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To the Graduate Council:

I am submitting herewith a dissertation written by Lawrence Edward Moore entitled "Studies of Tetrakis(Pyridine Base)Nickel(II) Perchlorate and Bisperchloratotetrakis(Pyridine Base)Nickel(II) Complexes." I recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.


Major Professor

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STUDIES OF TETRAKIS(PYRIDINE BASE)NICKEL(II) PERCHLORATE AND
BISPERCHLORATOTETRAKIS(PYRIDINE BASE)NICKEL(II) COMPLEXES

A Dissertation
Presented to
the Graduate Council of
The University of Tennessee

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
Lawrence Edward Moore

August 1964

DEDICATED TO

MY MOTHER

589146

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CHAPTER I

INTRODUCTION

A. Some Theoretical Aspects of Nickel(II) Complexes

The stereochemistry of nickel(II) compounds has been one of the most active and controversial fields of research in inorganic chemistry during the last 10 years. The multitude of colorful nickel compounds has intrigued chemists for a much longer time, but only in relatively recent years have such tools as visible and infrared absorptiometry, group theory and quantum mechanics, magnetic measurements, x-ray studies, and conductance measurements been brought to bear effectively to unravel the questions on stereochemistry in metal complexes.

In general, the arrangement of ligands about the nickel(II) ion may be regarded as either octahedral, tetrahedral, or square planar. Since the subject is very closely connected with ligand-field theory, it is appropriate to discuss the ligand-field theory of the d^8 system along with the stereochemistries of the nickel(II) ion, following, in general, the review by Miller.¹

By far, the largest class of nickel compounds are those of 6-coordinate nickel(II). The six ligands are thought of as being situated at the corners of an octahedron with the nickel ion located at the center. In a cubic octahedral field (six identical ligands), the 5-fold degenerate 3d orbitals are split into an orbital triplet and an orbital doublet as

depicted in Figure 1 (a). The triplet t_{2g} level lies lower in energy than the doublet e_g level.^{*} Hence the lowest energy electron configuration may be written $(t_{2g})^6(e_g)^2$. There is only one way of arranging the electrons in this configuration, and it is therefore non-degenerate and not liable to Jahn-Teller distortions. The two electrons in the e_g orbitals are spin parallel (hence a triplet ground state), and, since there is no resultant orbital angular momentum for the $(t_{2g})^6(e_g)^2$ ground state, one expects to find magnetic moments close to the spin-only value of 2.83 Bohr magnetons (B. M.). For regular octahedral nickel(II) compounds, magnetic moments normally fall in the range 3.0-3.3 B. M.; these higher values are readily explained when the orbital angular momentum arising from the first excited state is considered.

Interpretation of near-infrared and visible spectra using ligand field theory has developed from the basic principles^{**} set forth by Orgel.² Figure 2 is a simplified Orgel diagram showing the splittings of the lower four free-ion electronic states by a regular octahedral field. Transitions may take place from the ${}^3A_{2g}$ ground state^{***} to higher triplet states; hence, three bands should appear in the spectrum,

*The conventional symbols are as follows: orbital triplet, d_{xy} , d_{yz} , $d_{zx} \equiv d_{\pi}$; in octahedral field, t_{2g} , in tetrahedral, t_2 ; orbital doublet, $d_{x^2-y^2}$; $d_{z^2} \equiv d_{\sigma}$; in octahedral field, e_g ; in tetrahedral, e .

**The idea behind crystal field theory occurred to J. Becquerel in 1929, and in that same year H. Bethe formulated the idea into an exact theory. Van Vleck and Mulliken furthered the development of crystal and ligand field theories, and Orgel introduced the subject to the experimental chemist.

***The symbols are those of Mulliken. See reference 3, p. 71.

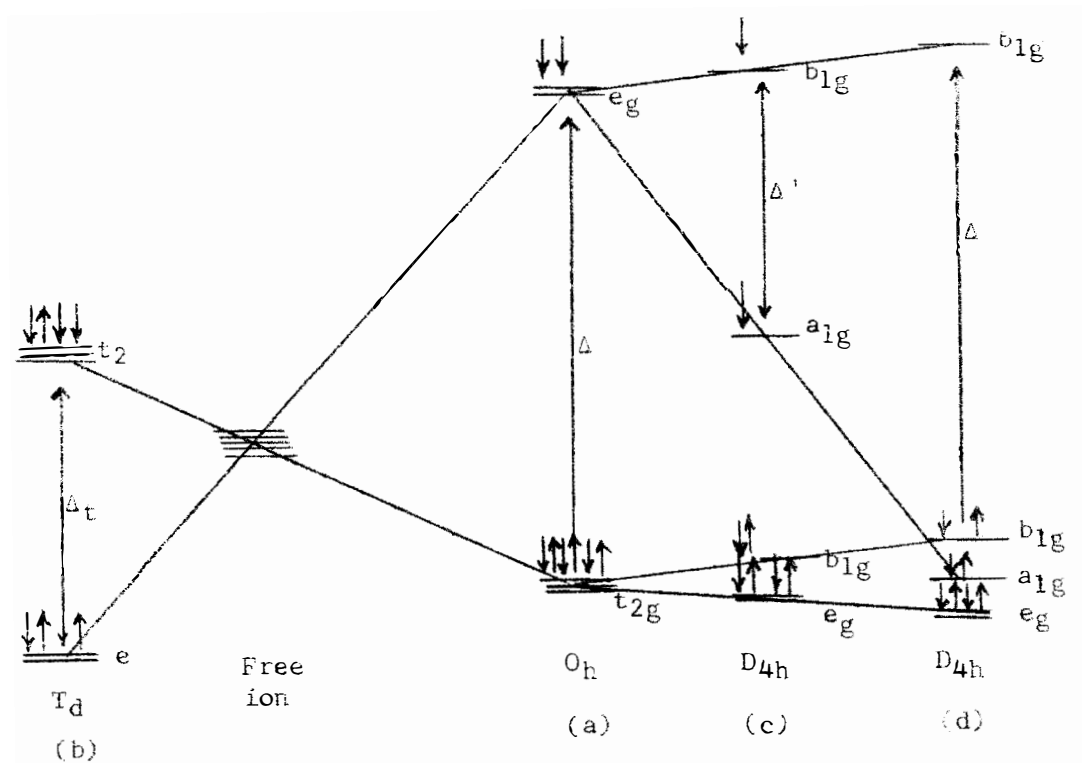


Figure 1. Splitting of 3d-orbitals in (a) octahedral, (b) tetrahedral, (c) weak, and (d) strong tetragonally distorted octahedral fields.

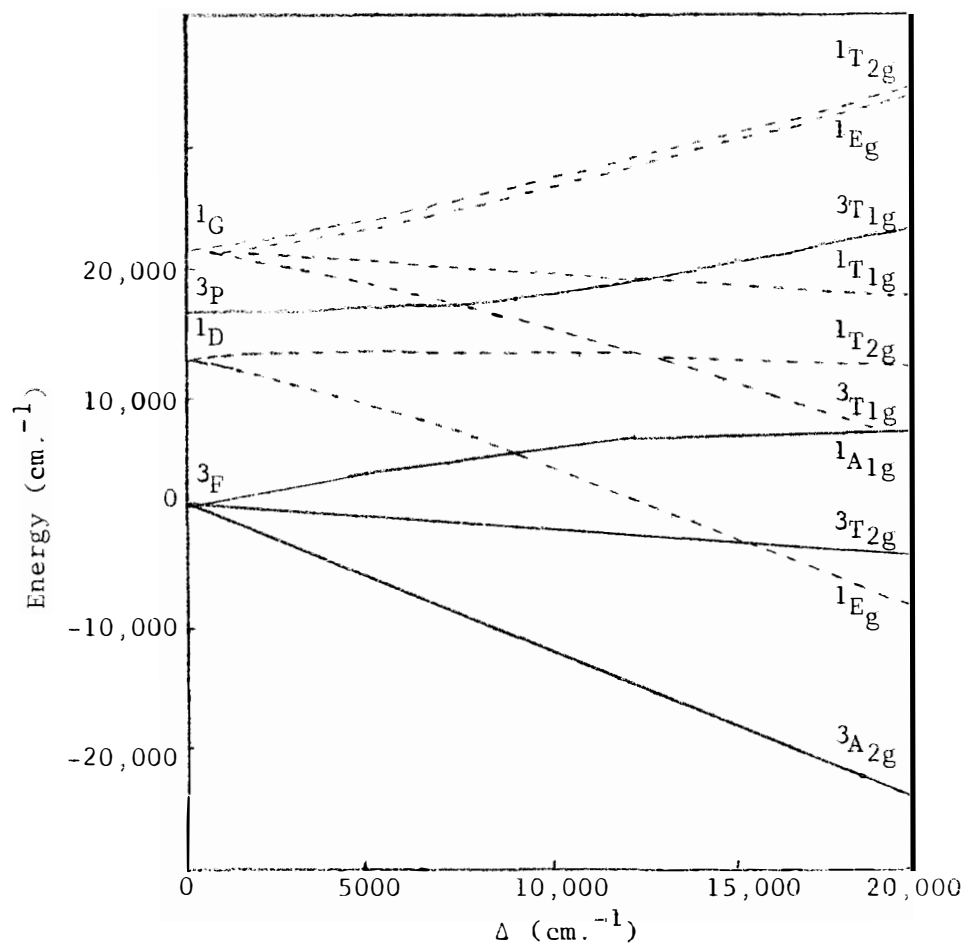


Figure 2. Energy levels for Ni^{+2} ion (d^8) in an octahedral field.

and these are indeed observed for numerous octahedral nickel(II) complexes. The classic examples are the spectra of the hexaquo nickel(II) ion and the trisethylenediaminenickel(II) ion as shown in Figure 3.⁴ The bands may be assigned as in Table I. The splitting of the center band in the spectra of the hexaquo and many other nickel complexes has been the subject of considerable controversy.^{5,6} The symmetry-forbidden nature of the transitions results in the characteristic low intensities of the bands: absorptivity indexes fall in the range 1 to 50. The position of the visible band results in colors for octahedral nickel(II) compounds ranging from green to blue and violet as the field strength increases.

It was long believed that many seemingly 4-coordinate paramagnetic nickel(II) compounds were tetrahedral in structure. The emergence of ligand-field theory was followed by the re-examination of these supposedly tetrahedral complexes in view of the calculation showing that the crystal-field stabilization energy works out to be $0.84\Delta^*$ greater for an octahedral complex than for a tetrahedral complex with the same ligands.¹ Although other factors (entropies, solvation energies, etc.) play a part in governing the relative stabilities of complexes, the 20-40 kilocalories per mole difference in stabilization energy (corresponding to 0.84Δ) leads one to expect octahedral complexes to form with nickel (II) so long as two extra ligands are available. Re-examination showed

^{*} Δ is the energy corresponding to the orbital splitting in the octahedral case. Δ_t is the splitting for a tetrahedral complex.

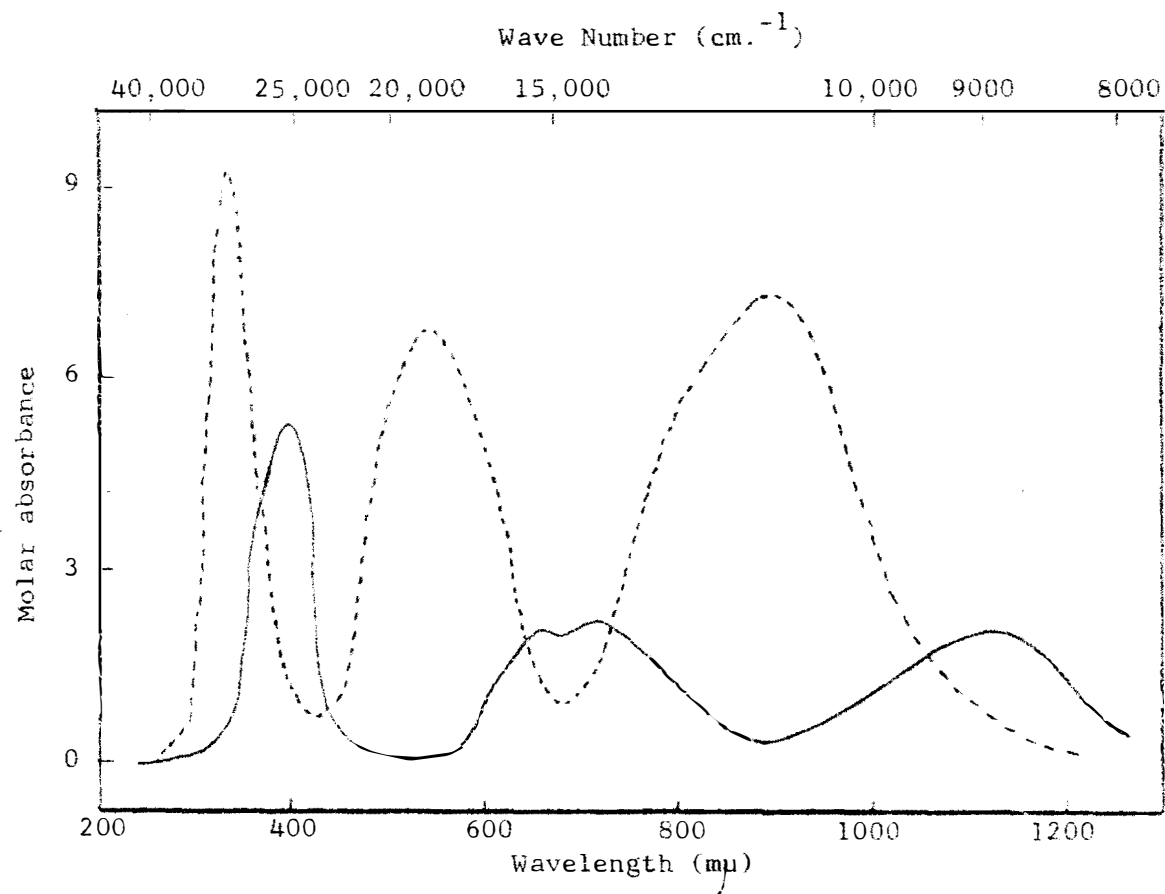


Figure 3. Near-infrared and visible absorption spectra of octahedral complexes of nickel(II); $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$ (—) and $[\text{Ni}(\text{en})_3]^{+2}$ (-----).

