983.05	A_g
602	2924.84	A_g	638	2983.13	A_u
603	2932.01	A_g	639	2983.98	A_u
604	2932.19	A_u	640	2984.00	A_g
605	2932.99	A_g	641	2988.48	A_u
606	2933.08	A_u	642	2988.48	A_g
643	2989.41	A_g	678	3040.86	A_g
644	2989.64	A_u	679	3041.14	A_u
645	2990.81	A_g	680	3041.77	A_g
646	2990.83	A_u	681	3041.95	A_u
647	2992.37	A_u	682	3042.46	A_g
648	2992.45	A_g	683	3043.68	A_g
649	2999.30	A_g	684	3043.72	A_u
650	2999.37	A_u	685	3046.92	A_g
651	2999.84	A_g	686	3047.07	A_u
652	3000.06	A_u	687	3047.58	A_u
653	3001.02	A_g	688	3047.95	A_g
654	3001.48	A_u	689	3048.28	A_g

Table A2.1 Continued

655	3005.97	A_g	690	3048.29	A_u
656	3006.03	A_u	691	3049.57	A_g
657	3008.22	A_u	692	3049.64	A_u
658	3008.22	A_g	693	3052.67	A_u
659	3008.59	A_g	694	3053.37	A_g
660	3008.72	A_u	695	3054.18	A_u
661	3010.48	A_u	696	3055.10	A_g
662	3010.62	A_g	697	3056.64	A_u
663	3011.25	A_u	698	3056.66	A_g
664	3011.65	A_g	699	3070.15	A_g
665	3015.61	A_g	700	3070.26	A_u
666	3015.63	A_u	701	3073.66	A_g
667	3020.47	A_g	702	3076.40	A_u
668	3020.56	A_u	703	3104.96	A_u
669	3023.15	A_g	704	3105.52	A_g
670	3023.22	A_u	705	3183.24	A_u
671	3035.01	A_g	706	3184.84	A_g
672	3035.05	A_u	707	3283.62	A_g
673	3038.75	A_g	708	3283.72	A_u
674	3038.83	A_u	709	3401.30	A_g
675	3039.13	A_u	710	3403.19	A_u

Table A2.1 Continued

676	3039.78	A_g	711	3526.00	A_u
677	3040.79	A_u	712	3526.95	A_g

A2.2.2 Spin density calculations

Shown in **Figure A2.11** and **Table A2.2**.

A2.2.3. Additional Hirshfeld surface results

Shown in **Figure A2.12**.

A2.3. Additional results for **Ni-MST-H₂O**

A2.3.1. PXRD of **Ni-MST-H₂O**

Shown in **Figure A2.13**.

A2.3.2. Additional FIRMS results

Shown in **Figures A2.14-15**.

A2.3.3. Additional INS results

Shown in **Figures A2.16-18**.

A2.3.4. Additional Hirshfeld surface results

Shown in **Figure A2.19**.

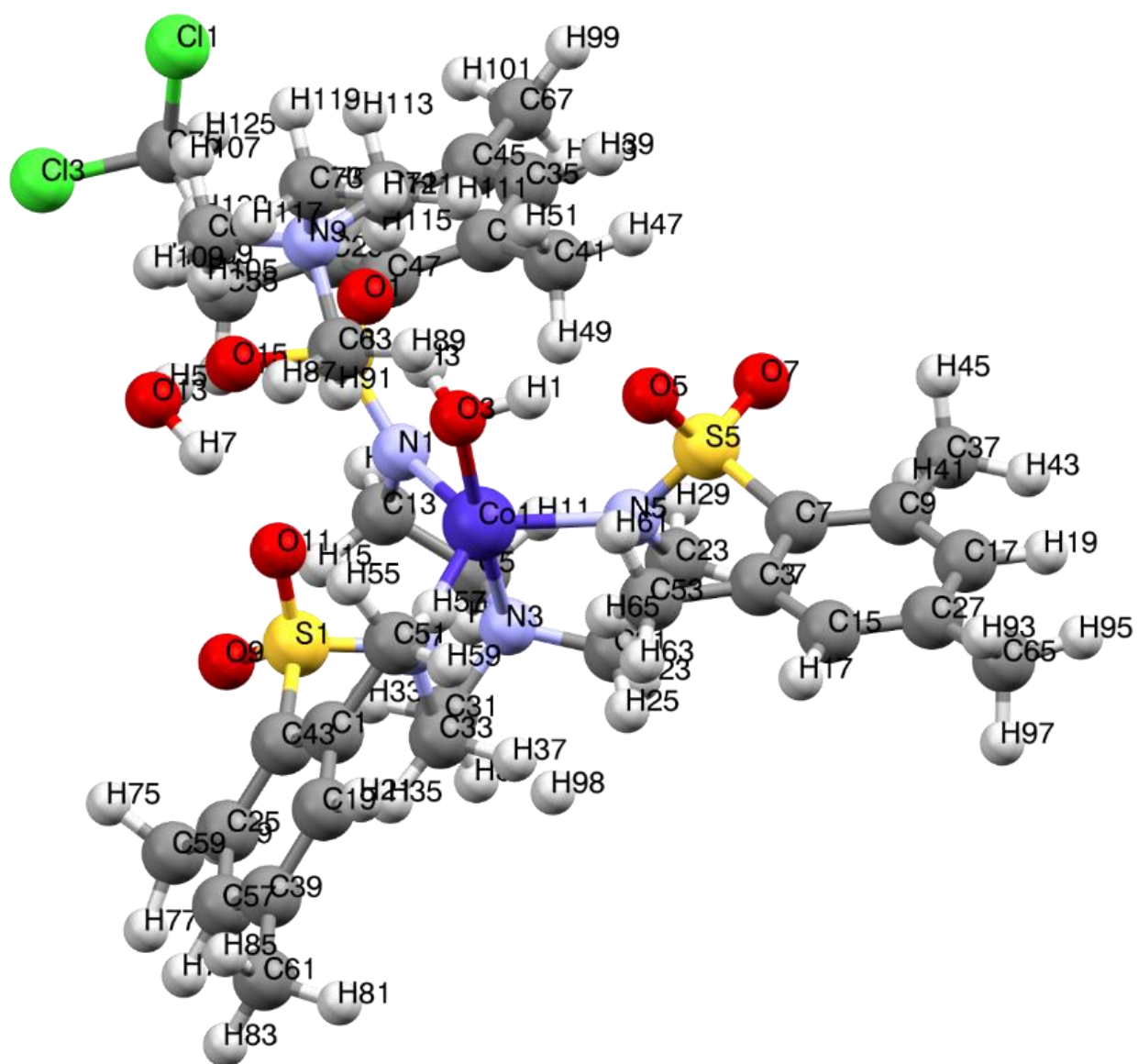


Figure A2.11. Structure of Co-MST-H₂O with labels associated with spin density calculations.

Table A2.2. Spin densities of atoms from VASP calculations for **Co-MST-H₂O**. There is a second identical molecule in the lattice, and its spin density is not listed.

Atom label	Spin density	Atom label	Spin density	Atom label	Spin density
H1	0	H81	0	C35	0
H3	0	H83	0	C37	0
H5	0	H85	0	C39	0.001
H7	0	H87	0	C41	0
H9	0.001	H89	0	C43	0.002
H11	0	H91	0	C45	0.001
H13	0.001	H93	0	C47	0.002
H15	0.001	H95	0	C49	0
H17	0	H97	0	C51	0
H19	0	H99	0	C53	0
H21	0	H101	0	C55	0
H23	0.001	H103	0	C57	0
H25	0	H105	0	C59	0
H27	0.001	H107	0	C61	0
H29	0.001	H109	0	C63	0
H31	0.001	H111	0	C65	0
H33	0	H113	0	C67	0
H35	0.001	H115	0	C69	0
H37	0	H117	0	C71	0

Table A2.2. Continued

H39	0	H119	0	C73	0
H41	0	H121	0	C75	0
H43	0	H123	0	N1	0.037
H45	0	H125	0	N3	0.045
H47	0	C1	0.001	N5	0.036
H49	0	C3	0.001	N7	0.037
H51	0	C5	0	N9	0
H53	0	C7	0.002	O1	0
H55	0	C9	0.001	O3	0.03
H57	0	C11	0.001	O5	0
H59	0	C13	-0.001	O7	0.006
H61	0	C15	0	O9	0.004
H63	0	C17	0	O11	0.001
H65	0	C19	0	O13	0
H67	0	C21	-0.001	O15	0.006
H69	0	C23	-0.001	S1	0.004
H71	0	C25	0.002	S3	0.005
H73	0	C27	0.001	S5	0.004
H75	0	C29	0.001	C11	0
H77	0	C31	0	C13	0
H79	0	C33	-0.001	Co1	2.627

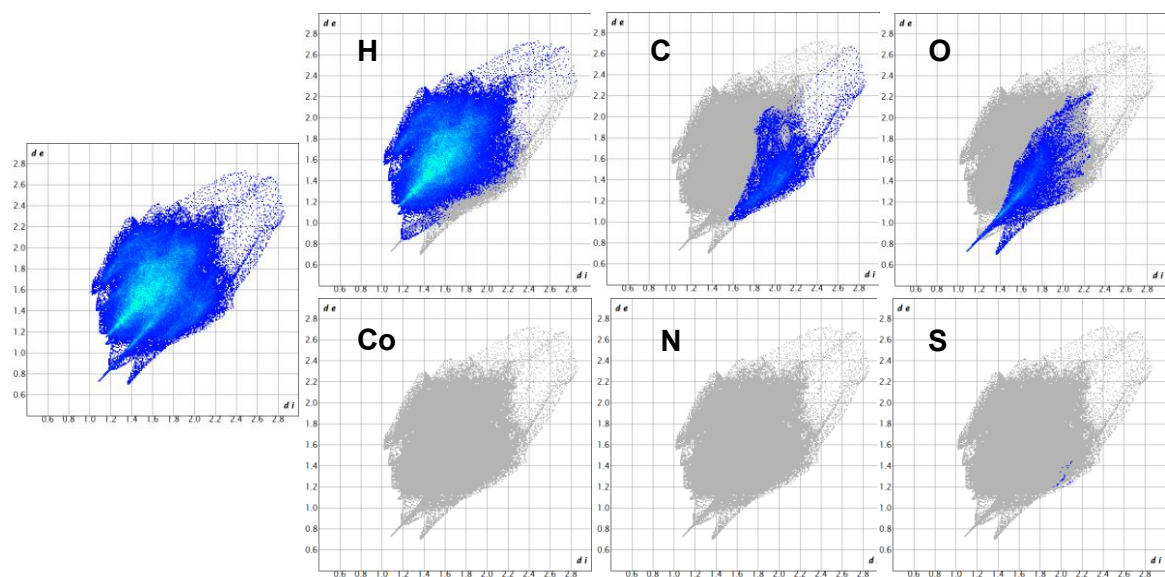


Figure A2.12. Fingerprint plots for the **Co-MST-H₂O⁻** anion showing the interactions of the listed element inside the Hirshfeld surface to all outer atoms.

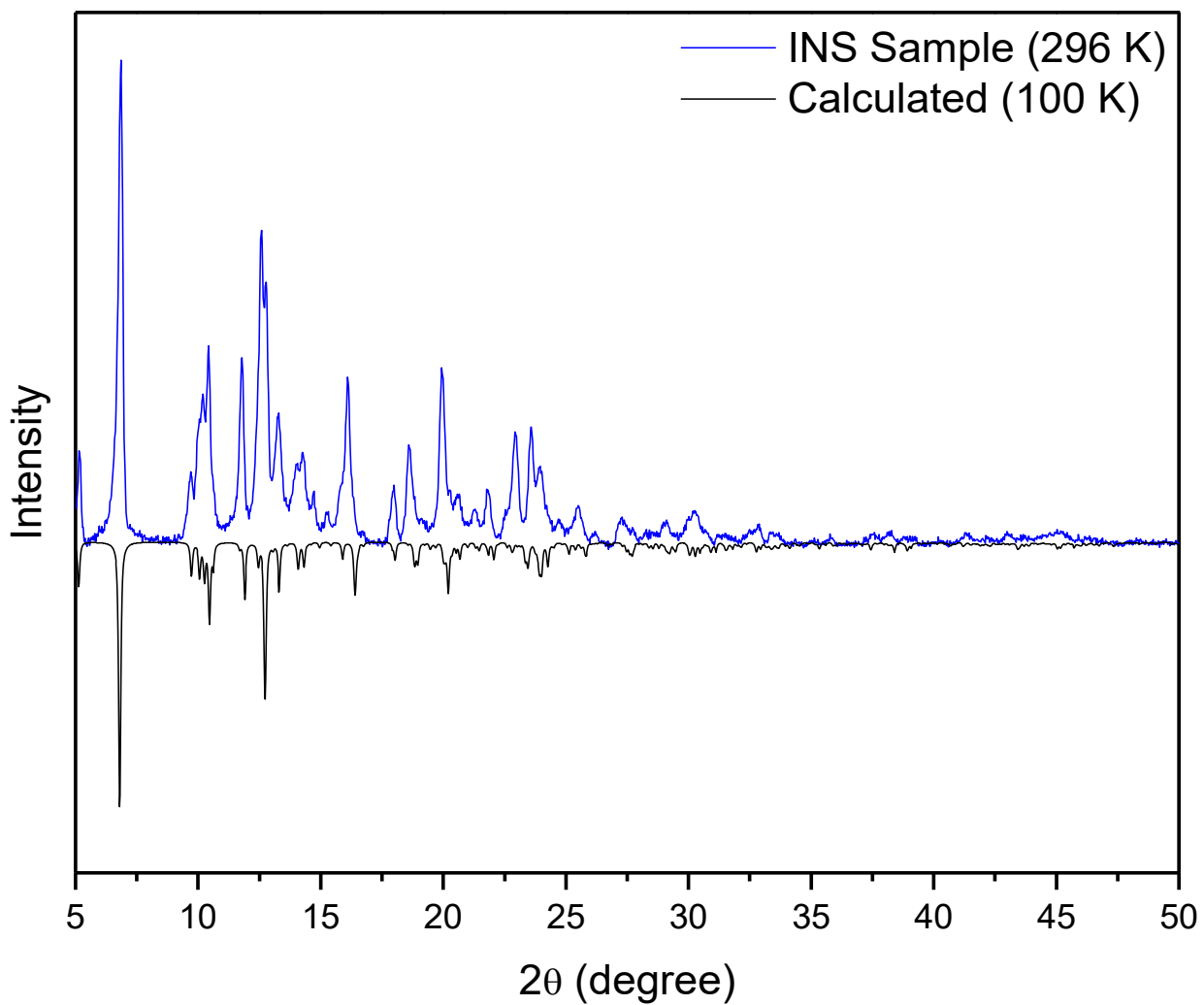


Figure A2.13. PXRD pattern of the **Ni-MST-H₂O** sample for INS compared to the calculated pattern from reported structure.¹⁰⁶