TABLE I
APPROXIMATE BAND POSITIONS FOR OCTAHEDRAL NICKEL(II) COMPLEXES

Transition	$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ cm. ⁻¹	$[\text{Ni}(\text{en})_3]^{2+}$ cm. ⁻¹
${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{2g}$	9,000	11,000
${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g}(\text{F})$	14,000	18,500
${}^3\text{A}_{2g} \longrightarrow {}^3\text{T}_{1g}(\text{P})$	25,000	30,000

without exception that the complexes in question were octahedral rather than tetrahedral: water or other solvent molecules which had been overlooked, or polymeric species, were found to account for occupation of the 5th and 6th coordination positions.

The search for tetrahedrally coordinated nickel(II) intensified; the first definitive case reported (1954) was in the spinel, NiCr_2O_4 .⁷ Since then, nickel(II) has been found to exist in tetrahedral environments in certain halide melts, in mixed crystals based on oxide or chloride lattices, and in complexes having bulky ligands. Some representative octahedral complexes are the blue $[\text{NiCl}_2(\text{OP}\phi_3)_2]$ (where $\text{OP}\phi_3$ is triphenylphosphine oxide), $[\phi_4\text{As}]_2[\text{NiCl}_4]$ (where $\phi_4\text{As}^+$ is the tetraphenylarsonium ion), and $[\text{Ni}(\phi_3\text{AsC})_2\text{Br}_2]$ (where $\phi_3\text{As}\bullet$ is triphenylarsine oxide).⁴

In a regular tetrahedral field, the 5-fold degeneracy of the 3d orbitals is split, as with an octahedral field, into an orbital triplet and an orbital doublet; however, the doublet e level lies lower than the triplet t_2 level in the tetrahedral case, as shown in Figure 1 (b). The ground state electronic configuration is therefore $(e)^4(t_2)^4$.

Since the ground state has 3-fold degeneracy (the 8th electron can be placed in any of three t_2 orbitals), there is a resultant angular momentum contribution to the magnetic moment. Thus, regular tetrahedral complexes should have a moment between 3.5 and 4.2 B. M.

The Orgel diagram for tetrahedral nickel(II), shown in Figure 4, has the energy levels inverted from those of the octahedral case. The

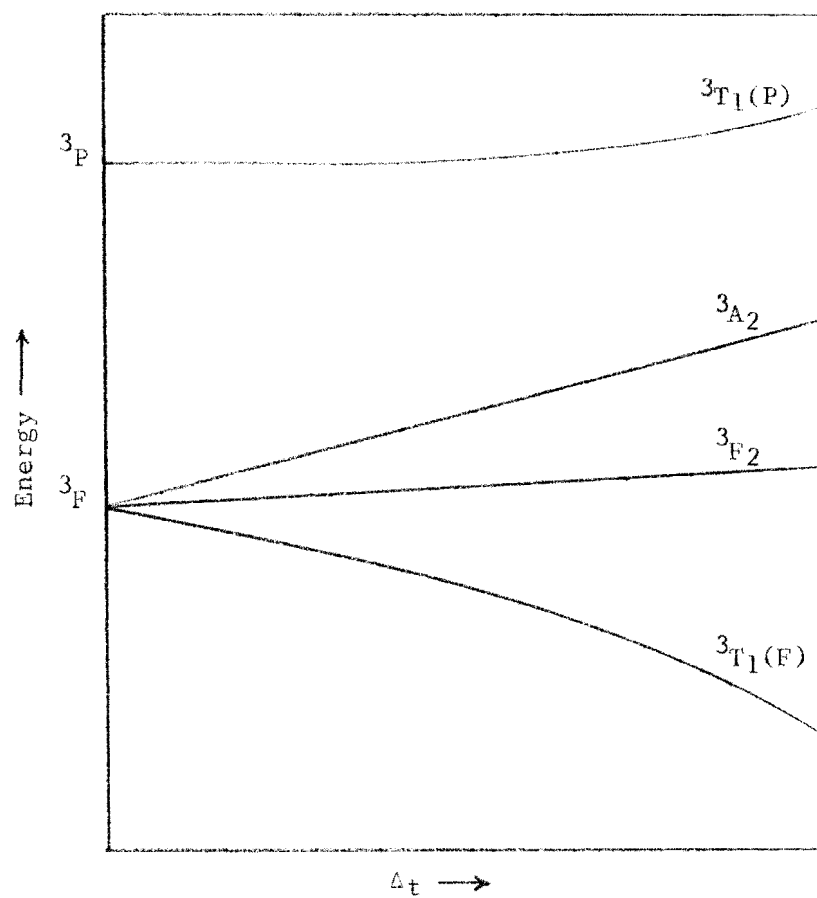


Figure 4. Triplet energy levels of a d^8 ion in a tetrahedral field.

ground state, ${}^3T_1(F)$, has the same symmetry properties as the higher ${}^3T_1(P)$ level, and the two states influence each other; since all transitions are from the ${}^3T_1(F)$ level, no transition corresponds to the splitting Δ_t . Three transitions to higher triplet states are possible, but since Δ_t is much smaller than in the octahedral case, the first transition, to ${}^3T_2$, lies well into the infrared and has not been observed. The spectrum of $[\text{Ni}(\text{O}_3\text{AsO})_2\text{Br}_2]$, as shown in Figure 5, is typical of nickel(II) ions in tetrahedral fields. The absorption band at about $15,000 \text{ cm}^{-1}$ is assigned to the $T_1(F) \rightarrow T_1(P)$ transition; the one at $7000\text{--}8000 \text{ cm}^{-1}$, to the $T_1(F) \rightarrow A_2$ transition. A notable feature of the spectra of tetrahedral nickel(II) complexes is the relatively high intensities of the bands. Since there is no center of symmetry in the point group T_d , there is mixing of the nickel d_{xy} -, d_{yz} -, and d_{zx} -orbitals with the p-orbitals. Thus, the transitions have some d-p character and are therefore not forbidden. This results in higher intensities (about 200 l./mole cm.) than the nearly pure d-d transitions of octahedral complexes.

The well known square-planar complexes of nickel(II) are best considered as the limit of tetragonal distortion of octahedral complexes. Referring to Figure 1 (c,d) one can see the effect on the energy levels of moving the ligands on the z-axis away from the nickel. As the e_g level splits into a_{1g} and b_{2g} levels in going from O_h to D_{4h} symmetry, the complex will remain paramagnetic so long as the separation energy between the a_{1g} and b_{2g} levels is less than the energy required to pair

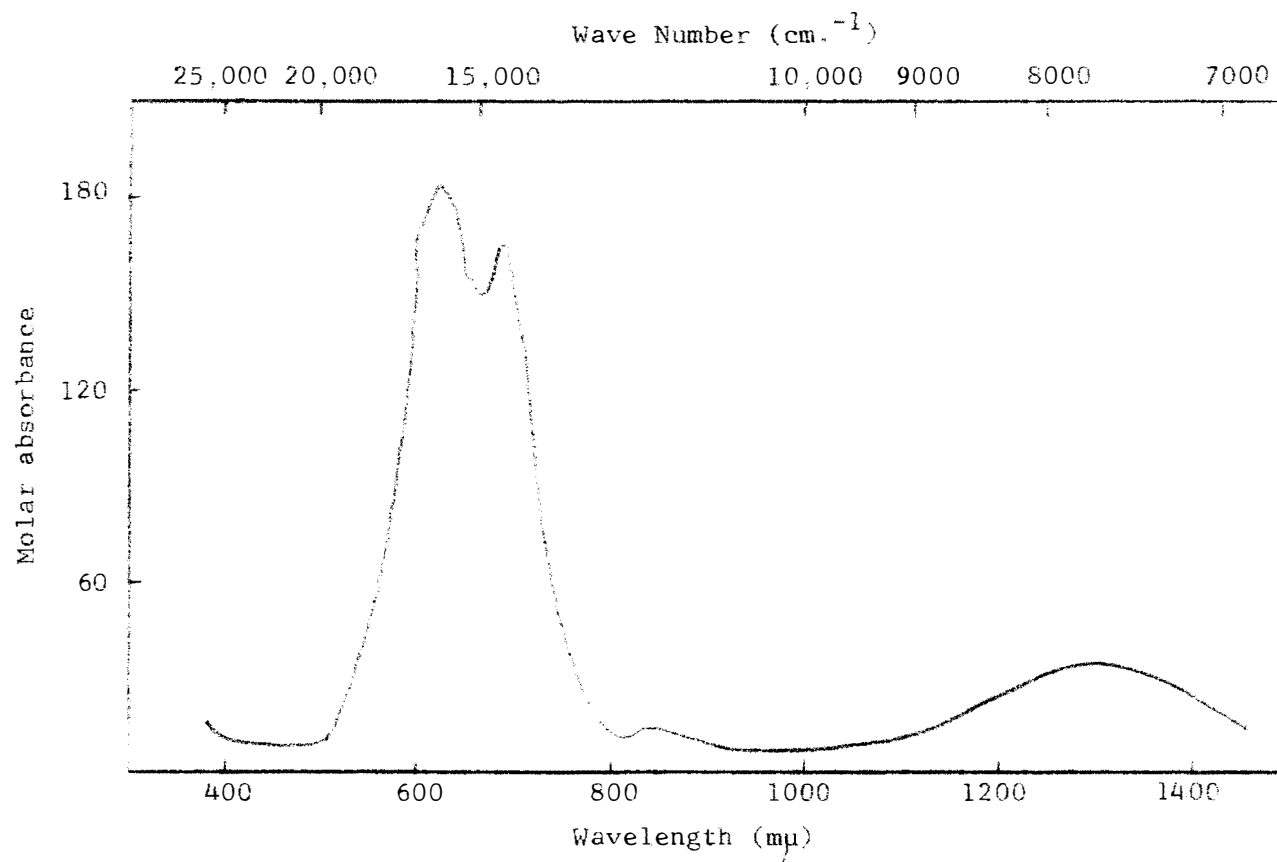


Figure 5. Visible and near-infrared absorption spectrum of a typical tetrahedral complex of nickel(II), $[\text{Ni}(\text{Ø}_3\text{AsO})_2\text{Br}_2]$.

two electrons (Figure 1 (c)); at greater distortions, the complex becomes diamagnetic (Figure 1 (d)). It is important to note that at the magnetic change-over there is no sharp change in the orbital scheme or in the nature of the bonding. Hence the classification of complexes as square-planar or tetragonally distorted octahedral is quite arbitrary. Interpretation of absorption spectra is often quite difficult. However, weak tetragonal distortion is usually recognized by a splitting of the first octahedral band, which is no longer a simple $t_{2g} \rightarrow e_g$ transition; strongly distorted "square-planar" complexes may show only a single band in the 22,000-23,000 cm^{-1} region of the spectrum.

B. Survey of Important Work Involving Substituted Pyridine Complexes

Transition metal complexes containing pyridine have been known and extensively studied for many years. The first report of nickel perchlorate-pyridine complexes was the paper of Weinland, Effinger, and Beck⁸ which appeared in 1927. These workers described the preparation of two blue complexes which they formulated $[\text{Ni}(\text{C}_5\text{H}_5\text{N})_6](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $[\text{Ni}(\text{C}_5\text{H}_5\text{N})_4](\text{ClO}_4)_2$. In 1943, Sinha and Ray⁹ reported a pale green complex of the composition $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{C}_5\text{H}_5\text{N}$; and, in 1958, Sinha¹⁰ reported complexes formulated as $\text{Ni}(\text{C}_5\text{H}_5\text{N})_6(\text{ClO}_4)_2$ and $\text{Ni}(\text{C}_5\text{H}_5\text{N})_4(\text{ClO}_4)_2$. All of the formulations are incorrect and incomplete in some detail.

In contrast to the perchlorate salt, the nickel halide and pseudo-halide complexes with pyridine have been carefully studied. An example

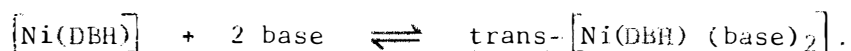
is the recent work by Brown, Nuttall, and Sharp.¹¹ Thermogravimetric studies were made for the thermal decomposition of dichlorotetrapyridine-nickel(II). Stages in the decomposition and analyses corresponded to the empirical formulas $\text{Ni}(\text{C}_5\text{H}_5\text{N})_2\text{Cl}_2$ and $\text{Ni}(\text{C}_5\text{H}_5\text{N})\text{Cl}$. Spectral studies on the complex and its decomposition products showed that the nickel was in an octahedral environment in all three and that the mono- and di-pyridine species were polymeric, containing chloride bridges.

Early work on substituent effects compared the coordinating ability of pyridine with that of other bases. Larsson¹² reported dissociation constants for silver complexes with ammonia, diethyl amine, aniline, *p*-toluidine, and pyridine as early as 1934. This work was later disputed and corrected. For many years in succeeding studies with other metal ions, work followed this idea of comparing pyridine, primary, secondary, and other tertiary amines.

Only in recent years have inorganic chemists become interested in the substituted pyridines as ligands, especially from the point of view of substituent effects. Bruhlman and Verhoeck¹³ included several alkyl-substituted pyridines in a study comparing the first formation constants for silver-amine complexes with the acid dissociation constants of the corresponding ammonium ions. They found, upon plotting $\text{p}K_1$ for the complexes against $\text{p}K_a$ for the ammonium ions, that two straight lines resulted: one for the pyridines and primary aliphatic amines, and one for the secondary amines. It is significant to note that the slopes of the two lines were about one-fourth in both cases, indicating a much smaller

range of basic strengths toward the silver ion than toward the hydrogen ion. A number of years later, Murmann and Basolo¹⁴ extended the study of formation constants of silver(I) with some additional pyridine bases. They found that variations in the stability of the complexes could not be explained solely on the basis of the base strengths of the pyridines, but that pi-bonding must be considered.