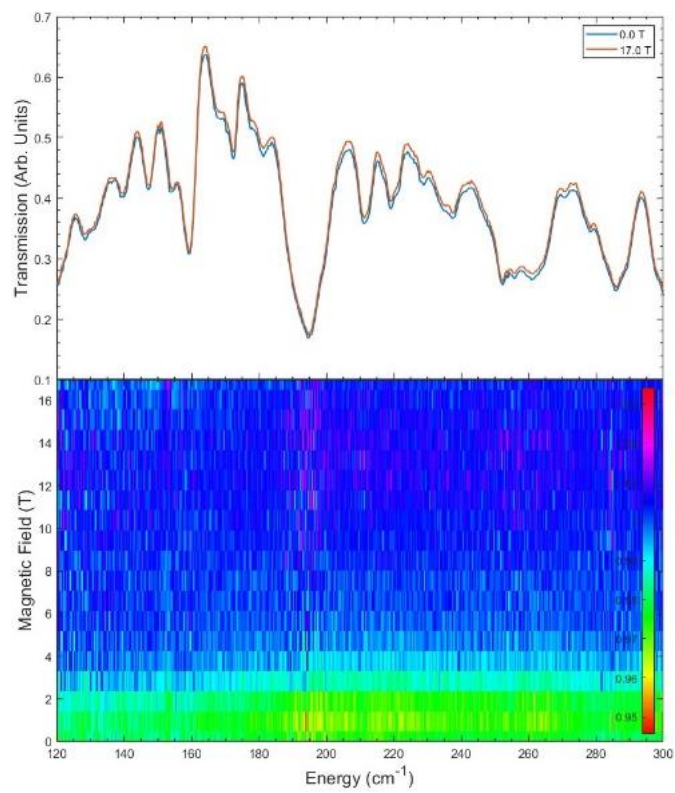


Figure A2.14. FIRMS and contour plot of spectra of **Ni-MST-H₂O** with no distinct magnetic peak.

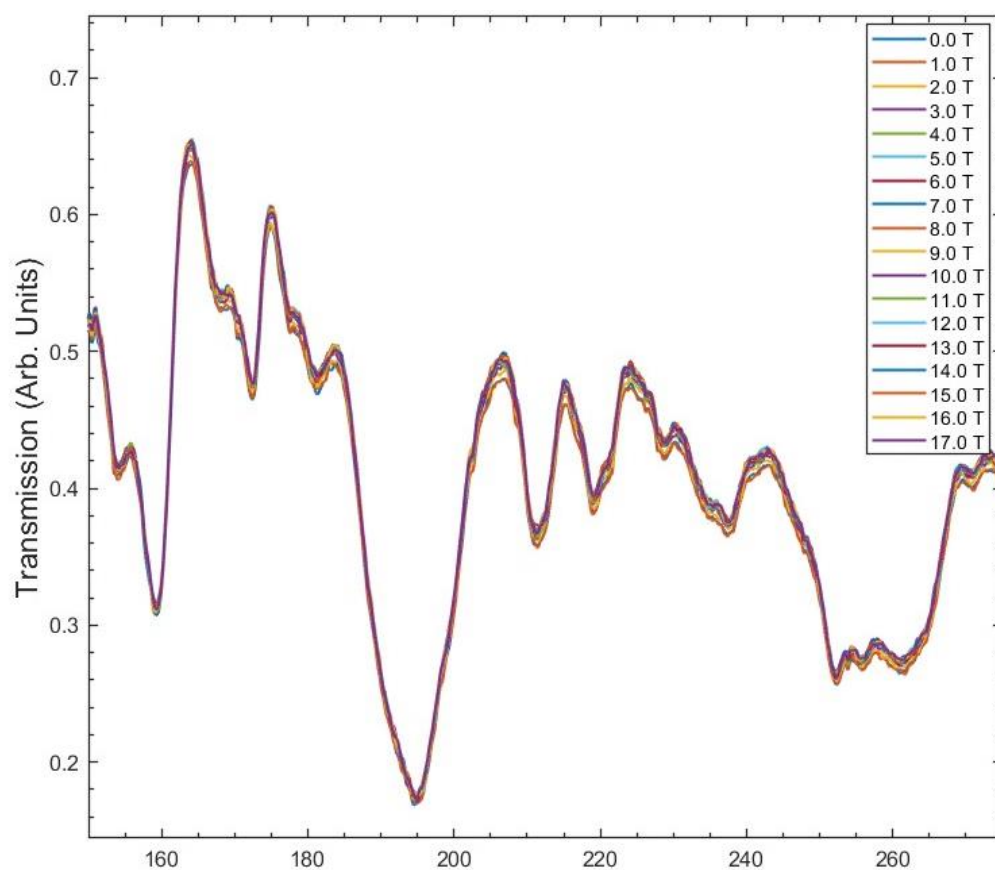


Figure A2.15. Averaged spectral data for **Ni-MST-H₂O** with all T-values showing vibrational features near the expected magnetic transition. There are several strong phonons in this region, which may be coupled to magnetic transitions.

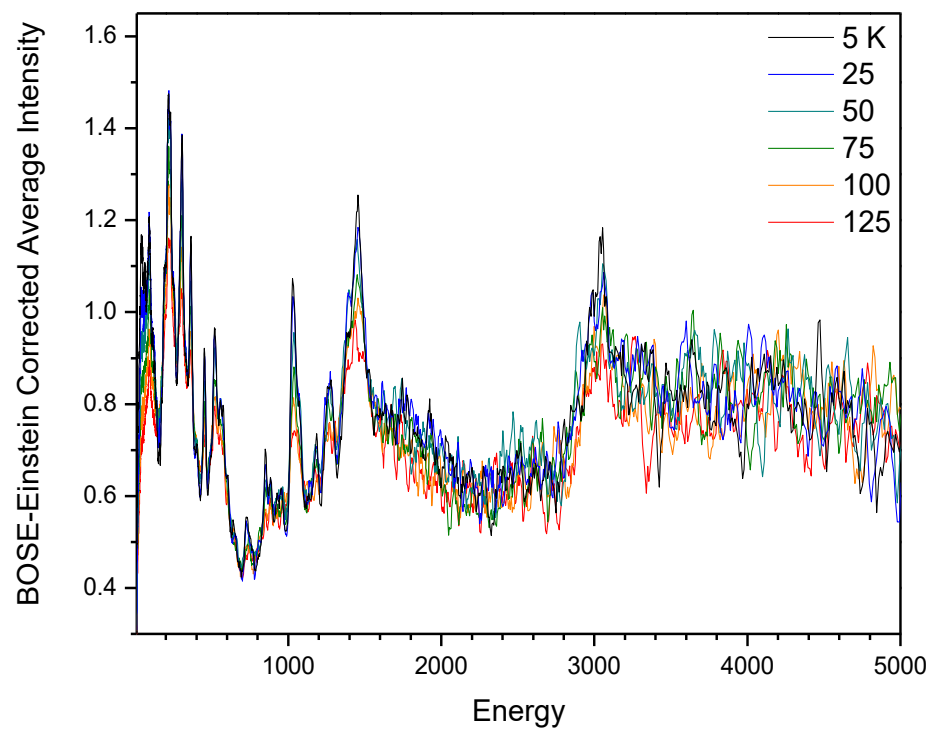


Figure A2.16. INS spectra of **Ni-MST-H₂O** at 10-5000 cm⁻¹.

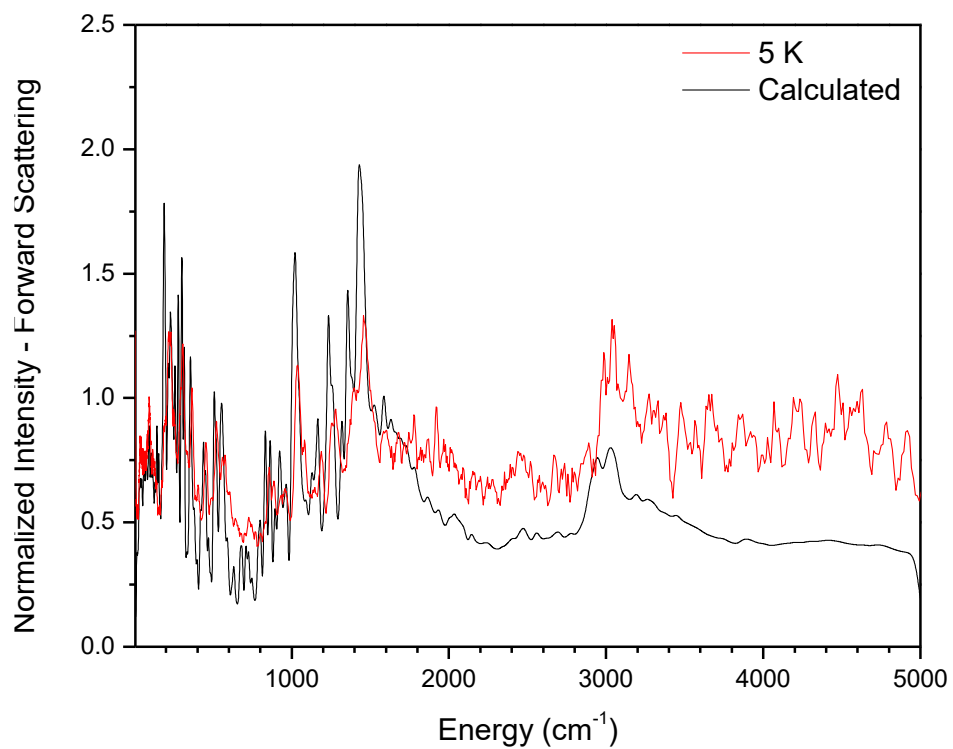


Figure A2.17. Calculated vs experimental spectra of **Ni-MST-H₂O** at 10-5000 cm⁻¹.

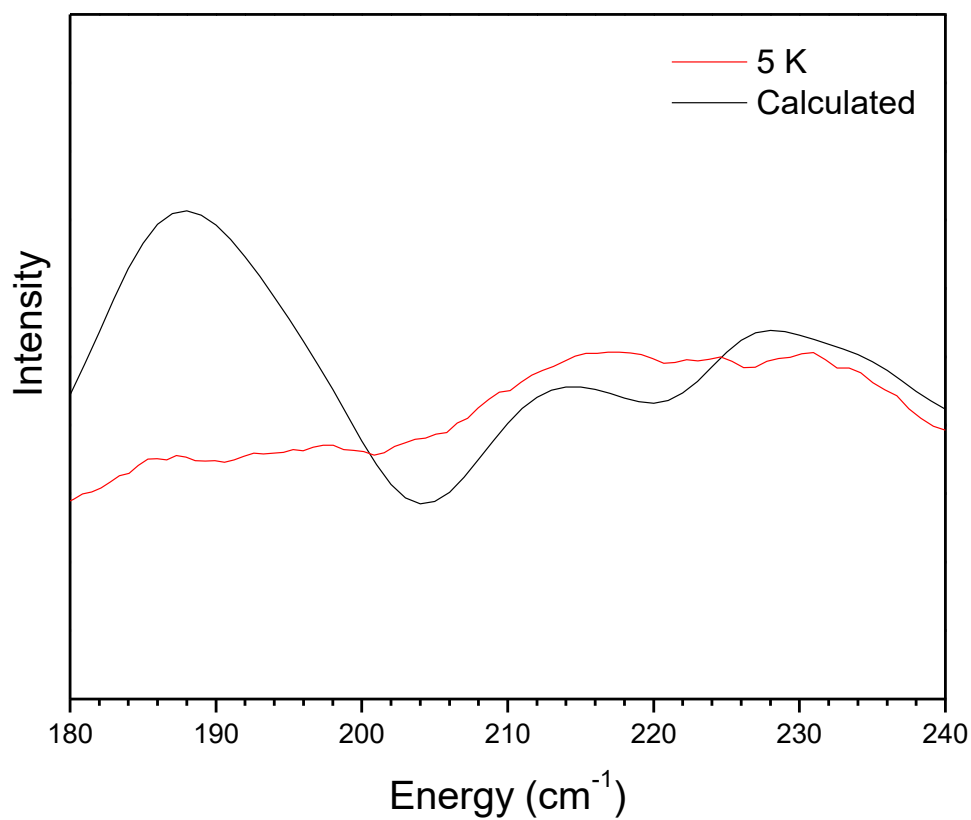


Figure A2.18. INS spectra of **Ni-MST-H₂O** showing calculated and experimental phonons in the 180-240 cm⁻¹ region. A comparison of the calculated INS spectrum with observed INS spectrum in the 180-240 cm⁻¹ region in the figure below does not clearly show the magnetic peak.