Sacconi, Lombardo, and Paoletti¹⁵ determined formation constants and thermodynamic functions for complexes of heterocyclic bases with diacetyl-bisbenzoylhydrazonenickel(II) ($[\text{Ni}(\text{DBH})]$) in benzene solutions. The reaction consisted simply of the addition of two molecules of base to the axial positions of the square-planar nickel complex:



The free energy and enthalpy changes were found to move in the same direction as values of pK_a for the protonated bases in water when steric effects were not involved. The entropy changes divided the bases studied into three groups: the saturated bases piperidine and pyrrolidine has ΔS values for the reaction of about -20 entropy units (e.u.), the non-ortho-substituted pyridines gave ΔS values of -30.1 to -33.1 e.u., and the ortho-substituted pyridines gave ΔS values of -39.7 to -43.5 e.u. The more negative ΔS values for the second group were interpreted as evidence for d-pi bonding between the nickel and the pyridines resulting in restriction of rotation about the Ni-N bond; the third group involved steric hindrance to rotation in addition to pi-bonding effects giving still more negative ΔS values.

The effect of varying ring substituents on the clathrating properties of tetrapyridine complexes with metal(II) halides and pseudo-halides has been probably the most extensive study in the area of substituted pyridine complexes. It was inspired by the petroleum industry's search for improved separation methods: Schaeffer, Dorsey, Skinner, and Christian¹⁶ observed the sharp selectivity of inorganic hosts having the general formula $M(X-py)_4A_2$ toward organic guest molecules and subsequently prepared more than 40 complexes of this type, with M = divalent Mn, Ni, Co, Fe, Cu, and Zn, with X = alkyl, amino, cyano, bromo, and other ring substituents, and with A = thiocyanate, cyanate, chloride, and acetate anions. The compounds were studied only for their potential uses as selective clathrating agents. Other workers have investigated other properties of a very few of these compounds.^{17,18,19,20}

Probably the first systematic studies of spectral and magnetic properties of substituted pyridine complexes with transition metal ions were reported in the papers of Buffagni, Vallarino, and Quagliano^{21,22} appearing in April and May 1964, and in the paper of Moore, Gayhart, and Bull²³ appearing in May 1964. The two papers by the former group reported preparations of various dimethylpyridine (lutidine) complexes of nickel(II) salts having both coordinating and non-coordinating anions. The complexes were found to fit one of the following formulations: $[NiL_2A_2]$, $[NiL_4A_2]$, or $[NiL_4]A_2$ where L = lutidine and A = monovalent anion. Tetrahedral, square-planar, or distorted octahedral structures were assigned to the complexes on the bases of their spectral and magnetic properties. The work of the latter group is included in this dissertation.

C. Purpose of This Research

It has been pointed out that the tools and theories necessary for structural determinations of transition metal complexes are available, and, during the last decade, have been particularly well developed for nickel(II) complexes. When the research for this thesis was undertaken, however, very little work had been done to characterize the complexes of transition metal ions with substituted pyridines. The pyridine bases seemed especially well suited for an investigation of substituent effects on the donor properties of the ligand because of the stability of the ring, the possibility of pi-bonding, and the ready availability of pyridines with a wide variety of ring substituents. Thus it was determined that a study would be made of the substituent effects on the spectra, magnetism, and structure of substituted-pyridine complexes of nickel(II).

In order to simplify interpretation of the visible spectra using ligand-field theory, a cubic field about the nickel ion was deemed desirable. For this reason, the perchlorate salt of nickel was chosen since perchlorate was widely recognized as a "non-coordinating anion;" thus, it was reasoned, all six positions about the nickel ion would be left for pyridine coordination. This proved to be wishful thinking: syntheses for the previously unreported nickel perchlorate-substituted-pyridine complexes had to be devised, in many of the complexes perchlorate was found to be coordinated to the nickel; in none of them were six monodentate pyridines coordinated to the nickel in a solid, anhydrous complex. These results complicated the interpretation of the visible spectra.

Likewise the synthetic problem was complicated in some cases by the clathration of solvent. These effects added many interesting aspects to the original problem.

CHAPTER II

EXPERIMENTAL

A. Reagents

1. Hexaquaonickel(II) Perchlorate

Hexaquaonickel(II) perchlorate ($[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$) obtained from the G. Frederick Smith Chemical Company was used without further purification in a portion of this work. However, the greater portion of this reagent used was prepared by Robert B. Gayhart, National Science Foundation Summer Undergraduate Research Participant, using the following procedure.

Perchloric acid was added slowly to an aqueous nickel(II) carbonate slurry until only a small amount of the solid carbonate remained. The carbonate was removed by filtration and the filtrate evaporated slowly on a hot plate until crystallization occurred. After cooling, the well-formed green crystals of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ were collected by suction filtration, washed in succession with cold ethanol and ether, and dried in vacuo. The product was not analyzed.

2. Pyridine Bases

The pyridines used in this study were obtained from several sources. In general, the liquid pyridines were dried and purified by distillation through an 8-cm. fractionating column from barium oxide or potassium hydroxide. The distillation apparatus was assembled from

a Metroware kit. The solid 4-aminopyridine was purified by sublimation or by two recrystallizations from acetone, and the solid 4-cyanopyridine by recrystallization from acetone. A few of the materials were used as received without further purification. The various pyridine derivatives that were used are tabulated in Table II (common symbols are also indicated); in the case of liquids, the drying agent in the distillation is given in column 2, the boiling range or melting point of the purified material is given in column 3; and the source of the material is given in the last column.

3. Solvents

Merck reagent benzene and "Baker Analyzed" reagent toluene, methanol, and acetone were used as solvents throughout this work. Spectroscopic grade dichloromethane from Fisher Scientific Company and nitromethane from Eastman Kodak were used. Practical grade 2,2-dimethoxypropane was obtained from Matheson Coleman and Bell. Other solvents (ethanol, ether, etc.) were reagent grade chemicals.

B. Syntheses

1. General

The compounds prepared for study were of two types: tetrakis-(pyridine base)nickel(II) perchlorate ($[\text{Ni}(\text{X-py})_4](\text{ClO}_4)_2$) and bisperchloratotetrakis(pyridine base)nickel(II) ($[\text{Ni}(\text{X-py})_4(\text{ClO}_4)_2]$). These compounds are hygroscopic in varying degrees; thus, removal and exclusion

TABLE II
PYRIDINE BASES

Compound	Drying Agent ^a	b.p./m.p. ^b	Source ^c
4-Aminopyridine (4-NH ₂ py)	S	158°	R
2,2'-Bipyridine (bipy)	S	--	S
3-Bromopyridine (3-Brpy)	KOH	170-173°	R
4-Chloropyridine Hydrochloride	S	--	C
3-Cyanopyridine	S	--	R
4-Cyanopyridine	S	--	R
5,6-Dimethyl-1,10-phenanthroline Monohydrate	S	--	S
2,6-Dimethylpyridine (2,6-lut)	-	--	P
3,5-Dimethylpyridine (3,5-lut)	BaO	169-172°	R
4-Ethylpyridine (4-etpy)	KOH	165.5-166.5°	R
4-Isopropylpyridine (4-ippy)	(BaO (KOH	176-178° 178-180°	R
4-Methanolpyridine	S	--	A
2-Methylpyridine (2-pic)	BaO	142-143°	E
3-Methylpyridine (3-pic)	BaO	141-145°	E
4-Methylpyridine (4-pic)	KOH	142-144°	E
3-Propanolpyridine	BaO	v	R
Pyridine (py)	BaO	113.5-114.5°	B,M

^aS indicates a solid pyridine derivative.

^bA dash indicates the compound was used without further purification; v indicates distilled at reduced pressure.

^cSymbols are as follows: A--Aldrich Chemical Co., Inc.; B--"Baker Analyzed" reagent; C--Columbia Organic Chemicals Co., Inc.; E--Eastman Organic Chemicals; M--Mallinckrodt Analytical Reagent; P--Paragon Testing Laboratories; R--Reilly Tar and Chemical Corporation; and S--G. Frederick Smith Chemical Company.

of water proved to be the key to their preparation. Azeotropic distillation and/or reaction with 2,2-dimethoxypropane (DMP) was used in some of the preparations. The all-glass distilling apparatus, assembled from Metroware, consisted of a round-bottomed flask for the reaction mixture, a fractionating distilling head having an 8-cm. jacketed column and a water-jacketed condenser, and a receiving flask. The reaction flask was heated with a heating mantle and, when necessary, stirred with magnetic stirring.

For some of the preparations, drastic means were not necessary to remove water and the reactions were carried out in open vessels. In a couple of cases the bisaquotetrakis(pyridine base)nickel(II) perchlorate complex ($[\text{Ni}(\text{X-py})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$) was prepared and converted to the desired product by further drying in an oven. The particular synthetic procedure for each of the new compounds and the analytical data are given in sections 2-14 of this chapter. Analyses were performed by Galbraith Laboratories and by Weiler and Strauss Microanalytical Laboratory. The majority of the compounds did not melt, but decomposed slowly over a wide temperature range. In a few cases, definite melting and decomposition temperatures have been noted.

A number of attempts to prepare complexes in these series with other substituted pyridines was unsuccessful. These attempts are described briefly in section 15 of this chapter.

2. Diaquotetrapyridinenickel(II) Perchlorate, $[\text{Ni}(\text{C}_5\text{H}_5\text{N})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$

Into a 20-ml., round-bottomed flask was placed 0.5 g. of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ and 10-15 ml. of pyridine. The flask was attached to the distillation apparatus described in section 1, and the pyridine-water azeotrope was removed by distillation. When the temperature reached 112° , the distillation was stopped. The blue product was isolated using suction filtration, triturated and washed several times with dry ether, and then dried for 12 hours over P_2O_5 at 78° and 15 mm.

Anal. Calcd. for $[\text{Ni}(\text{C}_5\text{H}_5\text{N})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$: C, 39.37; H, 3.96; N, 9.18. Found: C, 38.84; H, 4.59; N, 9.07.

3. Diperchloratotetrapyridinenickel(II), $[\text{Ni py}_4 (\text{ClO}_4)_2]$

a. From $[\text{Ni py}_4 (\text{H}_2\text{O})_2](\text{ClO}_4)_2$. The product prepared in section 2 lost water upon being stored in a desiccator over barium oxide for several months. Infrared spectra and analysis showed the new material to be $[\text{Ni py}_4 (\text{ClO}_4)_2]$.

Anal. Calcd. for $[\text{Ni}(\text{C}_5\text{H}_5\text{N})_4(\text{ClO}_4)_2]$: C, 41.85; H, 3.51; N, 9.76. Found: C, 42.11; H, 3.49; N, 9.90.

b. Using 2,2-dimethoxypropane. To a solution of 11 g. (0.03 mole) of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ in 25 ml. of acetone was added 9.7 ml. of pyridine and 24 ml. of DMP. The mixture was stirred and heated at $50-80^\circ$ in an open 250-ml. conical flask for 24 hours. The original volume was maintained until near the end of the 24-hour period by occasional additions of benzene. At the beginning of the last hour, 10 ml. of DMP was added and the mixture brought to a gentle boil. After boiling for an hour,

the fine blue product was collected by suction filtration. It was washed twice with a 50:40:10 mixture of benzene, DMP, and acetone. At no time was the product allowed to become dry on the filter. It was bottled wet and dried in a vacuum oven at 40° and 1 mm. for 5 hours. Analysis indicated almost 2 moles of benzene present per mole of complex (Calcd. for $\text{Ni}(\text{C}_5\text{H}_5\text{N})_4(\text{ClO}_4)_2 \cdot 2\text{C}_6\text{H}_6$: C, 52.6; H, 4.42; N, 7.67. Found: C, 52.50; H, 4.32; N, 8.48). The product was further dried for 5 days at 50° and 1 mm., after which time weight loss became negligible.

Anal. Calcd. for $[\text{Ni}(\text{C}_5\text{H}_5\text{N})_4(\text{ClO}_4)_2]$: C, 41.85; H, 3.51; N, 9.76. Found: C, 41.61; H, 3.61; N, 9.38.

4. Bis perchloratobis(2,2'-bipyridine)nickel(II), $[\text{Ni}(\text{bipy})_2(\text{ClO}_4)_2]$

To a solution of 2.2 g. (6 mM) of hexaquonickel(II) perchlorate in 25 ml. of acetone contained in a 125-ml. conical flask was added 5 ml. of DMP, 3.4 g. (30 mM) of lithium perchlorate, and a solution of 0.94 g. (6 mM) of 2,2'-bipyridine in 50 ml. of benzene. A rose precipitate, probably tris(2,2'-bipyridine)nickel(II) perchlorate, $[\text{Ni}(\text{bipy})_3](\text{ClO}_4)_2$, formed immediately. The mixture was stirred and heated at 60-70° on a magnetic-stirrer hot plate for 2-3 hours. The rose precipitate slowly changed to a purple precipitate of $[\text{Ni}(\text{bipy})_2(\text{ClO}_4)_2]$. An additional 5 ml. of DMP was added, and the flask stoppered and allowed to stand overnight at room temperature to ripen the precipitate. The product was then collected by filtration with suction and washed twice with small portions of absolute ethanol containing a little DMP; it was not allowed to become dry on the filter. The wet product was transferred to a

sample bottle and dried in a vacuum oven at 75° and 1 mm. for several hours.

Anal. Calcd. for $[\text{Ni}(\text{C}_5\text{H}_8\text{N}_2)_2(\text{ClO}_4)_2]$: C, 42.14; H, 2.83; N, 9.83. Found: C, 42.33; H, 2.70; N, 9.69.