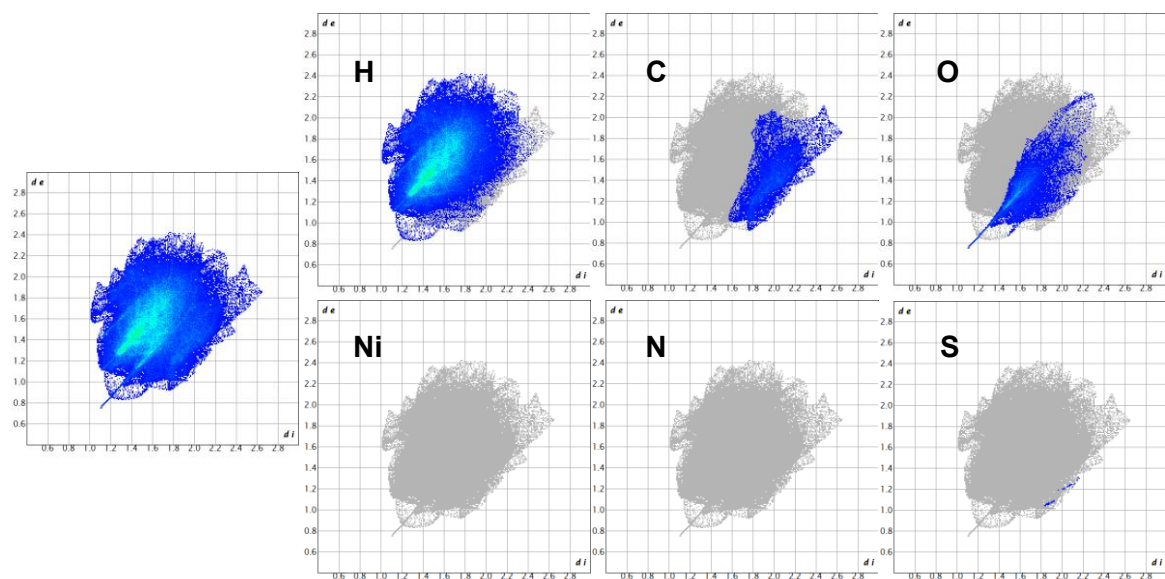


Figure A2.19. Fingerprint plots for Ni-MST-H₂O⁻ showing the interactions of the listed element inside the Hirshfeld surface to all outer atoms.

A2.4. Spin densities in $[\text{Co}(\text{12-crown-4})_2](\text{I}_3)_2$ and $\text{Co}(\text{AsPh}_3)_2\text{I}_2$

A2.4.1 Spin densities in $[\text{Co}(\text{12-crown-4})_2](\text{I}_3)_2$

Single-molecule magnet (SMM) properties of $[\text{Co}(\text{12-crown-4})_2](\text{I}_3)_2$ were reported by Chen and coworkers.²⁰² Its magnetic transitions, spin Hamiltonian parameters, and spin-phonon properties have been probed by advanced spectroscopies.¹³⁹ Its spin densities have been calculated by a DFT calculation similar to that used to calculate the spin densities in **Co-MST-H₂O**. The spin densities are reported here.

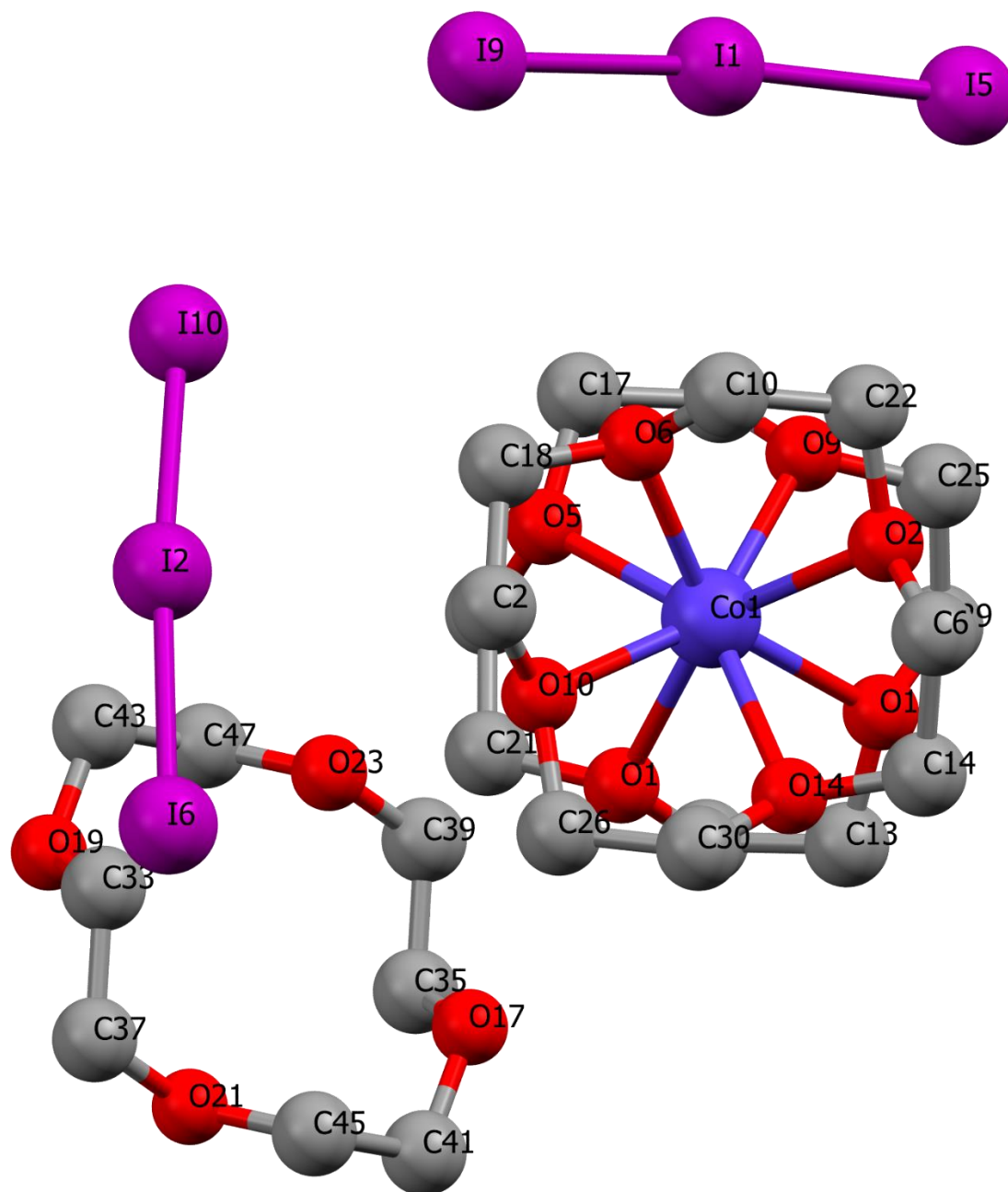


Figure A2.20. Model for the spin densities of $[\text{Co}(\text{12-crown-4})_2](\text{I}_3)_2$.

Table A2.3. Spin densities of atoms from VASP calculations for [Co(12-crown-4)₂](I₃)₂. There is a second identical molecule in the lattice, and its spin density is not listed.

Atom Label	Spin Density	Atom Label	Spin Density
H1	0.000	H80	0.000
H2	0.000	H82	0.000
H5	0.001	H84	0.000
H6	0.001	H86	0.000
H9	0.000	H88	0.000
H10	0.000	H90	0.000
H13	0.001	H92	0.000
H14	0.001	H94	0.000
H17	0.000	H96	0.000
H18	0.000	C1	0.001
H21	0.001	C2	0.001
H22	0.001	C5	0.001
H25	0.000	C6	0.001
H26	0.000	C9	0.001
H29	0.000	C10	0.001
H30	0.000	C13	0.000
H33	0.000	C14	0.000
H34	0.000	C17	0.000
H37	0.000	C18	0.000

Table A2.3. Continued

H38	0.000	C21	0.000
H41	0.000	C22	0.000
H42	0.000	C25	0.000
H45	0.000	C26	0.000
H46	0.000	C29	0.001
H49	0.000	C30	0.001
H50	0.000	C33	0.000
H53	0.000	C35	0.000
H54	0.000	C37	0.000
H57	0.000	C39	0.000
H58	0.000	C41	0.000
H61	0.001	C43	0.000
H62	0.001	C45	0.000
H65	0.000	C47	0.000
H66	0.000	O1	0.016
H68	0.000	O2	0.016
H69	0.000	O5	0.017
H72	0.000	O6	0.017
H74	0.000	O9	0.016
H76	0.000	O10	0.016

Table A2.3. Continued

H78	0.000	O13	0.016
O14	0.016	I1	0.000
O17	0.000	I2	0.000
O19	0.000	I5	0.000
O21	0.000	I6	0.000
O23	0.000	I9	0.000
Co1	2.819	I10	0.000
Total	2.615		

Table A2.4. Summary of spin densities for [Co(12-crown-4)₂](I₃)₂

Atoms	Ranges of spin densities
Co ^{II}	2.819
O	0.000–0.017
I	0.000
C	0.000–0.001
H	0.000–0.001

A2.4.2. Spin densities in $\text{Co}(\text{AsPh}_3)_2\text{I}_2$

Magnetic properties of $\text{Co}(\text{AsPh}_3)_2\text{I}_2$ were previously studied by Saber and Dunbar, showing slow magnetic relaxation and SMM behavior with easy-axis ZFS ($D = -74.7 \text{ cm}^{-1}$, $E = -0.82 \text{ cm}^{-1}$) from magnetometric studies.²⁰¹ Its spin Hamiltonian parameters and spin-phonon properties have been probed by advanced spectroscopies.⁹⁶ Its spin densities have been calculated by a DFT calculation similar to that used to calculate the spin densities in **Co-MST-H₂O**. The spin densities are reported here.

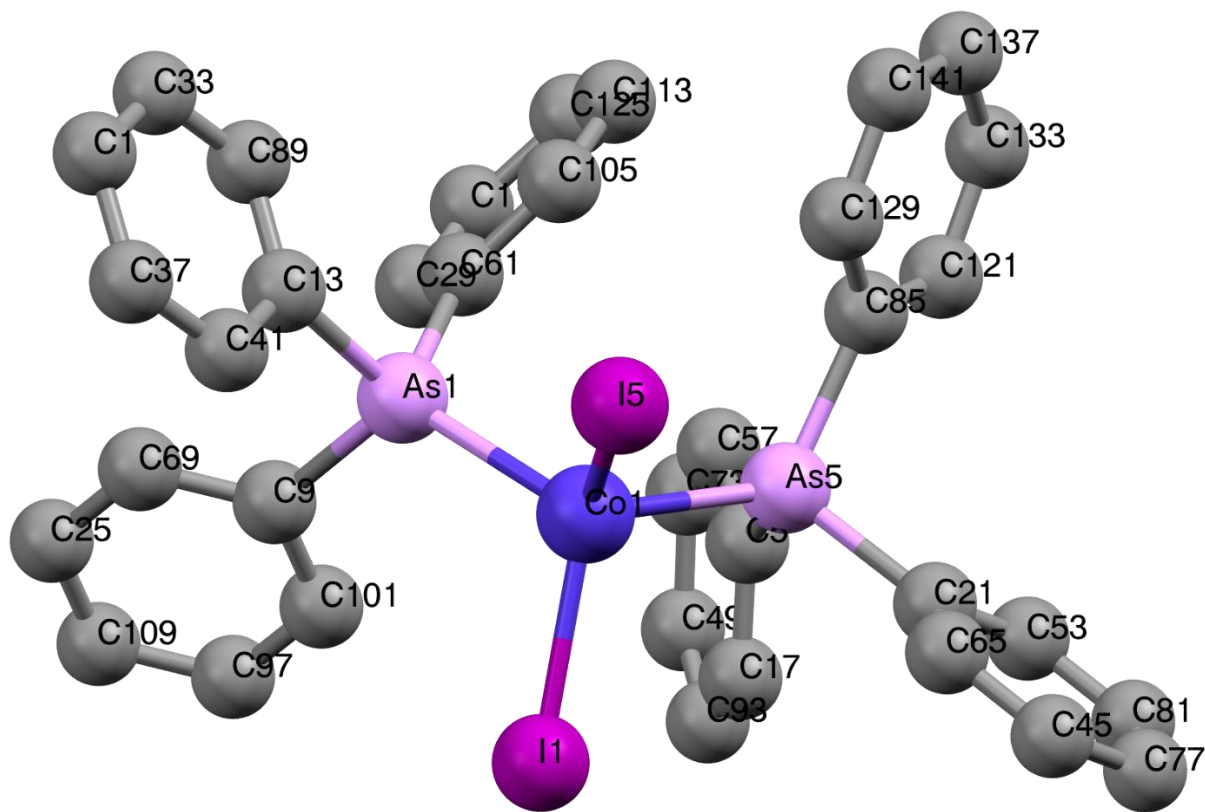


Figure A2.21. Model for the spin densities for $\text{Co}(\text{AsPh}_3)_2\text{I}_2$.

Table A2.5. Spin densities of atoms from VASP calculations for $\text{Co}(\text{AsPh}_3)_2\text{I}_2$. There are three other identical molecules in the lattice and their spin densities are not listed.

Atom label	Spin density	Atom label	Spin density
H1	0.000	C25	0.000
H5	0.000	C29	0.001
H9	0.000	C33	0.000
H13	0.000	C37	0.000
H17	0.000	C41	0.000
H21	0.000	C45	0.000
H25	0.000	C49	0.003
H29	0.000	C53	0.001
H33	0.000	C57	0.002
H37	0.000	C61	0.003
H41	0.000	C65	0.000
H45	0.000	C69	0.001
H49	0.000	C73	0.000
H53	0.000	C77	0.000
H57	0.000	C81	0.000
H61	0.000	C85	0.005
H65	0.000	C89	0.001
H69	0.000	C93	0.000
H73	0.000	C97	0.000

Table A2.5. Continued

H77	0.000	C101	0.000
H81	0.000	C105	0.001
H85	0.000	C109	0.001
H89	0.000	C113	0.000
H93	0.000	C117	0.000
H97	0.000	C121	0.002
H101	0.000	C125	0.001
H105	0.000	C129	0.000
H109	0.000	C133	0.001
H113	0.000	C137	0.000
H117	0.000	C141	0.000
C1	0.001	Co1	2.558
C5	0.003	As1	0.015
C9	0.004	As5	0.019
C13	0.003	I1	0.067
C17	0.003	I5	0.064
C21	0.002	Total	2.7635

Table A2.6. Summary of spin densities for $\text{Co}(\text{AsPh}_3)_2\text{I}_2$

Atoms	Ranges of spin densities
Co^{II}	2.558
I	0.064–0.067
As	0.015–0.019
C	0.000–0.005
H	0.000

Addenda for Chapter 3

A3.1. Experimental section

The reactions were carried out in room temperature aerobic conditions. Unless otherwise noted, chemicals and solvents were obtained from commercial sources and used without purification. Triethylamine was distilled before use. Elemental analysis was conducted by Galbraith Laboratories, Inc., Knoxville, Tennessee.

A3.1.1. Synthesis of *n*-(2'-pyridinyl)acetoacetamide (paaH) (**2**)

Compound **2** was synthesized as previously reported, and purified using a silica gel column.³⁷⁹ Purity was confirmed by ¹H NMR.

A3.1.2. Synthesis of [Dy₃(μ₃-OH)(teaH₂)₃(paa)₃]Cl(OMe)·PhCN·3MeOH (**Dy₃-2**)

Dy₃-2 was synthesized using a procedure similar to that reported.²⁶¹ Solvents were changed from MeCN/MeOH to PhCN/MeOH. In addition, Et₂O vapor diffusion (**Figure A3.1**) was used to grow crystals large enough for single-crystal X-ray and neutron diffraction (**Figure A3.2**). Into a solution of PhCN/MeOH (1:1 v/v, 14 mL), 0.38 g (1.0 mmol) of DyCl₃·6H₂O is dissolved (with 10 min mixing), followed by the addition of 0.18 g (1.0 mmol) of paaH and 0.55 mL (0.40 g, 4.0 mmol) of NEt₃. The solution is mixed for a few minutes, and then 0.13 mL (1.0 mmol) triethanolamine (teaH₃) is added. The solution is stirred for 3 h. This mother liquor is then filtered through a fine filter paper before being placed inside an Et₂O vapor diffusion set up (**Figure A3.1**). Crystals are observed within 3-4 days, while large, hexagonal block-like crystals take up to 4 weeks to form, to give 0.252 g (0.144 mmol, 43% yield) of **Dy₃-2** based on DyCl₃·6H₂O. IR spectrum of a crystal is given in **Figure A3.3**. Elemental analysis - Calculated

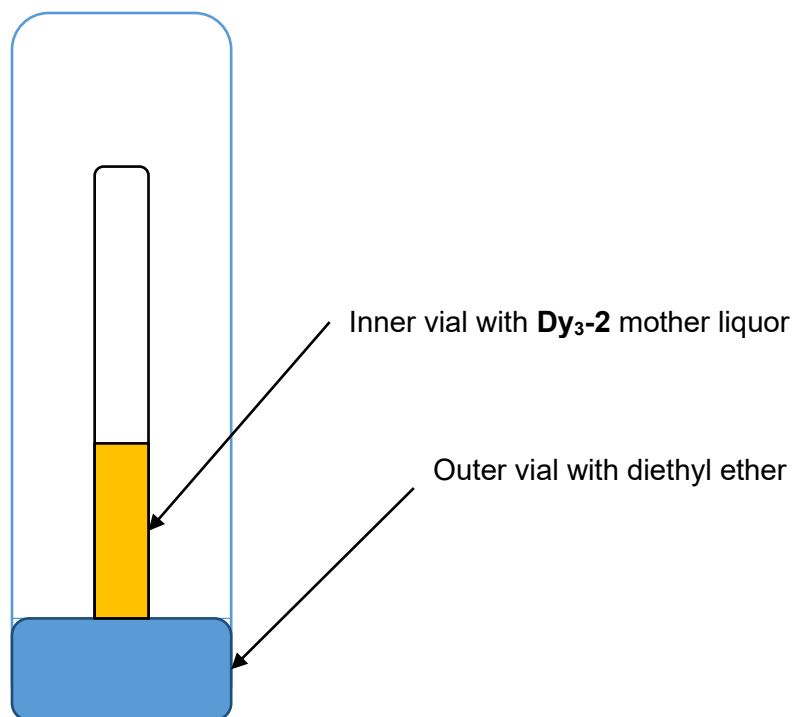


Figure A3.1. Depiction of diethyl ether vapor diffusion setup used for growth of **Dy₃-2** crystals. The system is sealed, and the ether vapor slowly mixes with the mother liquor of PhCN/MeOH to precipitate out crystals. Crystals are then removed from the walls of the inner vial for collection.

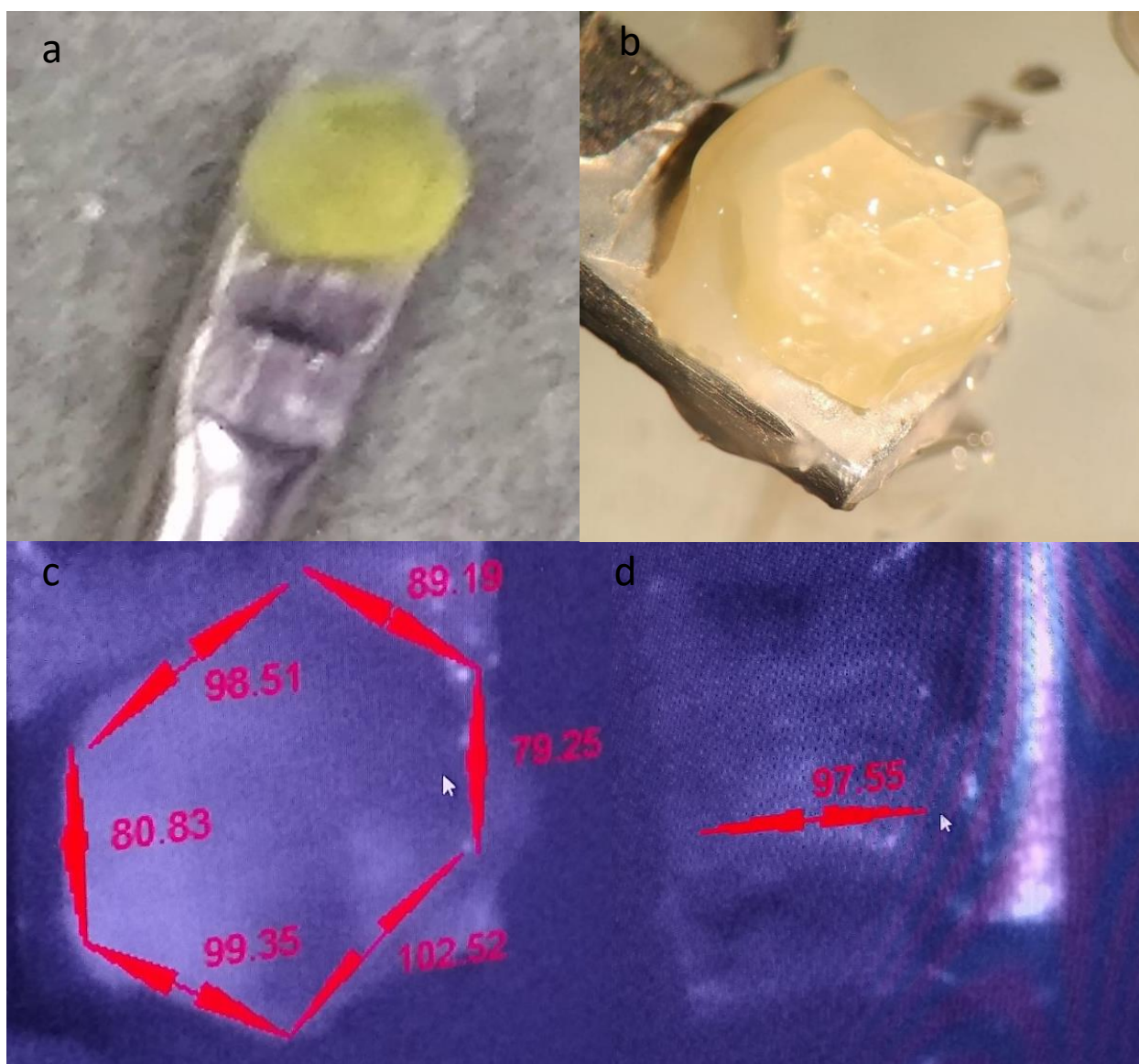


Figure A3.2. Images of the crystal used of PND experiment. a) is the sample before applying grease and measuring; b) the sample weeks after the experiment; c) and d) show the size of the crystal when mounted in the instrument.

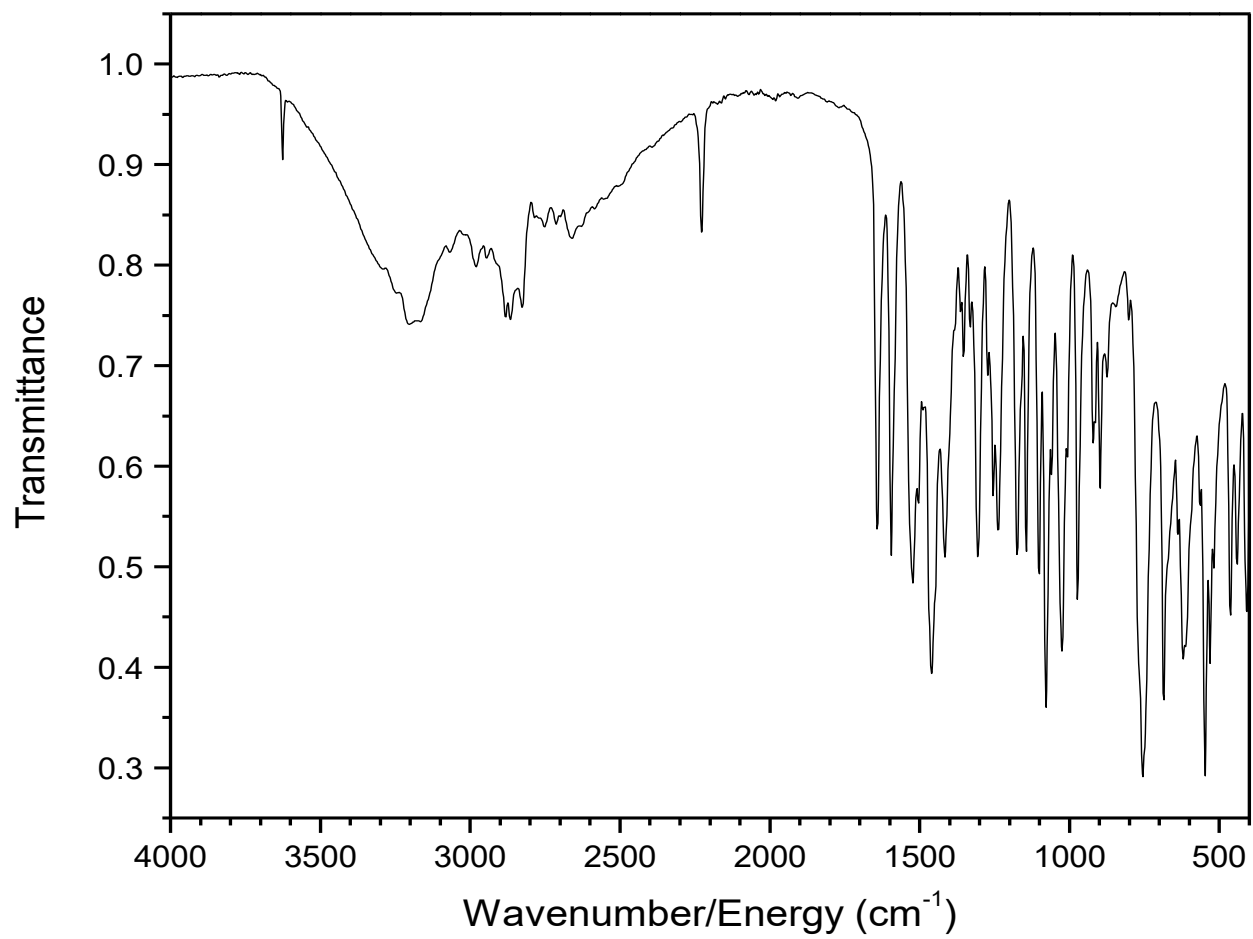


Figure A3.3. IR spectrum of a crystal of **Dy₃-2** at 23 °C.

for $C_{56}H_{90}ClDy_3N_{10}O_{20}$: C, 38.52; H, 5.19; N, 8.02. Found: C, 37.14; H, 4.99; N, 8.09. The lower C and H percentages may be a result of solvent loss from the crystals. The crystals are typically kept inside the solution that they grew from until use.