5. Bisperchloratotetrakis(3-bromopyridine)nickel(II), $[\text{Ni}(\text{3-Brpy})_4(\text{ClO}_4)_2]$

a. By azeotropic distillation. Into a round-bottomed flask were placed 14 ml. of 3-bromopyridine, 3.0 g. of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$, and 25 ml of benzene. The flask was attached to the usual distillation apparatus, and water was removed by distillation of the benzene-water azeotrope. When the vapor temperature reached 80°, the flask was removed and cooled in an ice bath. The light blue product which formed was collected by suction filtration, transferred to a sample bottle, and dried in a vacuum desiccator at reduced pressure.

Anal. Calcd. for $[\text{Ni}(\text{3-BrC}_5\text{H}_4\text{N})_4(\text{ClO}_4)_2]$: C, 27.00; H, 1.81; N, 6.30. Found: C, 27.23; H, 1.88; N, 5.85.

b. Using 2,2-dimethoxypropane. The procedure described in paragraph 3 (b) was used to prepare this complex. There was a tendency for an oil to form when the ratio of benzene to acetone was large. Cooling was necessary before filtering to obtain a reasonable yield.

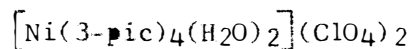
6. Tetrakis(4-aminopyridine)nickel(II) Perchlorate, $[\text{Ni}(\text{4-NH}_2\text{py})_4](\text{ClO}_4)_2$

To 1.3 g. of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ and 25 ml. of absolute ethanol contained in a 50-ml. round-bottomed flask were added 5 ml. of DMP and 2.1 g. of 4-aminopyridine. The flask was attached to a distillation apparatus

and the contents refluxed for a few minutes. The lower boiling components were removed by distillation until the temperature reached a constant 78°. After cooling to room temperature, the yellow product was collected by suction filtration, washed twice with ethanol, and dried in a vacuum desiccator at 0.4 mm. The compound melts and detonates at 291-292°.

Anal. Calcd. for $[\text{Ni}(\text{4-NH}_2\text{C}_5\text{H}_4\text{N})_4](\text{ClO}_4)_2$: C, 37.86; H, 3.79; N, 17.68. Found: C, 38.01; H, 3.74; N, 17.64.

7. Bisaquotetrakis(3-methylpyridine)nickel(II) Perchlorate,



To 3.7 g. (0.01 mole) of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ in 6 ml. of 50 per cent ethanol was added 9 ml. of 3-methylpyridine. The blue solution which resulted was allowed to evaporate at room temperature for several days until almost no liquid remained. A blue crystalline mass had formed in the bottom of the beaker. This was removed and washed with ether containing a little ethanol, air-dried, and then ground with a mortar and pestle. It was further dried at 50° and 16 mm.

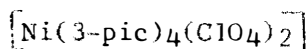
Anal. Calcd. for $[\text{Ni}(\text{3-CH}_3\text{C}_5\text{H}_4\text{N})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$: C, 43.27; H, 4.84; N, 8.41. Found: C, 43.36; H, 4.68; N, 8.14.

8. Tetrakis(3-methylpyridine)nickel(II) Perchlorate, $[\text{Ni}(\text{3-pic})_4](\text{ClO}_4)_2$

A sample of $[\text{Ni}(\text{3-pic})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ was dried in a vacuum oven at 70° and 1 mm. until weight loss was negligible and the product was uniformly bright yellow.

Anal. Calcd. for $[\text{Ni}(\text{3-CH}_3\text{C}_5\text{H}_5\text{N})_4](\text{ClO}_4)_2$: C, 45.80; H, 4.48; N, 8.89. Found: C, 45.80; H, 4.47; N, 8.74.

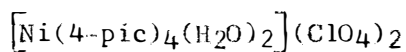
9. Bisperchloratotetrakis(3-methylpyridine)nickel(II),



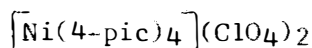
In a gloved bag that had been flushed with dry air, a sample of $[\text{Ni}(\text{3-pic})_4](\text{ClO}_4)_2$ was transferred to a clean glass ampule. The ampule was sealed and then heated at 165-170° in an oven overnight. Upon cooling, the blue product, $[\text{Ni}(\text{3-pic})_4(\text{ClO}_4)_2]$, was obtained. It was necessary to handle the product in a dry atmosphere. The product could be converted back to tetrakis(3-picoline)nickel(II) perchlorate by heating in a sealed ampule at 70° for a week, or by exposing to a moist atmosphere for several hours and then drying again at 70° in vacuo.

Anal. Calcd. for $[\text{Ni}(\text{3-CH}_3\text{C}_5\text{H}_4\text{N})_4(\text{ClO}_4)_2]$: C, 45.80; H, 4.48; N, 8.89. Found: C, 45.59; H, 4.56; N, 8.69.

10. Bisaquotetrakis(4-methylpyridine)nickel(II) Perchlorate,



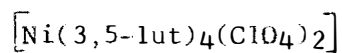
To a saturated aqueous solution of 3.7 g. of $[\text{Ni}(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ was added 9 ml. of 4-methylpyridine. Twenty ml. of saturated sodium perchlorate solution was added. The solution was cooled, and the blue crystals which formed were collected by suction filtration. The product was washed with a little cold ethanol and then with ether. It was air dried.

11. Tetrakis(4-methylpyridine)nickel(II) Perchlorate,

a. From $[\text{Ni}(4\text{-pic})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$. The blue $[\text{Ni}(4\text{-pic})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ was dried in an oven at 130° until a uniformly yellow product was obtained and weight loss was negligible.

b. By azeotropic distillation. Into a 25-ml., round-bottomed flask were placed 1 g. of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ and 15 ml. of 4-methylpyridine. Solvent was distilled from the flask, as described previously, until the vapor temperature reached 143° and very little solvent remained. The yellow product was collected by suction filtration, washed with ether containing a little DMP, and dried to constant weight at 130° in an oven.

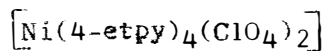
Anal. Calcd. for $[\text{Ni}(4\text{-CH}_3\text{C}_5\text{H}_4\text{N})_4](\text{ClO}_4)_2$: C, 45.80; H, 4.48; N, 8.89. Found: C, 45.87; H, 4.66; N, 8.62.

12. Bisperchloratotetrakis(3,5-dimethylpyridine)nickel(II),

Into a 100-ml., round-bottomed flask were placed 25 ml. of benzene, 14 ml. of 3,5-dimethylpyridine, 5 ml. of DMP, and 3.0 g. of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$. The low-boiling components were distilled from the mixture in the usual way, the distillation being stopped when the temperature reached a constant 80° . Well-formed blue crystals of the product separated. After cooling, the supernatant liquid was decanted from the flask and the crystals transferred to a sample bottle and dried in a vacuum desiccator at reduced pressure.

Anal. Calcd. for $[\text{Ni}(\text{3,5}-(\text{CH}_3)_2\text{C}_5\text{H}_3\text{N})_4(\text{ClO}_4)_2]$: C, 49.00; H, 5.29; N, 8.16. Found: C, 49.24; H, 5.40; N, 7.99.

13. Bisperchloratotetrakis(4-ethylpyridine)nickel(II),

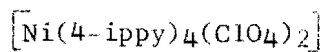


To 10 ml. of 50 per cent ethanol in a small beaker were added 3.6 g. of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$, 7 ml. of 4-ethylpyridine and 1 ml. of acetone. Upon standing for 2 days, large, deep blue crystals formed. These were dried in a vacuum oven at 80° and 1 mm. for several days until weight loss became negligible, yielding a light blue powdery product of $[\text{Ni}(\text{4-etpy})_4(\text{ClO}_4)_2]$. The dry material detonates at about 380°.

Anal. Calcd. for $[\text{Ni}(\text{4-C}_2\text{H}_5\text{C}_5\text{H}_4\text{N})_4(\text{ClO}_4)_2]$: C, 49.00; H, 5.29; N, 8.16. Found: C, 49.07; H, 5.35; N, 8.20.

An attempt to prepare this complex by azeotropic distillation resulted in an explosion. Into a 50-ml., round-bottomed flask were placed 5.1 g. of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ and 25 ml. of 4-ethylpyridine. The flask was attached to the distillation apparatus. After most of the water had been distilled from the mixture, the volume was considerably reduced, so additional 4-ethylpyridine was added, and heating was continued. An explosion occurred as the temperature reached about 145°.

14. Bisperchloratotetrakis(4-isopropylpyridine)nickel(II),



To 50 ml. of benzene in a round-bottomed flask were added 3.6 g. (0.01 mole) of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$, 5.3 ml. of 4-isopropylpyridine, and

10 ml. of DMP. Distillation was carried out, as described previously, until the volume was reduced to 5-10 ml. The blue product was collected by suction filtration (but was not allowed to dry on the filter) and dried in a vacuum desiccator at reduced pressure.

The product was soluble in benzene and toluene, from which unstable yellow solids were obtained upon evaporation of the solvents. The yellow solids lost enclathrated solvent rapidly upon standing to give the blue complex again.

Anal. Calcd. for $[\text{Ni}(\text{4-i-C}_3\text{H}_7\text{C}_5\text{H}_4\text{N})_4(\text{ClO}_4)_2]$: C, 51.77; H, 5.97; N, 7.56. Found: C, 52.38; H, 6.07; N, 7.26.

15. Attempted Preparations

a. With 4-chloropyridine. Samples of 4-chloropyridine hydrochloride were neutralized with sodium hydroxide and extracted into either benzene or chloroform. Addition of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ to the extracts and dehydration by addition of DMP or by azeotropic distillation usually gave mixtures of yellow and chartreuse solid products. Washing the product with benzene gave a blue solution and left a yellow insoluble material. Evaporation of the benzene solution gave a blue solid which became yellow upon drying. The latter yellow material gave the following analysis: C, 32.64; H, 2.74; N, 7.27; calculated for $\text{Ni}(\text{4-ClC}_5\text{H}_4\text{N})_4(\text{ClO}_4)_2$: C, 33.74; H, 2.27; N, 7.87.

b. With 3-cyanopyridine. From a mixture of 2 g. of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ and 4 g. of 3-cyanopyridine in 25 ml. of toluene was obtained

a blue product by distillation of the toluene-water azeotrope. The product did not come to constant weight upon drying.

Evaporation of a 50:25:25 acetone-ethanol-water solution containing 3.6 g. of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ and 7 g. of 3-cyanopyridine gave a blue oil. The oil was dissolved in 100 ml. of acetone, and 10 ml. of DMP was added. Upon warming, a blue precipitate formed. The solid was collected by filtration, washed, and dried. It did not come to constant weight. The infrared spectrum indicated that water was present.

Anal. C, 37.59; H, 3.01; N, 13.65. Calcd. for $[\text{Ni}(3\text{-CNC}_5\text{H}_4\text{N})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$: C, 40.59; H, 2.84; N, 15.78.

c. With 4-cyanopyridine. A solution of 4.2 g. (0.04 mole) of 4-cyanopyridine in 30 ml. of warm isopropanol was added to a concentrated aqueous solution of 3.6 g. (0.01 mole) of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$. Evaporation of the solution gave an oil. Pumping on the oil in a vacuum desiccator removed the remaining solvent and gave a plastic solid. The oil could not be made to crystallize from chloroform, benzene, or dioxane. A portion of the oil was stirred and warmed with a 50:50 mixture of benzene and DMP. A violet precipitate formed, which, upon continued heating, changed to a light blue powder. The blue powder was isolated by suction filtration, washed, and dried at 60° and 1 mm. The infrared spectrum indicated that no water was present and that perchlorate was coordinated.

Anal. C, 32.30; H, 2.53; N, 11.79. Calcd. for $\text{Ni}(4\text{-CNC}_5\text{H}_4\text{N})_4(\text{ClO}_4)_2$: C, 42.76; H, 2.39; N, 16.62.

A solution of 4.2 g. (0.04 mole) of 4-cyanopyridine in 15 ml. of acetone was added to a solution of 3.6 g. (0.01 mole) of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ in 7 ml. of acetone. To this solution was added 0.5 ml. of DMP and 10 ml. of benzene; the mixture was warmed and evaporated until a fine violet solid began separating. The flask and contents were cooled in an ice bath, and the solid collected by suction filtration. It was washed with dry benzene and then with dry ether and dried in a vacuum desiccator. The infrared spectrum indicated that water was present.

Anal. C, 32.05; H, 2.92; N, 11.81.

d. With 4-methanolpyridine. About 0.5 g. of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ was dehydrated by warming with 30 ml. of DMP. The excess DMP was decanted from the resulting brown oil, and the latter was dissolved in 20 ml. of acetone. Solid 4-methanolpyridine was added to the solution with warming until it was saturated. Addition of ether to the green solution did not cause precipitation. The solvent was evaporated, yielding a green oil. This was made to crystallize by boiling with successive 20 ml. portions of benzene. The green product was redissolved in acetone and again crystallized by the same treatment. It was isolated by suction filtration and air dried; m.p. 125-128°.

Anal. C, 42.32; H, 4.62; N, 7.13. Calcd. for $\text{Ni}(4\text{-HOCH}_2\text{C}_5\text{H}_4\text{N})_4\text{-(ClO}_4)_2$: C, 41.5; H, 4.06; N, 8.07.

e. With 2-methylpyridine. To 5.0 g. of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ was added 5.5 ml. of 2-methylpyridine. Heat was evolved, and a pasty green mass resulted which slowly solidified. The solid was dried in a vacuum

desiccator, ground to a powder, and further dried over barium oxide. It did not come to constant weight, even after drying several days, and smelled strongly of 2-methylpyridine.