A3.2. Physical measurements

A3.2.1. X-ray crystallography

Single-crystal X-ray diffraction data for **Dy₃-2** was collected using a Bruker D8 Venture at 100 K with Mo $K\alpha$ radiation. Data collection and integration was completed using APEX 3 programs, reduced using Bruker SAINT, and corrected for absorption using the SADABS multi-scan program. Reflections were merged using SHELXL, with computing graphics by Olex2.³⁸⁰⁻

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Table A3.1. Crystallographic details for **Dy₃-1** (previously reported by Langley et al.^{261,276}) and **Dy₃-2**

	Dy₃-2	Dy₃-1 ^{261, 276}
Formula	Dy ₃ C ₅₆ H ₉₀ N ₁₀ O ₂₀ Cl	Dy ₃ C ₄₇ H ₈₁ O ₂₀ N ₁₀ Cl ₂
Formular weight	1746.32	1664.55
Temperature (K)	100(2)	123(2)
Crystal system	Trigonal	Trigonal
Space group	<i>P</i> $\bar{3}$ <i>c</i> 1 (165)	<i>P</i> $\bar{3}$ (147)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	17.5420(6), 17.5420(6), 26.4299(13)	17.5986(3), 17.5986(3), 13.1888(5)
α , β , γ (°)	90, 90, 120	90, 90, 120
<i>V</i> (Å ³)	7043.4(6)	3537.46(16)
<i>T</i> (K)	100(2)	123(2)
<i>Z</i>	4	2
ρ_{calc}	1.647	1.555
λ (Å)	0.71073	0.71073
Data measured	269480	36880
Independent reflections	7678	5400
Parameters	397	308
Restraints	73	51
<i>R</i> 1 ^a [<i>I</i> > 2σ(<i>I</i>)], <i>wR</i> 2 ^a (All data)	0.0227, 0.0594	0.0247, 0.0680
Goodness of fit	1.120	1.128

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$;

$w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = [2F_c^2 + \text{Max}(F_o^2, 0)] / 3$

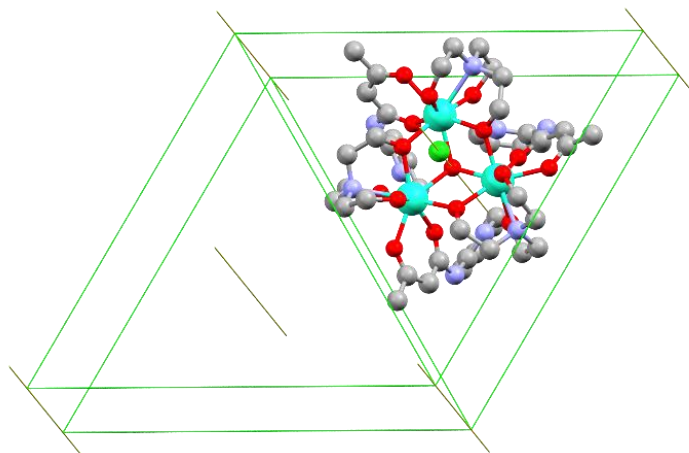


Figure A3.4. Rotational symmetry elements for **Dy₃-2**. Green lines show 2-fold rotation, while yellow lines show 3-fold rotation. There is a 3-fold rotation through the center of the **Dy₃-2** molecule.

Table A3.2. Continuous shape measurements (CShM) for **Dy3-2** and **Dy3-1**. Values closer to zero show a better fit to the symmetry described.

<i>CShM</i>	<i>Symmetry</i>	Dy3-2	Dy3-1
Octagon	D_{8h}	31.829	31.968
Heptagonal pyramid	C_{7v}	23.728	23.736
Hexagonal bipyramid	D_{6h}	14.289	14.214
Cube	O_h	12.171	12.177
Square antiprism	D_{4d}	2.508	2.579
Triangular dodecahedron	D_{2d}	1.344	1.368
Johnson - Gyrobifastigium (J26)	D_{2d}	9.743	9.686
Johnson - Elongated triangular bipyramid (J14)	D_{3h}	26.979	26.938
Johnson - Biaugmented trigonal prism (J50)	C_{2v}	2.150	2.142
Biaugmented trigonal prism	C_{2v}	2.098	2.099
Snub disphenoid (J84)	D_{2d}	2.378	2.378
Triakis tetrahedron	T_d	12.591	12.665
Elongated trigonal bipyramid	D_{3h}	22.562	22.551

The best symmetrical fit for both **Dy₃-1** and **Dy₃-2** is the triangular dodecahedron showing local D_{2d} symmetry. Minor differences in bonding and bond angles are observed in the local geometry between these two complexes. These differences in local symmetry around the Dy³⁺ ion may lead to changes in the magnetic character of these complexes.

Reference polyhedral and cartesian coordinates were generated using the cif previously discussed for **Dy₃-2** in the CrystalExplorer program.^{170, 173} Cartesian coordinates were then used to make an input file for *Continuous Shape Measurement (CShM)* following typical procedures referenced in the manual.^{383, 384} Cartesian coordinates for **Dy₃-1** were taken from a previously reported cif.²⁶¹

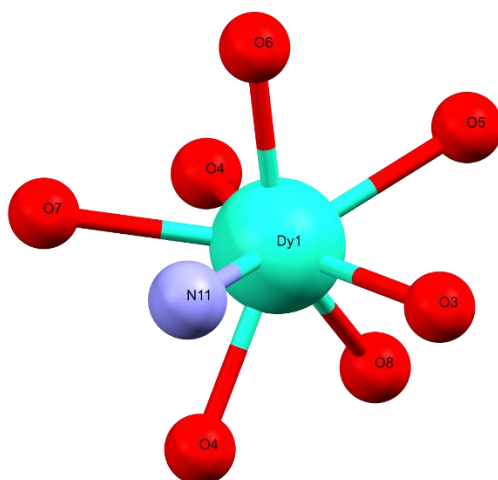


Figure A3.5. The **Dy₃-2** model used for *CShM*.

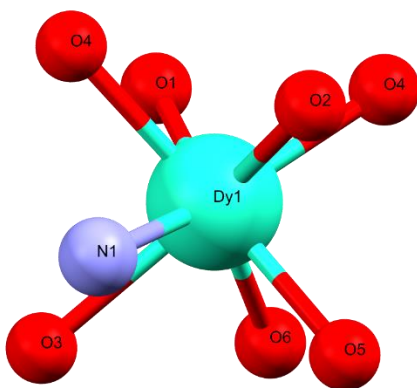


Figure A3.6. The **Dy₃-1** model used for *CShM*.

A3.2.3. Magnetic susceptibility measurements

DC magnetic susceptibility measurements were completed using a Quantum Design MPMS-7 T at the SmartState Center for Experimental Nanoscale Physics, University of South Carolina. Magnetization by variable temperature and variable magnetic field was collected. Measurements were taken of a powdered sample as well as single crystals oriented in multiple directions. Single crystals were coated with a thin layer of silicon grease to protect the crystal from degradation.

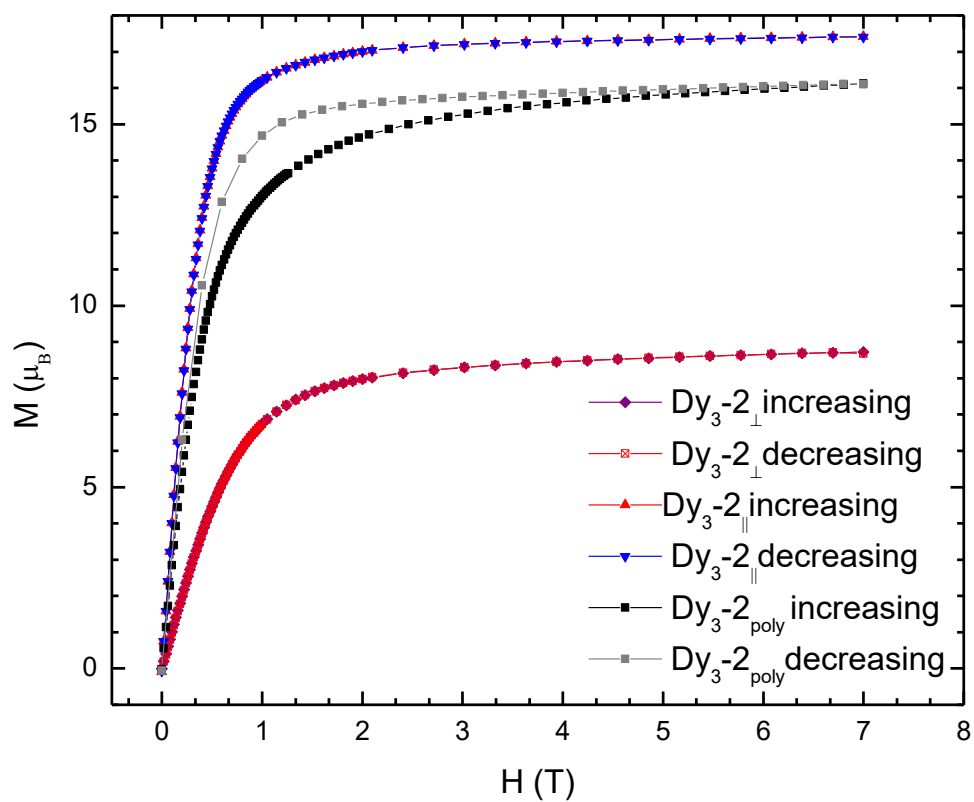


Figure A3.7. M vs H plots for **Dy₃-2_{poly}**, **Dy₃-2_l**, and **Dy₃-2_⊥**. This is data from **Figure 3.5** compiled together to show magnetic anisotropy of the single crystal sample orientation.

A3.2.4. Polarized neutron diffraction (PND)

The HB-3A DEMAND³⁰¹ at the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL) was used to perform the polarized single crystal neutron diffraction measurements with a polarized neutron beam of 1.542 Å from a bent Si-220 monochromator³⁰² and a calibrated neutron polarization of 76%. The sample was measured at 5 K with $H//ab$ and a permanent magnetic set was used to fix the field to 0.6 T. The CrysPy software⁶⁹ was used to analyze the measured flipping ratios.

A3.2.5. Neutron diffraction under variable-magnetic fields

The HB-3A DEMAND³⁰¹ at the High Flux Isotope Reactor (HFIR), Oak Ridge National Laboratory (ORNL) was used to perform the single crystal neutron diffraction measurements. The sample was measured at 1.5 K with a variable magnetic field ranging from 0 to 4 T. Data subtraction and integration was completed using FulProf.^{303, 304}

Addenda for Chapter 4

A.4.1. Synthesis

A4.1.1. Crystal growth trials

In attempts to obtain more crystalline products and grow crystals suitable for SCXRD, a variety of testing were performed. These variations include changes in the concentration of reactants from 1.0mmol of Ni(II) salts to a 20% scale, or 0.2 mmol of Ni(II) salts, within the same 7 mL of solvent. The second main variation was to change solvent. This included a 5:2 ratio of water/alcohol as well as the 4:3 ratio of water to alcohol. Alcohols that were used in the tests were methanol, ethanol, isopropanol, and *t*-butanol. Of all these tests, the alcohols producing the most crystalline materials were ethanol and isopropanol. Butanol decreased crystalline size and increased the amount of powder produce. Methanol seemed to not change the crystallization of the products. The reaction conditions that produced the highest volume of crystalline product was at a 25% scale of reactants within a 4:3 water/ethanol solvent.

There were also attempts at reducing reaction time from 144 h to 72 h. This led to the completion of the reaction when checked by PXRD and IR, but the product was a very fine powder, even when a 25% scale was used.

NiBaO-*d_n* and **NiBeO-*d_n*** were synthesized using the standard reaction conditions (7 mL of water and 144 h at 170 °C and concentrations (1.0 mmol) with the partially deuterated ligands.

A4.1.2. Deuteration reactions

Deuteration of 1,2-di(pyridin-4-yl)ethane (bpa) and 1,2-di(pyridin-4-yl)ethene (bpe) was completed as described in the experimental portion of the text. There were other reactions and attempts for deuteration, with very low levels of success. These included the use of WCl₆ and

C_6D_6 ,³²⁶ or the use of Pd/C with D_2O ,^{325, 327} which were similar to previously reported H/D exchanges. These H/D exchange reactions gave significantly lower levels of deuteration than the base-mediated reaction during initial testing and therefore were not studied further.

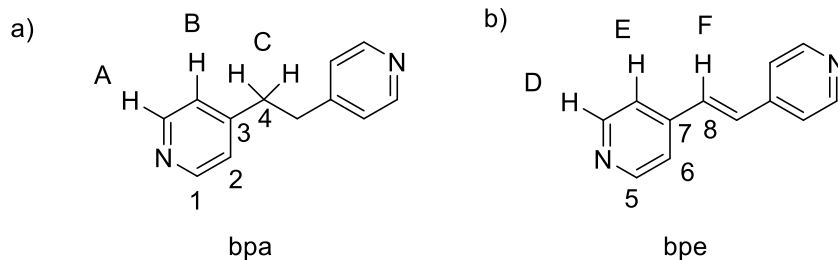


Figure A4.1. Schematic showing locations of H atoms for H/D exchange for a) bpa and b) bpe.

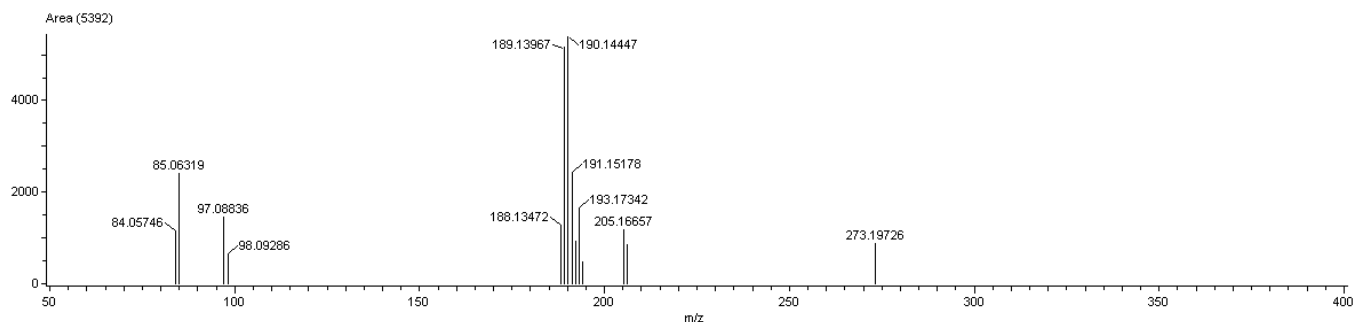


Figure A4.2. Mass spectrometry data representative of bpa deuteration. Without any deuterium, bpa should have a main mass peak of 184. Each main mass peak of 1 m/z higher should be correlated to an H-D exchange. The two strongest peaks at 189 and 190 m/z are related to bpa- d_5 and bpa- d_6 , respectively.

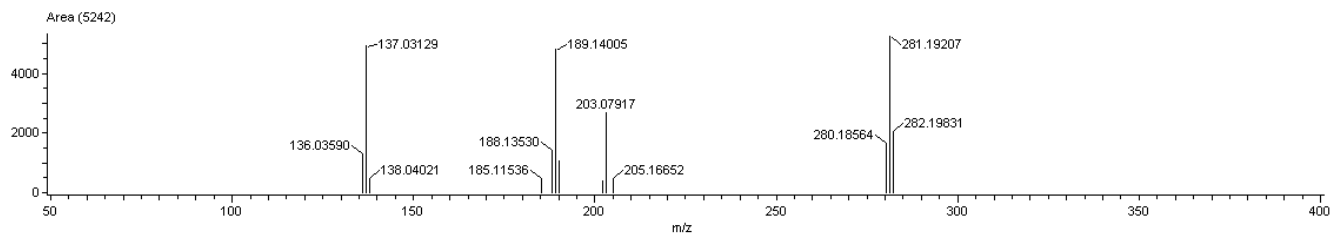


Figure A4.3. Mass spectrometry data representative of bpe deuteration. Without any deuterium, bpe should have a main mass peak of 182. The two strongest peaks at 188 and 189 m/z are related to bpe- d_6 and bpe- d_7 , respectively.

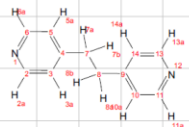


Figure A4.4. ^1H NMR of bpa standard before deuteration.

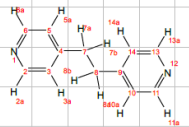


Figure A4.5. ^1H NMR of bpa after deuteration.

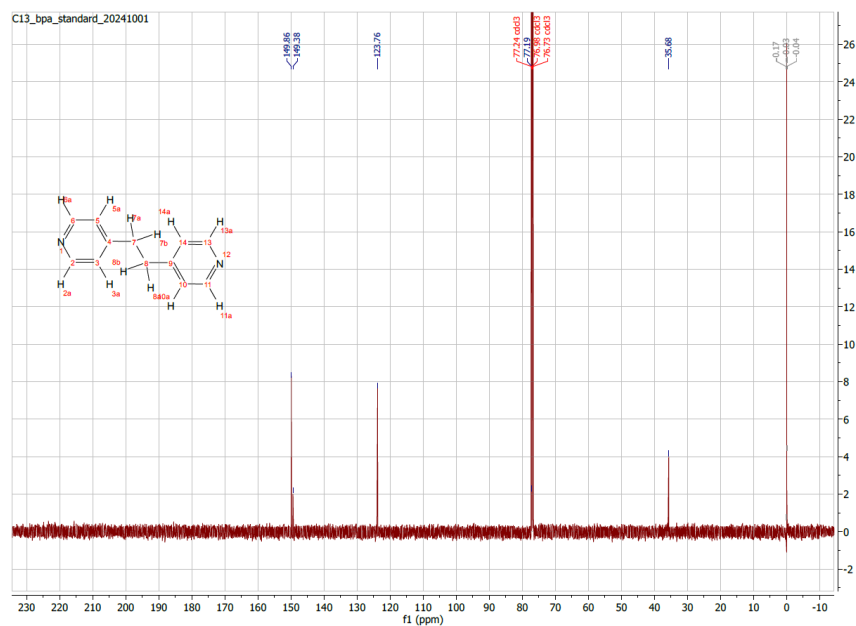


Figure A4.6. ^{13}C NMR of bpa standard before deuteration

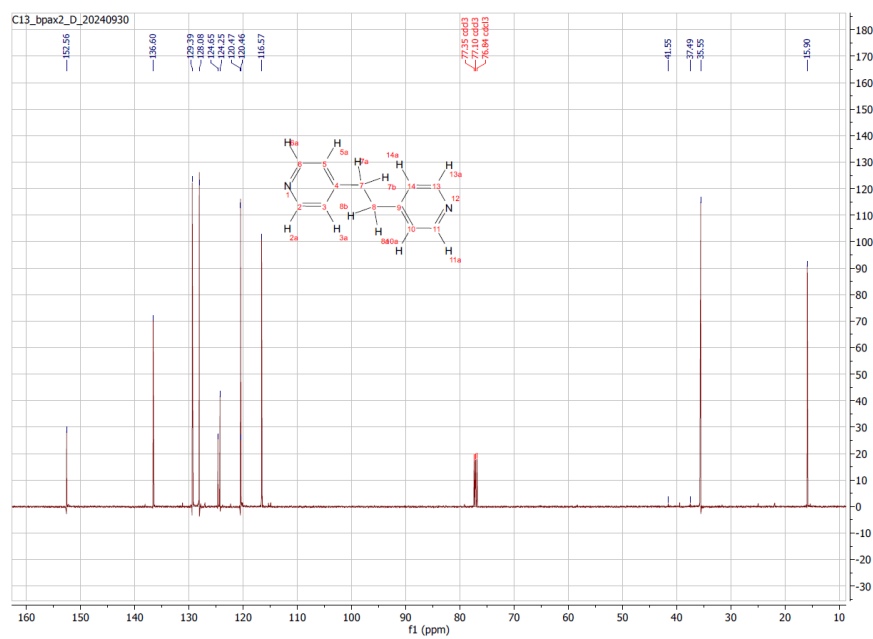


Figure A4.7. ^{13}C NMR of bpa after deuteration

A4.2. Physical measurements

A4.2.1. Variable temperature powder neutron diffraction

Additional variable temperature powder neutron diffraction plots of the low d-spacing region show that there is not significant data to reveal a phase change or the appearance of magnetic structure peaks in the PND data.

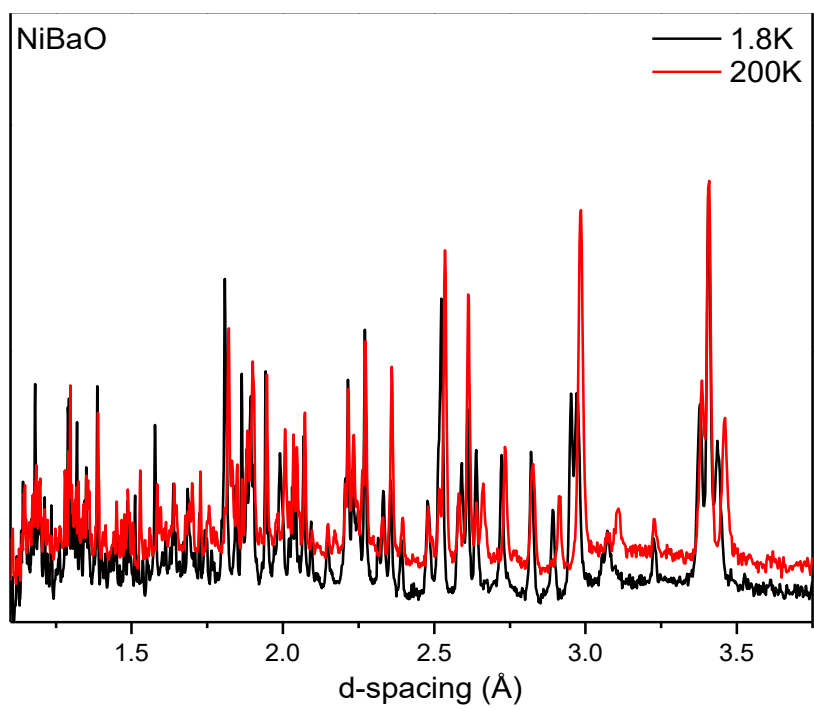


Figure A4.8. Emphasis on low d -spacing for **NiBaO**.

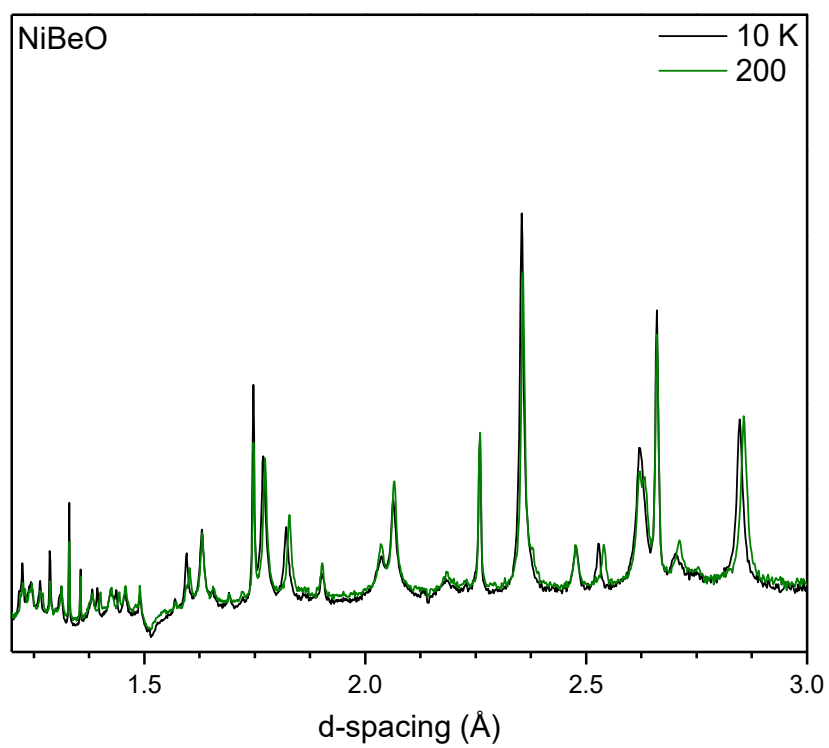


Figure A4.9. Emphasis on low d -spacing for **NiBeO**.