Anal. C, 37.85; H, 4.52; N, 7.04. Calcd. for $\text{Ni}(\text{2-CH}_3\text{C}_5\text{H}_4\text{N})_4(\text{ClO}_4)_2$: C, 45.80; H, 4.48; N, 8.89.

f. With 2,6-dimethylpyridine. To 4.0 g. of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ dissolved in a minimum amount of acetone was added 5.0 ml. of 2,6-dimethylpyridine. A green, gelatinous precipitate formed immediately. It was allowed to settle, and the solvent removed with a filter stick. The precipitate was washed with ethanol and then chloroform; the ethanol washings were pale green; the chloroform washings, yellow. The product did not appear a uniform green when dried.

g. With 4-propanolpyridine. The procedure described in section 15 (d) was tried using 4-propanolpyridine. A brown solid, which appeared to be a mixture, was obtained.

h. With 5,6-dimethyl-1,10-phenanthroline. To a hot solution of 2.2 g. (6 mM) of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ in 25 ml. of acetone was added 1.4 g. (6 mM) of 5,6-dimethyl-1,10-phenanthroline monohydrate as a slurry in 25 ml. of hot benzene containing 5 ml. of DMP. A salmon-pink precipitate formed immediately; it was probably tris(5,6-dimethyl-1,10-phenanthroline)-nickel(II) perchlorate. The solution was saturated with lithium perchlorate, but, after heating for several hours, no change was noted. The solid was collected by suction filtration, washed 6 times with ethanol containing a little DMP, and then dried at 70° and 1 mm.

Anal. C, 53.33; H, 4.10; N, 8.26. Calcd. for $[\text{Ni}(\text{C}_{14}\text{H}_{12}\text{N}_2)_3]-(\text{ClO}_4)_2$: C, 57.16; H, 4.11; N, 9.53.

A 0.3 g. sample of the above product and 0.3 g. of $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ were dissolved in a mixture of 5 ml. of water and 80 ml. of acetone to give a pink solution. Upon heating gently for an hour, the solution gradually became blue. The blue solution was left to evaporate at room temperature. After 3 days, a mixture of salmon-pink powder and well-formed blue-violet crystals had deposited. Attempts to separate the two products were not successful.

C. Visible and Near Infrared Spectra

Visible and near infrared spectra were obtained on a Cary Model 14 recording spectrophotometer manufactured by the Applied Physics Corporation.

A modification of the powder technique described by Maki²⁴ was used in obtaining absorption spectra of the powders. In a gloved polyethylene bag which had been flushed with dry air, about 0.1 g. of the sample was ground in Nujol with a mortar and pestle to give a mull. The Nujol coating protected the complex from atmospheric moisture for an hour or longer. The mull was spread on a quarter of filter paper cut from a 5.5 cm. circle, and, when necessary, additional Nujol was added to make the filter paper translucent. The sample was then suspended in the sample beam of the instrument. A second quarter of filter paper was wet with Nujol and suspended in the reference beam to equalize light scattering. The

spectrum of the sample was then obtained in the 6000-16,000 angstrom region using the infrared source and detector, and in the 3000-7000 angstrom region using the visible source and detector. The wavelength drive was set at speeds ranging from 10 to 50 angstroms per second.

For solution spectra, a sample was transferred to a weighed volumetric flask in a gloved bag which had been flushed with dry air, and the flask then was reweighed in order to determine the sample weight by difference. Solvent was then added to dissolve the sample and fill the flask to the mark. Spectra, in the ranges cited previously, were obtained in 1-, 2-, 5-, or 10-cm. matched quartz cells with solvent in the reference cell. All solutions were prepared and spectra run at $21 \pm 1^\circ$.

D. Infrared Spectra

Infrared spectra of the complexes were obtained using Nujol mulls between sodium chloride plates. The mulls were prepared by grinding a small amount of sample in Nujol with a small agate mortar and pestle. The mulls were prepared in a gloved bag which had been flushed with dry air, and were spread on the sodium chloride plates using a rubber policeman. Spectra in the 2-15 micron range were then obtained using the Beckman IR-5A, the Perkin Elmer Infracord, or the Perkin Elmer Model 21 recording spectrophotometers. The spectra were calibrated against polystyrene film. There was no evidence that the complexes reacted with the sodium chloride plates during the times required to get the spectra.

Preliminary work with the potassium bromide pellet technique indicated that the bromide ion replaced coordinated perchlorate in many of the complexes during the pellet-making process.

One solution spectrum was obtained: $[\text{Ni}(4\text{-ippy})_4(\text{ClO}_4)_2]$ in dichloromethane. The technique described in section C of this chapter was used in preparing the solution. The 0.025 mm. sodium chloride cell was filled with a syringe. The spectrum indicated that the complex reacted slowly with the cell walls.

E. Magnetic Moments

Magnetic susceptibilities of the complexes were measured using a Curie-Chaneveau torsion balance which was built in this department by G. K. Schweitzer and W. K. Witherspoon. The sample holder was a 12 x 17-mm. screw-cap vial suspended by a thread from the beam of the balance. Using this balance, it was necessary to determine the weight of the sample and the maximum total deflection of the beam due to the sample since the deflection is directly proportional to the gram magnetic susceptibility of the sample. (This differs from the more commonly used Guoy method in which the deflection is proportional to the volume magnetic susceptibility of the sample, and is hence dependent on particle size and packing for solid samples.) The balance was calibrated by measuring the total deflection of the beam caused by a weighed sample of mercury tetrathiocyanatocobaltate(II) which has a magnetic susceptibility of 16.44×10^{-6} per gram and has been recommended as a magnetic standard 25

The technique employed was as follows: The sample was transferred to the previously weighed sample holder in a gloved bag which had been flushed with dry air, and the holder was then reweighed to determine the sample weight by difference. It was then suspended from the beam of the balance. After waiting 15-30 minutes for beam vibrations to stop, maximum deflection readings were recorded when the magnet was moved away from the sample in each direction. The two values were added to give the total deflection. Several pairs of deflection readings were taken for each sample and the average total deflection determined. For each pair of readings, the sample holder was removed from the beam and then resuspended. The diamagnetic deflection due to the empty sample holder was measured in the same manner, and this value added to the total deflection of each sample to give the actual deflection due to the sample alone. The magnetic data are given in Table III.

The calculation of magnetic susceptibilities and magnetic moments was quite straightforward. The gram susceptibility X_g of a sample was calculated using the relation

$$X_g = \frac{X_g' m' \theta'}{m\theta} \quad (1)$$

where m is the sample weight and θ is the corrected total deflection for the sample; the primes refer to the corresponding quantities for the calibrant, mercury tetrathiocyanatocobaltate(II). The molar susceptibility X_M was obtained by multiplying X_g by the molecular weight M of the sample and then adding a diamagnetic correction. The diamagnetic corrections were obtained by adding atomic diamagnetic susceptibilities

TABLE III
MAGNETIC DATA

Compound	Molecular Weight	Sample Weight (g.)	Temperature (°K)	Corrected Deflection
Hg [Co(SCN) ₄]	---	0.1907	297	44.40
[Ni(3-Bzpy) ₄ (ClO ₄) ₂]	889.6	0.2903	297	16.73
[Ni(4-ippy) ₄ (ClO ₄) ₂]	742.4	0.2014	298	14.37
[Ni(3,5-lut) ₄ (ClO ₄) ₂]	686.2	0.2869	298	23.65
Correction for diamagnetism of empty sample holder: 4.67				
Hg [Co(SCN) ₄]	---	0.1617	298	39.21
[Ni(3-pic) ₄ (ClO ₄) ₂]	630.1	0.1919	301	0.50
[Ni(3-pic) ₄ (ClO ₄) ₂]	630.1	0.1256	300	13.53
[Ni py ₄ (ClO ₄) ₂]	610.0	0.1273	299	16.61
[Ni(bipy) ₂ (ClO ₄) ₂]	570.0	0.1607	301	16.45
Correction for diamagnetism of empty sample holder: 6.72				
Hg [Co(SCN) ₄]	---	0.1201	301	28.93
[Ni(4-etpy) ₄ (ClO ₄) ₂]	686.2	0.1288	300	11.66
[Ni(4-etpy) ₄ (ClO ₄) ₂]	686.2	0.2278	300	20.39
[Ni(4-pic) ₄ (ClO ₄) ₂]	630.1	0.4234	301	-1.66
[Ni(4-pic) ₄ (ClO ₄) ₂]	630.1	0.0731	301	-0.21
Correction for diamagnetism of empty sample holder: 7.24				
[Ni(4-NH ₂ py) ₄](ClO ₄) ₂	---	---	301	-0.75
Correction for diamagnetism of empty sample holder: 8.48				

tabulated by Figgis and Lewis.²⁶ From the molar susceptibility, the effective magnetic moment μ was computed by assuming a Curie temperature of 0°K and using the relation

$$\mu = 2.84 \sqrt{X_M \cdot T}. \quad (2)$$

F. Conductance Measurements

The same solutions used in the near-infrared-visible spectral studies were also used for conductance measurements. The cell constant of the conductance cell had previously been found to be 0.357 cm.^{-1} by T. C. Patterson. It was determined by measuring the resistance of the cell containing 0.0200 molar potassium chloride solution. The resistances of the samples were measured, and the equivalent conductances computed. All work was done at $25.5 \pm 0.5^\circ$. A Model RC-1 Conductivity Bridge made by Industrial Instruments, Inc. was used for the resistance measurements.

CHAPTER III

RESULTS AND DISCUSSION

A. General Properties of Complexes

The anhydrous complexes of nickel(II) perchlorate and pyridine bases substituted in the 3- and 4-positions were found to be either square-planar complexes having the general formula $[\text{Ni}(\text{X-py})_4](\text{ClO}_4)_2$ or tetragonally distorted octahedral complexes having the general formula $[\text{Ni}(\text{X-py})_4(\text{ClO}_4)_2]$. These conclusions are based on the analytical results, as given in Chapter II, and on the spectroscopic and magnetic data. Low intensity absorption bands in the visible region of the spectra are consistent with the assignment of trans (centrosymmetric D_{4h} symmetry) rather than cis (C_{2v} symmetry) configurations to the $[\text{Ni}(\text{X-py})_4(\text{ClO}_4)_2]$ complexes. From symmetry considerations of d-pi bonding possibilities²⁷ between the metal and the pyridine base, it seems most probable that the four pyridine molecules are co-planar in the xy-plane of the complex (as contrasted to a paddle-wheel arrangement of the pyridines).

The spectroscopic results will be discussed in more detail in section B of this chapter. At this point, however, it is appropriate to discuss some other characteristics of these compounds.

1. Description

The compounds which have been assigned a square-planar configuration are yellow in color. $[\text{Ni}(4\text{-pic})_4](\text{ClO}_4)_2$ was obtained as well-formed deep yellow crystals; $[\text{Ni}(3\text{-pic})_4](\text{ClO}_4)_2$, as a bright yellow powder; and $[\text{Ni}(4\text{-NH}_2\text{py})_4](\text{ClO}_4)_2$, as a dull yellow powder. When exposed to atmospheric moisture, the 4-methylpyridine and 3-methylpyridine complexes became blue, the former over a period of hours, the latter, in a matter of a few minutes. The 4-aminopyridine complex appeared to be stable to atmospheric moisture for at least several days.

The octahedrally coordinated complexes are blue in color. All except two were obtained as very fine powders. $[\text{Ni}(4\text{-ippy})_4(\text{ClO}_4)_2]$ crystallized as thin plates from 4-isopropylpyridine (but a powder resulted when the compound was obtained by crystallizing from chloroform or by decomposing the benzene clathrate). $[\text{Ni}(3,5\text{-lut})_4(\text{ClO}_4)_2]$ crystallized as octahedral crystals from benzene and from chloroform and as plates from carbon tetrachloride. All of the blue compounds are quite hygroscopic except $[\text{Ni}(3,5\text{-lut})_4(\text{ClO}_4)_2]$.

In general, both blue and yellow complexes are soluble in water, acetone, ethanol, and the component pyridine (if a liquid) giving blue or green solutions. The degree of solubility varies from slight for the 4-aminopyridine complex to very soluble for the pyridine complex. Solution is thought to take place in most cases by the addition or substitution of two molecules of solvent along the molecular axis perpendicular to the plane of the 4 pyridine ligands.

The principal exception to these generalizations about solubility is $[\text{Ni}(3,5\text{-lut})_4(\text{ClO}_4)_2]$. This compound is not soluble in water or 3,5-dimethylpyridine. It is slightly soluble in acetone, giving a blue solution, and readily soluble in chloroform, giving a yellow solution which becomes bluish upon cooling.

A few well formed crystalline octahedra of $[\text{Ni}(3,5\text{-lut})_4(\text{ClO}_4)_2]$ were examined under a polarizing microscope. The crystals were found to be anisotropic and dichroic.

2. Magnetism

The results of the magnetic studies and calculations are given in Table IV. Among the yellow complexes, $[\text{Ni}(4\text{-NH}_2\text{py})_4](\text{ClO}_4)_2$ and $[\text{Ni}(4\text{-pic})_4](\text{ClO}_4)_2$ were found to be diamagnetic, while $[\text{Ni}(3\text{-pic})_4](\text{ClO}_4)_2$ showed a small magnetic moment of 1.05 Bohr magnetons. The diamagnetism found in the first two cases is consistent with the assignment of square planar configurations to these compounds. The paramagnetism of the 3-methylpyridine compound, however, is of interest. There are two possible explanations: (1) the $^3\text{A}_{2g}$ state of the nickel may lie only slightly above the $^1\text{A}_{1g}$ ground state, thus allowing thermal excitation of an electron from the singlet ground state to the triplet excited state, or (2) the sample may have been a mixture of diamagnetic and paramagnetic species.