A.4.2.2. DC magnetic susceptibility

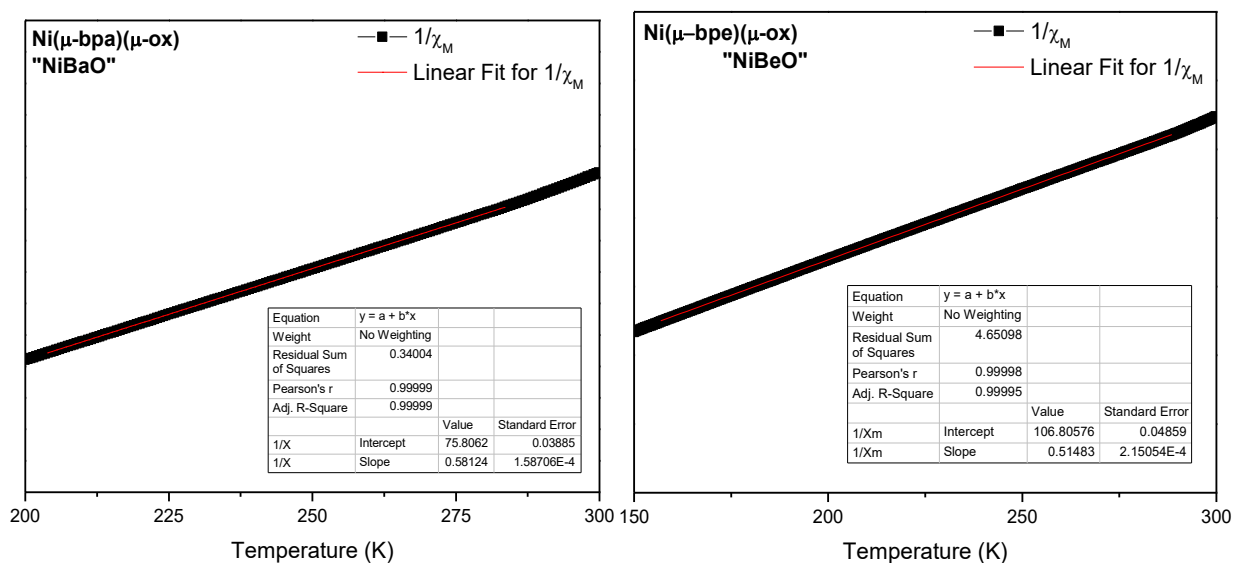


Figure A4.10. Fitting data for the high-temperature region of DC magnetometry.

A.4.2.2. Specific heat measurements

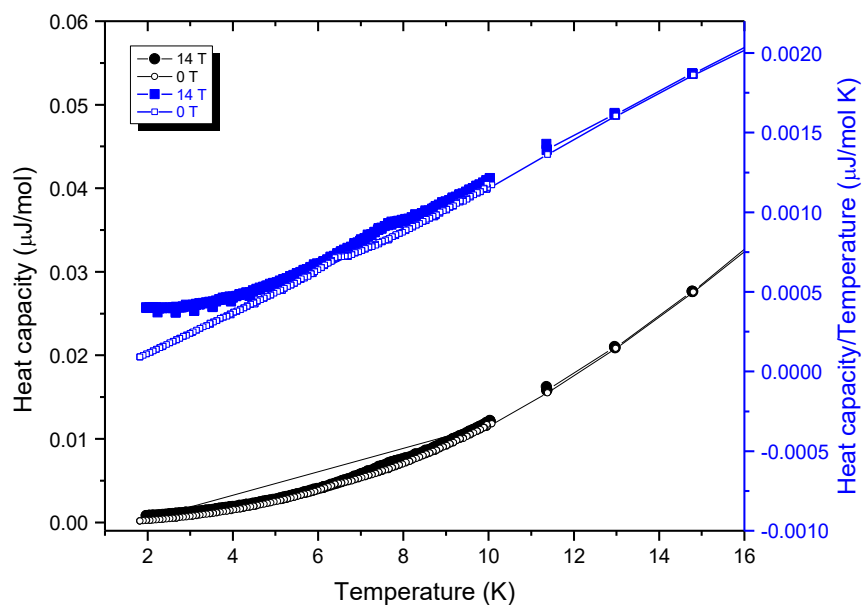


Figure A4.11. Heat capacity results of NiBaO from 1.8 K to 16 K at 0 and 14 T. There is no sharp uptick correlated to a phase change.

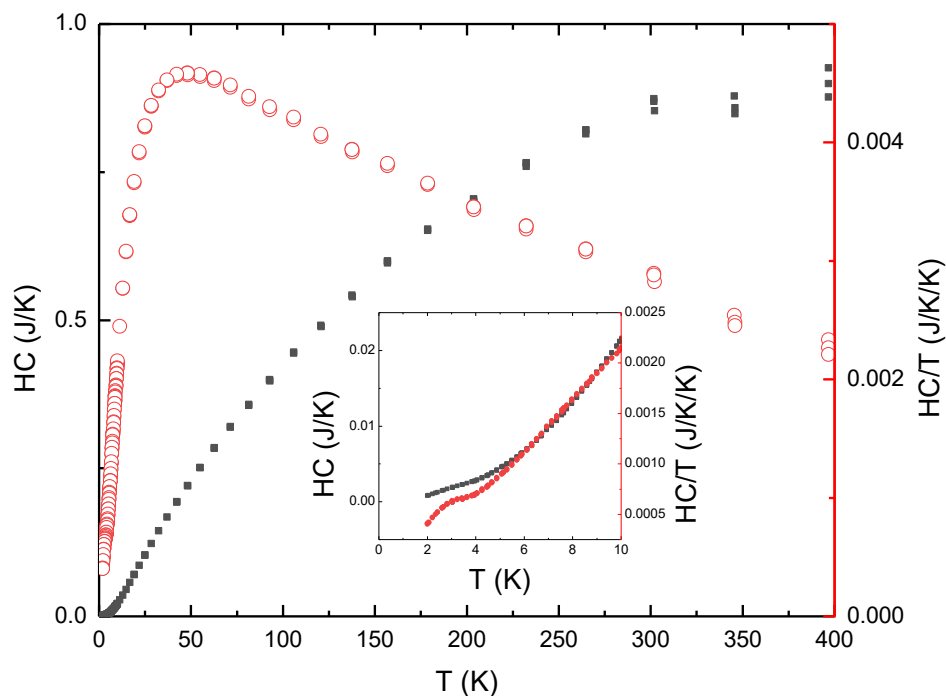


Figure A4.12. Heat capacity measurements of **NiBeO** from 1.8 K to 400 K. Inset is from 1.8 K to 10 K. There are no sharp changes indicating a phase change.

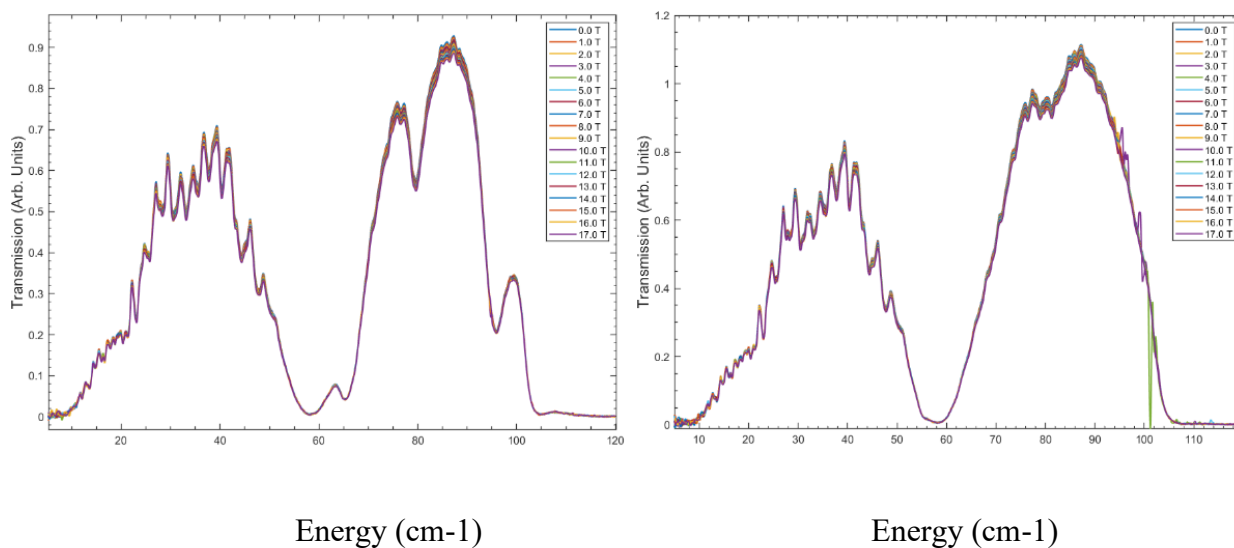


Figure A4.13. FIRMS spectra for (left) **NiBaO** and (right) **NiBeO**. There is no indication of magnetic transition within these spectra.

Table A5.1. Images of the reactions at different stages in the formation of CuO in three solutions

Notes	Acetone	Isopropanol	Water
Addition of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ to solvent with 3 min of mixing			
Addition of NaOH to solution with 3 min mixing			
After 10 min mixing			

Table A5.1. Continued

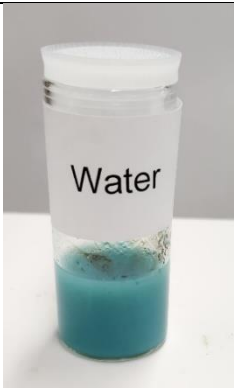
After 1 h mixing			
After 2 h mixing			
After 4 h mixing			

Table A5.1. Continued

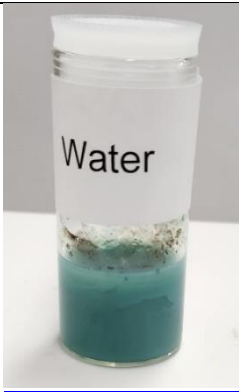
After 6 h mixing			
After 8 h mixing			
After 10 h mixing			

Table A5.1. Continued

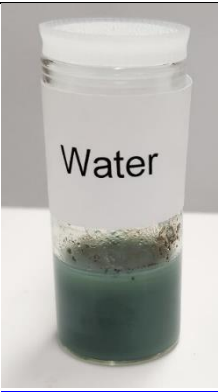
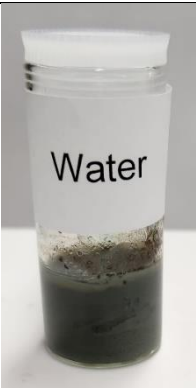
After 12 h mixing			
After 12 h mixing and settling for 1 min			
After 28 h mixing	No change from 12 h mark	No change from 12 h mark	

Table A5.1. Continued

After 72 h mixing and 5 min settling	No change from 12 h mark	No change from 12 h mark	
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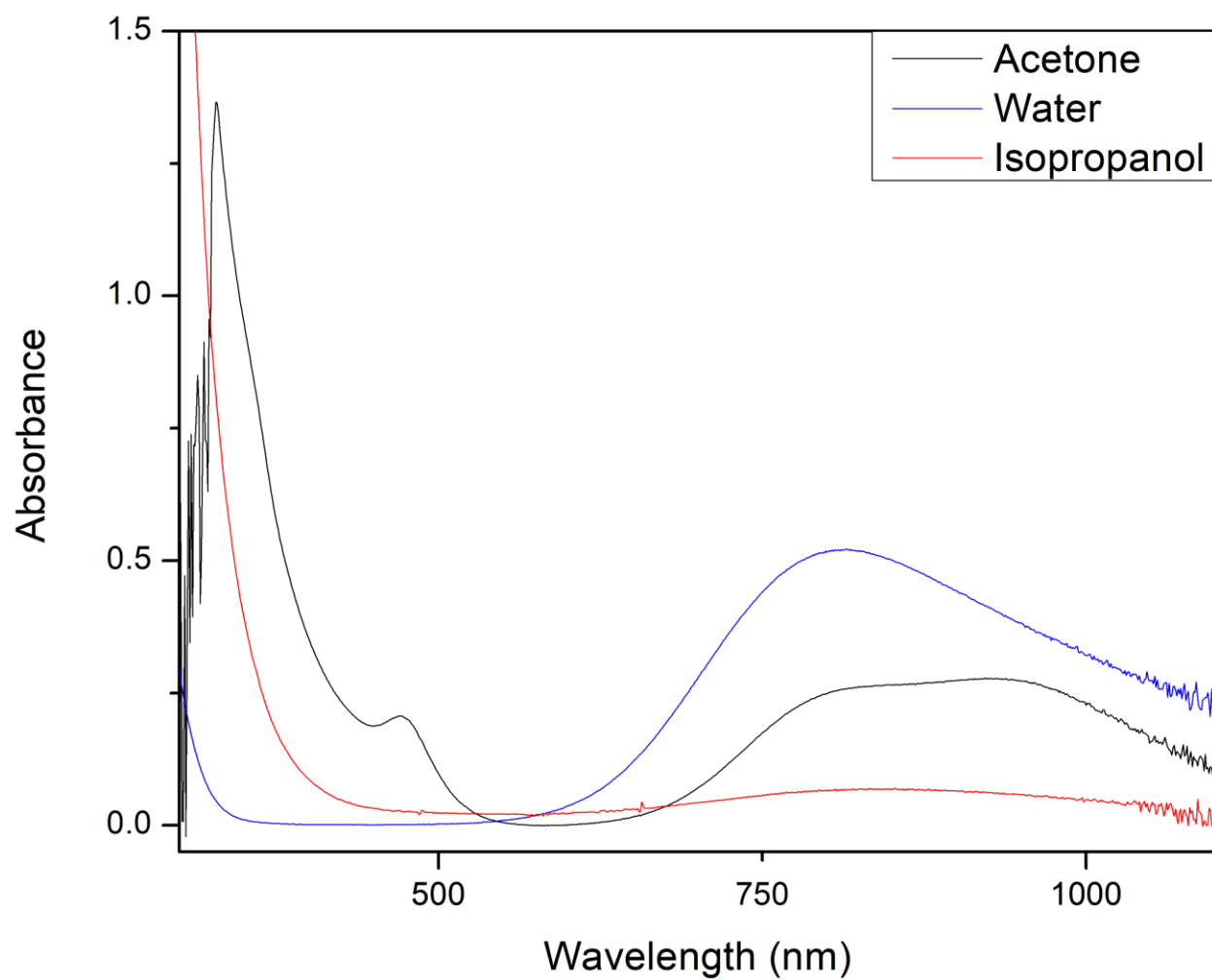


Figure A5.1. Full range of electronic absorption spectra at 300-1100 nm.