The fact that the yellow 3-methylpyridine complex can be readily converted to a blue modification having a magnetic moment of 3.46 B. M. by heating at 170° would seem to favor the first explanation. However,

TABLE IV
MAGNETIC RESULTS

Compound	χ_g $\times 10^6$	Molar Diamagnetic Correction $\times 10^6$	χ_M $\times 10^6$	μ B. M.
$[\text{Ni py}_4 (\text{ClO}_4)_2]$	8.85	300	5380	3.6
$[\text{Ni}(\text{bipy})_2 (\text{ClO}_4)_2]$	6.94	290	4240	3.2
$[\text{Ni}(3\text{-Br py})_4 (\text{ClO}_4)_2]$	4.07	410	4030	3.1
$[\text{Ni}(3\text{-pic})_4 (\text{ClO}_4)_2]$	7.30	350	4940	3.5
$[\text{Ni}(3,5\text{-lut})_4 (\text{ClO}_4)_2]$	5.82	390	4390	3.2
$[\text{Ni}(4\text{-etpy})_4 (\text{ClO}_4)_2]$	6.50	390	4860	3.4
$[\text{Ni}(4\text{-ippy})_4 (\text{ClO}_4)_2]$	5.04	440	4180	3.2
$[\text{Ni}(4\text{-NH}_2\text{py})_4] (\text{ClO}_4)_2$	--	--	--	Diamagnetic
$[\text{Ni}(3\text{-pic})_4] (\text{ClO}_4)_2$	0.18	350	450	1.0
$[\text{Ni}(4\text{-pic})_4] (\text{ClO}_4)_2$	--	--	--	Diamagnetic

one would expect a temperature-dependent magnetic moment in the case of a thermally accessible triplet state.²⁸ Although a thermostated magnetic balance was not available for temperature-dependency studies, a single magnetic moment determination was made on the yellow complex at about 70°. There was no significant change in the value of the magnetic moment from the 1.05-B. M. value observed at 28°.

The possibility of a mixture of diamagnetic and paramagnetic nickel species seems more probable. A recent x-ray study²⁹ of the weakly paramagnetic (2.58 B. M.) yellow form of bis(meso-stilbenediamine)nickel (II) dichloroacetate has shown that crystals of this yellow material consist of a mixture of paramagnetic octahedral molecules and diamagnetic planar molecules. By analogy, the yellow $[\text{Ni}(\text{3-pic})_4](\text{ClO}_4)_2$ may be similarly constituted.

Some samples of the yellow 3-methylpyridine complex could definitely be seen to contain some bluish crystals. These could be the diaquo complex, $[\text{Ni}(\text{3-pic})_4(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (however, the samples were handled in a dry atmosphere to avoid contact with moisture), or the anhydrous high temperature modification, $[\text{Ni}(\text{3-pic})_4(\text{ClO}_4)_2]$, which may form in small amounts at the 70°-80° temperatures required to prepare the yellow complex. When a sample of the yellow material was added to dichloromethane, part of the solid dissolved quickly, but some blue solid remained undissolved. Whether the blue solid formed due to a trace of moisture in the dichloromethane or whether it was originally present in the yellow sample was not determined. There is, therefore, at present no conclusive evidence to support either explanation.

The remaining complexes listed in Table IV are blue and have magnetic moments falling within or near the 3.0-3.3 B. M. range expected for octahedral nickel(II) complexes. No explanation can be offered for the slightly high value of 3.60 B. M. observed in the case of $[\text{Ni py}_4(\text{ClO}_4)_2]$.

3. Electrolytic Conductance

The results of the conductance measurements are given in Table V. In acetone solutions, values of the equivalent conductance were in the range 87-120 $\text{cm}^2 \text{ohm}^{-1} \text{mole}^{-1}$. One would expect much higher values for a 1:2 electrolyte since 10^{-4} molar solutions of 1:1 electrolytes in acetone have been reported to have equivalent conductances of 150-200 $\text{cm}^2 \text{ohm}^{-1} \text{mole}^{-1}$.³⁰ In the current study, however, the solutions were quite concentrated, and extensive ion association could have occurred, causing the low values. One important conclusion can be drawn: since the solutions did conduct, it is certain that at least some of the perchlorate was displaced from the coordination sphere during the solvation process.

For the solutions in which each complex was dissolved in its component pyridine, the values of the equivalent conductance ranged from 1.6 to 35 $\text{cm}^2 \text{ohm}^{-1} \text{mole}^{-1}$. Again the solutions were too concentrated for reliable determination of the nature of the electrolyte. Also, neither conductances in nor viscosities for the majority of these solvents have been reported in the literature; hence there is no other data available for comparisons. It is interesting to observe, however,

TABLE V
CONDUCTANCE MEASUREMENTS

Complex	Concentration in Moles/l. $\times 10^3$	Solvent	Resistance in Ohms ^a	Equivalent Conductance in cm^2 $\text{ohm}^{-1} \text{Mole}^{-1}$
$[\text{Ni py}_4 (\text{ClO}_4)_2]$	14.7	Acetone	239	102
$[\text{Ni(bipy)}_2 (\text{ClO}_4)_2]$	14.1	Acetone	211	120
$[\text{Ni(3-Br py)}_4 (\text{ClO}_4)_2]$	17.5	Acetone	232	88
$[\text{Ni(3-pic)}_4] (\text{ClO}_4)_2$	12.1	Acetone	260	113
$[\text{Ni(3-pic)}_4 (\text{ClO}_4)_2]$	10.0	Acetone	300	119
$[\text{Ni(4-pic)}_4] (\text{ClO}_4)_2$	21.5	Acetone	170	98
$[\text{Ni(3,5-lut)}_4 (\text{ClO}_4)_2]$	8.97	Acetone	330	120
$[\text{Ni(4-ippy)}_4 (\text{ClO}_4)_2]$	14.5	Acetone	234	105
$[\text{Ni py}_4 (\text{ClO}_4)_2]$	13.4	Py	751	35.4
$[\text{Ni(3-Br py)}_4 (\text{ClO}_4)_2]$	26.2	3-Br py	8350	1.6
$[\text{Ni(3-pic)}_4] (\text{ClO}_4)_2$	22.8	3-pic	690	22.7
$[\text{Ni(4-pic)}_4] (\text{ClO}_4)_2$	21.8	4-pic	748	21.9
$[\text{Ni(4-etpy)}_4 (\text{ClO}_4)_2]$	24.0	4-etpy	1500	9.9
$[\text{Ni(4-ippy)}_4 (\text{ClO}_4)_2]$	15.3	4-ippy	2630	8.9

^aCell constant, $k = 0.357 \text{ cm}^{-1}$.

that the three compounds having the smallest measured equivalent conductances in the pyridine solvents are the same three compounds which show splittings of the first absorption band in their near-infrared spectra. It is possible that in these solutions there is little tendency for the solvent to displace perchlorate from the coordination sphere of the nickel complex.

4. Clathration

Clathrates were observed to form with two complexes during this study, and it is suspected that enclathrated solvent may have been the cause of poor analytical results in some of the unsuccessful preparations. No attempt was made to study and characterize these intriguing compounds, but a brief description of some observed properties is of interest.

From the analytical results, the presence of enclathrated benzene in almost a 2:1 mole ratio was suspected in the original $[\text{Ni py}_4(\text{ClO}_4)_2]$ sample. The sample was decomposed in hydrochloric acid solution and this solution washed with heptane. The ultraviolet spectrum of the heptane extract confirmed the presence of benzene in the sample. The clathrate was a light blue powder, and the guest was apparently quite strongly held in the host lattice, for it was necessary to dry the compound at 50° and 1 mm. for 5 days to completely strip the benzene from the host. No color change was noted when the guest was removed and no significant changes occurred in the spectrum of the solid complex except the disappearance of the benzene bands from the infrared spectrum.

The yellow clathrate of benzene and $[\text{Ni}(4\text{-ippy})(\text{ClO}_4)_2]$ was discovered when a benzene solution of the complex was evaporated at 30-35° with a Rinco flash evaporator attached to a water aspirator. Under the same conditions a yellow toluene clathrate resulted upon evaporating a toluene solution. These clathrates were flaky crystalline materials, dry to the touch. They smelled strongly of benzene or toluene. The toluene clathrate was slightly more stable, but both lost guest molecules rapidly, leaving the host as a blue powder. At 35° and 18 mm., the yellow crystals of the clathrate burst apart, reverting to a blue powder in 2-3 minutes. When the solutions were evaporated at temperatures below 20° or above 50°, a considerable amount of blue solid crystallized, and the amount of yellow material crystallizing diminished rapidly at more extreme temperatures. The visible spectrum of the toluene clathrate was very similar to that of the square planar $[\text{Ni}(4\text{-pic})_4](\text{ClO}_4)_2$ complex discussed in the next section. No analyses were attempted because of the instability of the compounds. Evaporation of cyclohexane, acetone, and chloroform solutions of $[\text{Ni}(4\text{-ippy})_4(\text{ClO}_4)_2]$ gave only blue solids. It is thought, therefore, that a π -electron system, as found in aromatic hydrocarbons, is necessary for clathration to occur. This seems to indicate an interaction of the π -cloud of the guest with the host complex.

B. Spectroscopic Results

1. Infrared Spectra

a. Perchlorate bands. The perchlorate ion consists of a chlorine atom surrounded by four oxygen atoms situated at the corners of a regular tetrahedron; hence it belongs to symmetry point group T_d . The five atoms contribute 9 degrees of freedom, but due to the high symmetry of the ion there are only four normal modes. The assignments of the normal modes have been established from infrared and Raman spectral studies by several investigators.³¹⁻³³ These assignments are listed in Table VI. Of the four normal modes, only ν_3 , antisymmetric stretching, and ν_4 , antisymmetric bending, are infrared active. The former, occurring at 1110 cm^{-1} , appears in the infrared spectra of ionic perchlorates as a very broad, strong band with a poorly defined maximum; the latter occurs below the region accessible with sodium chloride optics, but is readily observed at 626 cm^{-1} with potassium bromide optics. The symmetric stretching frequency ν_1 , which is theoretically infrared inactive, usually appears very weakly at 932 cm^{-1} due to distortion of the ion in the crystal field.³⁴ The symmetric bending frequency ν_2 is assigned a frequency of 460 cm^{-1} from Raman spectra.

Figure 6 shows the infrared spectrum of the yellow $[\text{Ni}(\text{4-pic})_4]-(\text{ClO}_4)_2$ complex in the $7\text{-}12.5\text{ }\mu$ region, and the perchlorate bands of the yellow complexes are listed in Table VII along with the corresponding bands for some perchlorate salts. It can be seen that the strong, broad 1110 cm^{-1} band and the very weak 932 cm^{-1} band fit the requirements of

TABLE VI
VIBRATIONS OF THE ClO₄ GROUP

Symmetry	Modes ^a			
T _d	ν_1 A(R) sym. str. 932	ν_2 E(R) sym. bend. 460	ν_3 T ₂ (I,R) asy. str. 1110	ν_4 T ₂ (I,R) asy. bend. 626
C _{3v}	ν_2 A ₁ (I,R) Cl-O* str.	ν_6 E(I,R) rock.	ν_1 A(I,R) ClO ₃ sym. str.	ν_4 E(I,R) Cl-O* asy. bend.
			ν_3 A(I,R) ClO ₃ sym. bend.	ν_5 E(I,R) ClO ₃ asy. bend.

^aSymbols are as follows: *Coordinated oxygen; A, non-degenerate; E, doubly degenerate; T, triply degenerate; I, infrared active; R, Raman active; sym., symmetric; asy, antisymmetric; str., stretching; bend., bending.

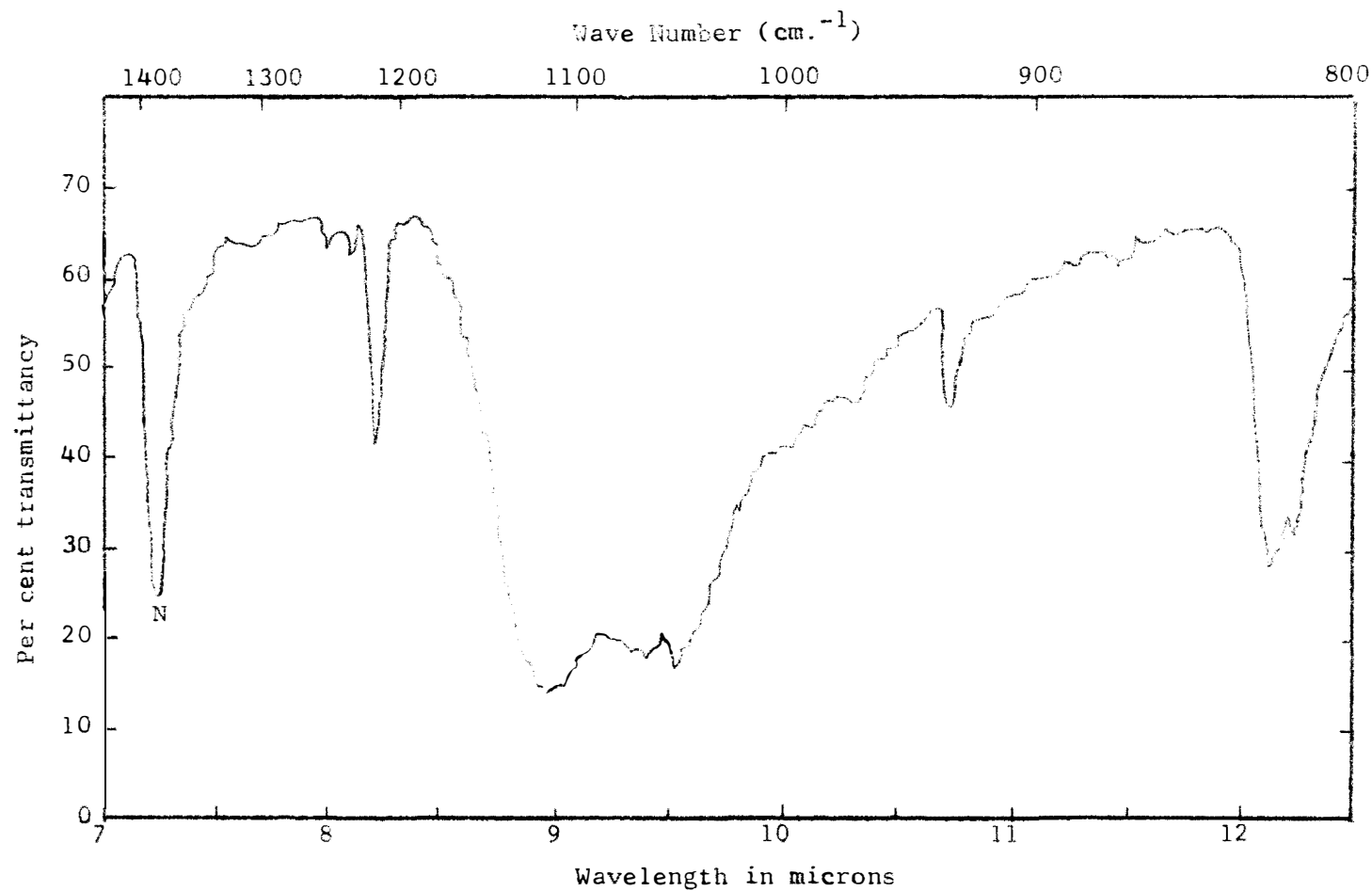


Figure 6. Infrared absorption of $[\text{Ni}(\text{4-pic})_4](\text{ClO}_4)_2$ (Nujol mull) showing per-chlorate ion absorption in 8-11 μ region.