Table A5.2. List of solutions, their relative polarities,^{a, 339, 385} and the near-IR absorptions

Solvent	Relative Polarity^{339, 385}	Local Maxima (nm)
Acetone	0.355	927
Isopropanol	0.546	855
Water	1.00	815

^a The relative polarities are normalized from measurements of the transition energy at 25 °C of the long-wavelength visible absorption of a standard pyridinium N-phenolate betaine dye in Ref. 385.

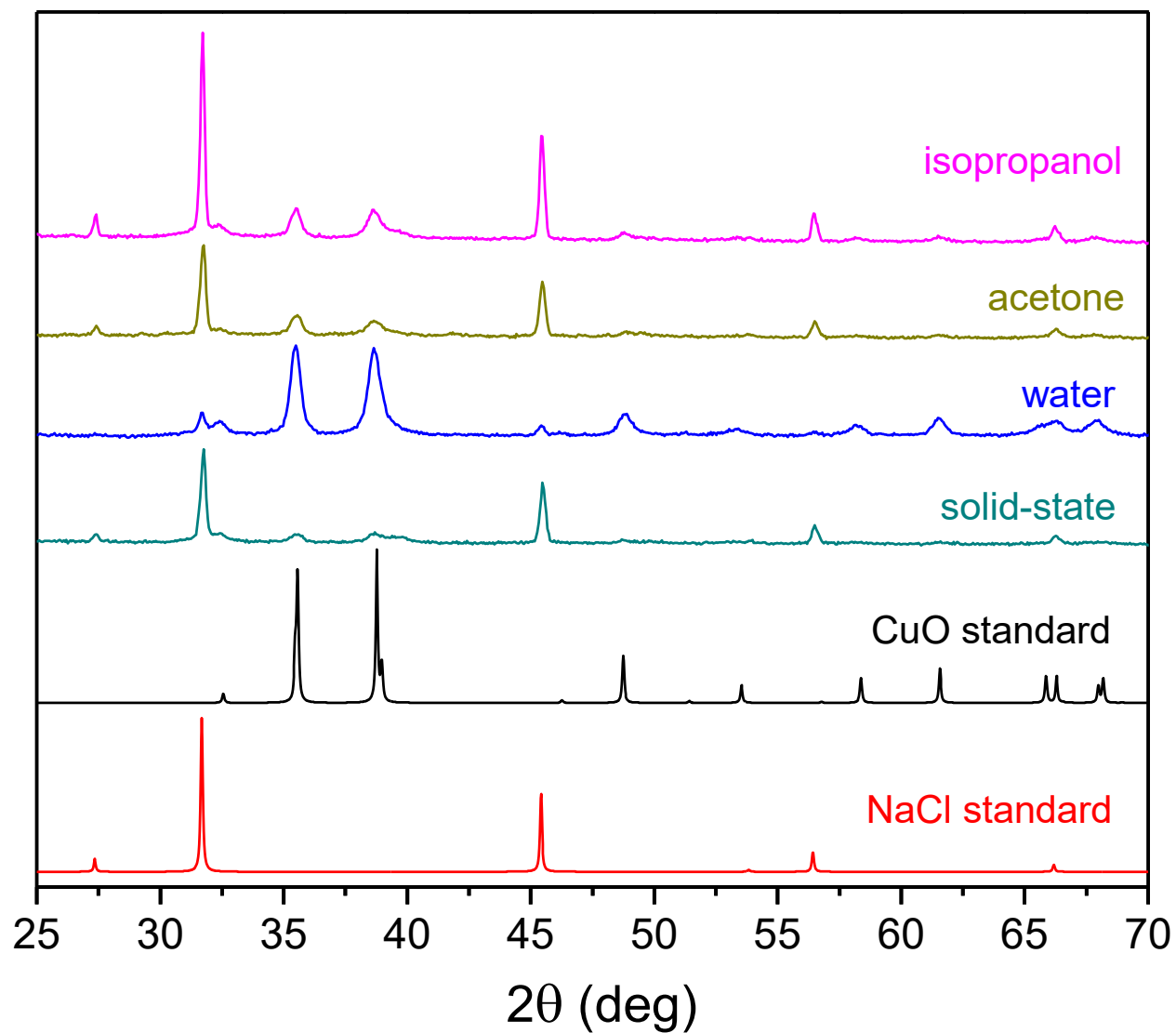


Figure A5.2. PXRD patterns of the products *without washing* from reactions conducted in isopropanol, acetone, water, and solid-state. The patterns of CuO and NaCl standards are given for comparison. The solids were heated in a 200 °C furnace for 20 min.

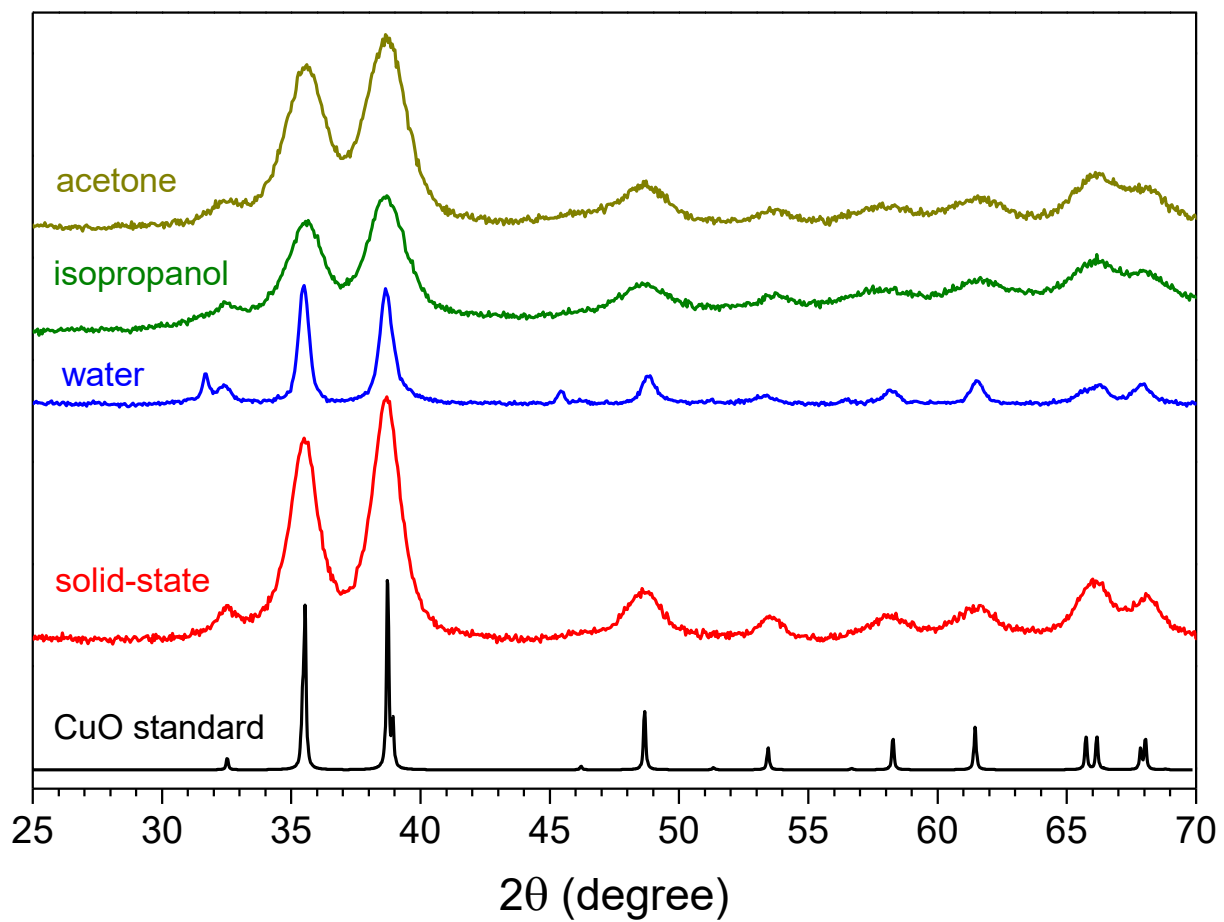


Figure A5.3. PXRD of CuO products dried with a heat gun. For the product from water, the solid was dried first, followed by washing. Trace NaCl diffraction peaks are visible in this PXRD pattern.

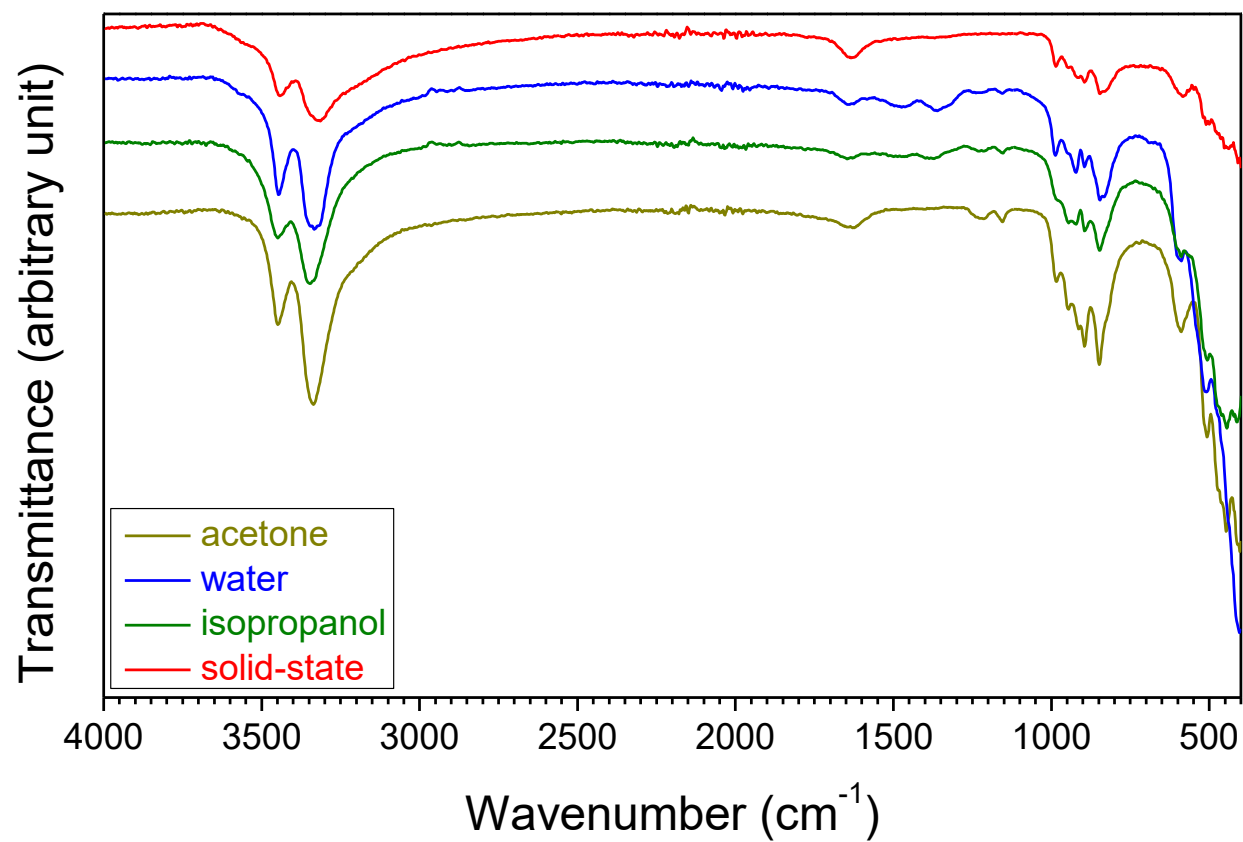


Figure A5.4. IR spectra of the products separated for clarity.

Vita

Michael J. Jenkins was born in Nampa, ID to Lawrence and Elaine Jenkins. He attended public school in the Vallivue School system, graduating from Vallivue Senior High School in 2012. He went on to attend Idaho State University and graduate with a B.S. in Chemistry. During undergraduate studies, Michael interned for ON Semiconductor in Pocatello in the EHS department focusing on improvements in wastewater treatment and updates to chemical monitoring. He also conducted undergraduate research under Dr. Andrew Holland, studying the formation of molecular precursors for I-III-VI₂ nanoparticles with photovoltaic applications. In 2020 Michael entered the graduate program of the University of Tennessee, where he studied molecular magnetism in the group of Dr. Zi-Ling Xue. During this time as a graduate student and researcher, he presented his work at the National Meeting of the American Chemical Society in August 2024 and co-authored several publications, including *Nat. Commun.* **2023**, *14*, 5454, with additional manuscripts in preparation for submission.