TABLE VII

INFRARED ABSORPTION OF ClO_4 IN $[\text{Ni}(\text{X-py})_4](\text{ClO}_4)_2$ COMPLEXES

Compound	Band Assignments ^a	
	T_d Symmetry	
	ν_3 $T_2(\text{I,R})$ Asy. Str.	ν_1 $A(\text{R})$ Sym. Str.
$[\text{Ni}(4\text{-pic})_4](\text{ClO}_4)_2$	1040-1130 s, b	931 w
$[\text{Ni}(3\text{-pic})_4](\text{ClO}_4)_2$	1085-1105 s	931 w
$[\text{Ni}(4\text{-NH}_2\text{py})_4](\text{ClO}_4)_2$	1050-1155 s, b	935 vw
KClO_4	1070-1165 s, b	942 w
$[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ ³⁴	1030-1190 s, b	930 w

^aA = non-degenerate; T = triply degenerate; I = infrared active; R = Raman active, s = strong; w = weak; vw = very weak; b = broad.

T_d symmetry very well and confirm the presence of ionic perchlorate in these complexes.

If the perchlorate group becomes coordinated through one of its oxygen atoms, this atom is no longer equivalent to the other three oxygen atoms, and the T_d symmetry of the perchlorate ion is reduced to C_{3v} symmetry in the perchlorato group. This reduction in symmetry results in a splitting of the two triply degenerate normal modes of vibration. Also, the two symmetric normal modes become infrared active since these vibrations are accompanied by a changing dipole moment. Table VI also shows the normal modes of the perchlorato group and correlates them with the modes of the perchlorate ion.

Figure 7 shows the infrared spectrum of the blue $[\text{Ni}(3,5\text{-lut})_4(\text{ClO}_4)_2]$ complex in the 7-12.5 μ region, and the perchlorate bands of the blue complexes are listed in Table VIII. In each case, the strong ν_1 and ν_4 bands appear at about 1030 and 1140 cm^{-1} , respectively; these arise from the splitting of the broad ν_3 band of ionic perchlorate. The chlorine-coordinated oxygen (Cl-O^*) stretching frequency ν_2 , corresponding to the inactive ν_1 mode in T_d symmetry, appears as a medium or strong band at about $925 \pm 5 \text{ cm}^{-1}$. The range of frequencies of this band is shifted to slightly lower energies than that observed for the inactive ν_1 band (932 cm^{-1}) in the ionic complexes. This shift may be interpreted as further evidence for coordination of the perchlorate group since coordination through a given oxygen atom would be expected to lower the bond order, and hence the vibrational frequency

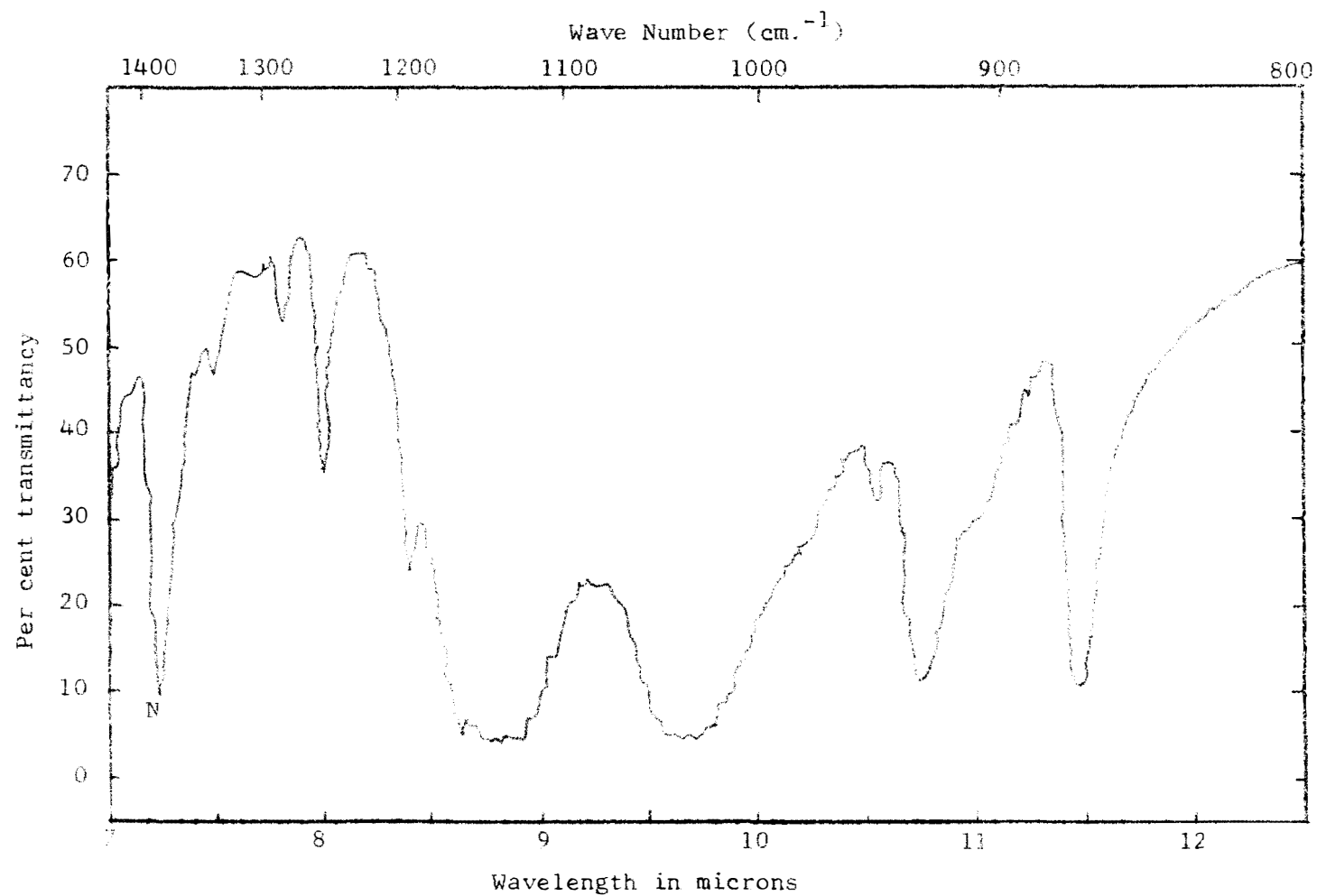


Figure 7. Infrared absorption of $[\text{Ni}(3,5\text{-lut})_4(\text{ClO}_4)_2]$ (Nujol mull) showing absorption of perchlorate group in 8-11 μ region.

TABLE VIII
INFRARED ABSORPTION OF ClO_4 IN $[\text{Ni}(\text{X-py})_4(\text{ClO}_4)_2]$ COMPLEXES

Compound	Band Assignments ^a C _{3v} Symmetry		
	A(I,R) ClO ₃ Sym. Str.	E(I,R) ClO ₄ [*] Asy. Bend	A ₁ (I,R) ClO ₄ [*] Str.
$[\text{Ni py}_4(\text{ClO}_4)_2]$	1032 s	1133 s	929 m
$[\text{Ni}(\text{bipy})_4(\text{ClO}_4)_2]$	1020-1040 s	1110-1145 s	923 m
$[\text{Ni}(3\text{-Brpy})_4(\text{ClO}_4)_2]$	1025 s	1140-1165 s	920 m
$[\text{Ni}(3\text{-pic})_4(\text{ClO}_4)_2]$	1020-1035 s	1123-1160 s	928 s
$[\text{Ni}(3,5\text{-lut})_4(\text{ClO}_4)_2]$	1025-1055 s	1115-1165 s	930 s
$[\text{Ni}(4\text{-etpy})_4(\text{ClO}_4)_2]$	1027 s	1130-1155 s	925 m
$[\text{Ni}(4\text{-ippy})_4(\text{ClO}_4)_2]$	1010-1045 s	1120-1160 s	920 s
HClO_4^{34}	1032	1312	739
$\text{ClO}_3\text{F}^{34}$	1061	1315	715

^aA = non-degenerate; E = doubly degenerate; I = infrared active; R = Raman active; s = strong; m = medium.

of the corresponding Cl-O* bond.³⁵ The corresponding shift has been reported for the sulfate ion³⁶ to be from 981 cm.⁻¹ (T_d) to 970 cm.⁻¹ (C_{3v}), which is about the same order of magnitude as the shift observed here. Perchlorate coordination to nickel through an oxygen atom is not, however, the equivalent of complete covalent bond formation. In the latter case, a much larger shift of the ν_2 band would be observed. For example, ν_2 occurs at 739 cm.⁻¹ in the spectrum of anhydrous perchloric acid³⁷ and at 715 cm.⁻¹ in the spectrum of perchloryl fluoride;³⁸ the corresponding shifts (from 932 cm.⁻¹ for ionic perchlorate) are thus 193 cm.⁻¹ for the Cl-OH stretch and 217 cm.⁻¹ for the Cl-F stretch.

On page 40, it was indicated that solution of the blue complexes was thought to involve the substitution of solvent for perchlorate in the coordination sphere. This is not, however, true in every case. The infrared spectrum of a dichloromethane solution of $[\text{Ni}(\text{4-ippy})_4(\text{ClO}_4)_2]$ showed perchlorate bands typical of coordinated perchlorate. When the spectrum was run again after a 15 minute interval using the same solution and cell, the ν_1 and ν_4 bands were considerably reduced in intensity and distorted, indicating that coordinated perchlorate was being replaced in the complex by chloride from the cell walls.

b. Pyridine bands. Infrared bands arising from vibrations of the pyridine ligands have been listed in Table IX for the 700-900 cm.⁻¹ and 1125-1650 cm.⁻¹ regions of the spectra. Bands have also been tabulated for the free pyridine bases in these same regions. Nujol absorption often prevented observation of bands in the neighborhood of 1380 and

TABLE IX
INFRARED BANDS OF FREE AND COMPLEXED PYRIDINE DERIVATIVES

Compounds	700-900 Cm.^{-1} Bands	1125-1650 Cm.^{-1} Bands ^a
py	703, 749	1439, 1482, 1572, 1580
$[\text{Ni py}_4(\text{ClO}_4)_2]$	703, 759, 763	N, N, 1598, 1632
bipy	756	1144, 1220, 1251, 1421, N, 1567, 1588
$[\text{Ni}(\text{bipy})_2(\text{ClO}_4)_2]$	733, 763	1163 sh, 1181, 1220, 1251, 1320, 1450, 1500, 1575, 1620
3-Brpy	700, 793	1194, 1224, 1325, 1418, 1468, 1567, 1580
$[\text{Ni}(\text{3-Brpy})_4(\text{ClO}_4)_2]$	682, 697, 717, 799	1205, 1233, 1332, 1425, N, 1560, 1595
4-NH ₂ py	811, 822, 844	1223, 1279, 1340, 1445, 1515, 1600, 1650
$[\text{Ni}(\text{4-NH}_2\text{py})_4](\text{ClO}_4)_2$	826, 846, 853 sh	1220, 1293, 1355, N, 1525, 1637, 1650 sh

TABLE IX (CONTINUED)

Compound	700-900 cm^{-1} Bands	1125-1650 cm^{-1} Bands ^a
3-pic	711, 793	1196, 1232, 1389, 1420, 1485, 1580, 1600
$[\text{Ni}(3\text{-pic})_4(\text{ClO}_4)_2]$	707, 798, 818	1204, 1250, N, N, 1492, 1590, 1615
$[\text{Ni}(3\text{-pic})_4](\text{ClO}_4)_2$	706, 807	1203, 1250, N, N, 1495, 1590, 1615
4-pic	712, 726, 796	1210, 1220, 1330 sh, 1380, 1408, 1450, 1492, 1561, 1605
$[\text{Ni}(4\text{-pic})_4](\text{ClO}_4)_2$	723, 814	1212, 1232, 1335, 1388, 1428, 1448, 1500, 1565, 1620
4-etpy	777, 824	1225, 1320, 1380, 1422, 1460, 1500, 1567, 1610
$[\text{Ni}(4\text{-etpy})_4(\text{ClO}_4)_2]$	789, 831	1215, 1233, 1435, 1515, 1567, 1625
3,5-lut	710, 858	1158, 1173, 1236, 1275, 1330, 1430, N, 1575, 1610
$[\text{Ni}(3,5\text{-lut})_4(\text{ClO}_4)_2]$	707, 760, 873	1160, 1192, 1251, 1283, 1335, N, N, N, 1610

TABLE IX (CONTINUED)

Compound	700-900 cm^{-1} Bands	1125-1650 cm^{-1} Bands
4-ippy	750, 819, 893	1221, 1240, 1314, 1368, 1390, 1414, 1460, 1493, 1555, 1600
$[\text{Ni}(4\text{-ippy})_4(\text{ClO}_4)_2]$	723, 765, 828, 895 sh	1235, 1250, 1317, N, N, 1430, N, 1505, 1555, 1595

^aN indicates bands obscured by Nujol absorption; sh = shoulder.

1465 cm^{-1} , and perchlorate absorption obliterated pyridine frequencies in the 950-1170 cm^{-1} range.

Strong bands in the 700-900 cm^{-1} region in spectra of aromatic hydrocarbons have been identified with motions of ring hydrogen atoms moving in phase out of the plane of the ring.³⁹ The frequencies of the out-of-plane hydrogen bending bands have been shown to depend on the number of adjacent hydrogen atoms around the ring and have been used to determine substitution patterns. The splitting of an intense in-phase, out-of-plane hydrogen bending mode upon complex formation has been interpreted as evidence for a cis configuration in a complex.⁴⁰ This interpretation has been shown to be unreliable in more recent work.^{41,42} Interaction between molecules in the unit cell, low lattice site symmetry for the complex, or slight rotations of the coordinated pyridine about the metal-nitrogen bond have also been invoked as causes for the splitting of bands in this region.

For the substituted pyridines used in this study, the number of bands appearing in the 700-900 cm^{-1} region could be predicted with a fair degree of accuracy from the known pattern of hydrogen atoms on the ring. The shifts and splittings of these bands upon complex formation could not be correlated, however, in any systematic manner.

Pyridine bands occurring at the low-frequency end of the 1125-1650 cm^{-1} range may arise from in-plane bending motions of ring hydrogens or possibly from ring vibrations; characteristic ring frequencies of aromatic compounds occur near the high-frequency end of this region.³⁹

Also some bands in this region may be attributed to overtones and combinations. Because many bands were too weak to be observed or were obscured by Nujol or perchlorate absorptions, detailed assignment of the bands which appeared was not feasible. The only general feature observed in this spectral region was a shift to higher frequencies by 5-50 cm^{-1} of many of the bands upon complex formation.

A strong band, showing slight splitting, appeared at 2340 cm^{-1} in the spectrum of $[\text{Ni}(\text{4-NH}_2\text{py})_2](\text{ClO}_4)_2$. The appearance of this band was considered unusual since no band appeared in the triple-bond region of the 4-aminopyridine spectrum. However, absorption bands in the 2300-3000 cm^{-1} region have been reported in the literature for alkylammonium salts.⁴³ These bands were attributed to N-H stretching modes which were shifted to lower frequencies by hydrogen bonding of the amine hydrogens to anions in the crystal. In $[\text{Ni}(\text{4-NH}_2\text{py})_4](\text{ClO}_4)_2$, there is also a possibility for hydrogen bonding, either between two amine groups, or between an amine group and the perchlorate anion. Such an occurrence would explain the 2340 cm^{-1} band in the spectrum of the complex.

2. Visible and Near-Infrared Spectra

a. Complexes in pyridine base solutions. In Table X are listed the frequencies of maximum absorbance, the molar absorptivity indexes, and the concentrations for solutions of the blue and yellow complexes in the component pyridine derivatives; only the complexes which were soluble in the (liquid) component pyridine could be studied.

TABLE X

VISIBLE AND NEAR-INFRARED BANDS OF $\text{Ni}(\text{X-py})_4(\text{ClO}_4)_2$ COMPLEXES IN X-py SOLUTIONS

Complex	Concentration $C \times 10^3$ Moles/l.	Absorption Maxima ($\lambda^2 \times 10^{-3} \text{ cm}^{-1}$) and Molar Absorbancy Index				
$[\text{Ni py}_4(\text{ClO}_4)_2]$	13.4	10.1 (3.6)	13.4 (1.7)	16.6 (6.0)	27.0 (11.6)	
$[\text{Ni}(3\text{-pic})_4(\text{ClO}_4)_2]$	22.8	10.1 (3.6)	13.4 sh	16.5 (5.7)	26.9 (10.1)	
$[\text{Ni}(4\text{-pic})_4](\text{ClO}_4)_2$	21.8	10.1 (3.8)	13.4 (1.6)	16.6 (6.5)	27.0 (12.9)	
$[\text{Ni}(3\text{-Brpy})_4(\text{ClO}_4)_2]$	26.2	8.8 (2.5) 11.6 (3.11)	13.4 sh	16.4 (6.8)	26.9 (13.7)	
$[\text{Ni}(4\text{-etpy})_4(\text{ClO}_4)_2]$	24.0	8.8 (4.4) 11.4 sh	13.1 sh	16.5 (11.9)	26.7 (28.4)	
$[\text{Ni}(4\text{-ippy})_4(\text{ClO}_4)_2]$	15.3	9.9 (4.2) 10.4 (4.4)	13.4 sh	16.5 (6.0)	27.0 (13.7)	

The spectra of the nickel complexes in pyridine (see Figure 8), 3-methylpyridine and 4-methylpyridine, are nearly identical and correspond to the spectra of regular octahedral nickel(II) complexes. The bands appearing at 10,100, 16,600, and 27,000 cm^{-1} may be assigned to the ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$, and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$ transitions, respectively. These assignments may be seen to fit the spin-allowed transitions expected for a Δ -value of 10,100 cm^{-1} from a study of Figure 2 (page 4). Also, they agree quite well with transitions calculated in either the weak-field or strong-field formalism. Using the strong-field matrices of Tanabe and Sugano,⁴⁴ (Table XI), the three spin-allowed transitions for nickel(II) are calculated to be 10,100, 16,400, and 27,600 cm^{-1} when Δ is assigned a value of 10,100 cm^{-1} from the experimental spectrum, and the Racah parameter B is assigned a value of 910 cm^{-1} . For the gaseous nickel(II) ion, B is 1080 cm^{-1} ;⁴⁵ hence, β , the ratio of B for the complex to B for the gaseous nickel(II) ion, is 0.771.

When the crystal-field matrix elements reported by Orgel² (Table XII) are solved in the weak-field formalism, the energies of the three spin-allowed transitions for nickel(II) are predicted to be 10,100, 17,200, and 27,000 cm^{-1} for assigned values of 10,100 cm^{-1} for Δ and 13,900 cm^{-1} for the splitting of the ${}^3\text{F}$ and ${}^3\text{P}$ multiplets (this reduction in the F-P splitting from 15,840 cm^{-1} corresponds to a β value of 0.878).

These two sets of predictions seem to be the best fits to the experimentally observed results which can be calculated using simple

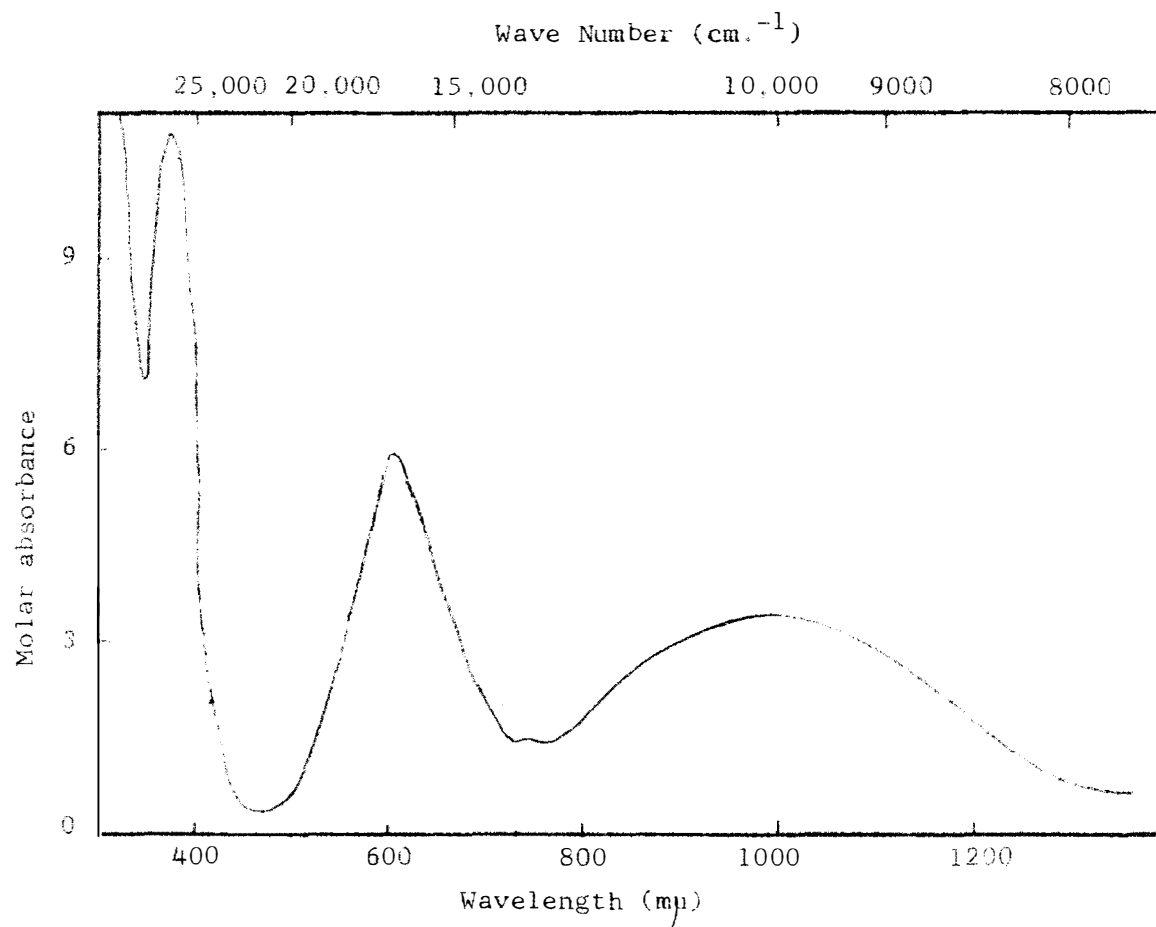


Figure 8. Visible and near-infrared absorption spectrum of $[\text{Ni py}_4(\text{ClO}_4)_2]$ in pyridine solution.

TABLE XI
TANABE-SUGANO MATRICES FOR CONFIGURATION $d^{2,8}$

	t^2	e^2
$1A_1$	$\begin{pmatrix} 10B + 5C - \Delta \\ \sqrt{6}(2B + C) \end{pmatrix}$	$\begin{pmatrix} \sqrt{6}(2B + C) \\ 8B + 4C + \Delta \end{pmatrix}$
$3A_2$	t^2 $(-8B + \Delta)$	
$1E$	t^2 $\begin{pmatrix} B + 2C - \Delta \\ -2\sqrt{3}B \end{pmatrix}$	e^2 $\begin{pmatrix} -2\sqrt{3}B \\ 2C + \Delta \end{pmatrix}$
$1T_1$	et $(4B + 2C)$	
$3T_1$	t^2 $\begin{pmatrix} -5B - \Delta \\ 6B \end{pmatrix}$	et $\begin{pmatrix} 6B \\ 4B \end{pmatrix}$
$1T_2$	t^2 $\begin{pmatrix} B + 2C - \Delta \\ 2\sqrt{3}B \end{pmatrix}$	et $\begin{pmatrix} 2\sqrt{3}B \\ 2C \end{pmatrix}$
$3T_2$	et $(-8B)$	

TABLE XII
ORTEL MATRICES FOR CONFIGURATION d^8

	$1G$	$1G$
$1A_{1g}$	$\begin{pmatrix} 0 & 4\sqrt{6} Dq \\ 4\sqrt{6} Dq & 4Dq \end{pmatrix}$	
	$3F$	
$3A_{2g}$	$12 Dq$	
	$1D$	$1G$
$1E_g$	$\begin{pmatrix} (24/7) Dq & (40\sqrt{3/7}) Dq \\ (40\sqrt{3/7}) Dq & (4/7) Dq \end{pmatrix}$	
	$1G$	
$1T_{1g}$	$(2 Dq)$	
	$3F$	$3P$
$3T_{1g}$	$\begin{pmatrix} -6 Dq & 4 Dq \\ 4 Dq & 0 \end{pmatrix}$	
	$1D$	$1G$
$1T_{2g}$	$\begin{pmatrix} -(16/7) Dq & (20\sqrt{3/7}) Dq \\ (20\sqrt{3/7}) Dq & -(26/7) Dq \end{pmatrix}$	
	$3F$	
$3T_{2g}$	$(2 Dq)$	

ligand-field theory. Here, cubic symmetry has been assumed, pi-bonding has been accounted for by a reduction of the F-P splitting from that observed in the gaseous ion, and spin-orbit coupling has been neglected. The fact that the observed band maxima do not fit exactly the calculated transition energies is not surprising for the bands are "vibronic" in origin; i.e., the bands are allowed only by a coupling of certain vibrational modes of the complex with the electronic wave functions; thus, the energies absorbed correspond to the sum of the energies necessary to cause an electronic transition and to excite a vibrational mode.

The weak band at about $13,400\text{ cm.}^{-1}$ in the spectra needs to be accounted for now. As was mentioned in Chapter I, the appearance of a fourth band (or splitting of the center band) in the spectra of many nickel(II) complexes has been the subject of some controversy. For a series of these complexes, including the hexaquonickel(II) ion, Jørgensen⁶ has assigned the corresponding weak bands in the spectra to a spin-forbidden transition, $^3A_{2g}(F) \rightarrow ^1E_g(D)$. Although spin-forbidden transitions are normally too weak to be observed, Jørgensen has contended that near the crossover point of the lowest singlet state with a triplet state, the states interact and the singlet state gains intensity from the triplet state. More specifically, states of the same J (the vector sum of L and S) interact as a function of the Landé multiplet splitting factor ζ_{nl} . For nickel(II), the interaction between the states with $J = 2$ is particularly strong. Figure 9 shows the Orgel diagram for nickel(II) which Jørgensen has developed from these considerations.

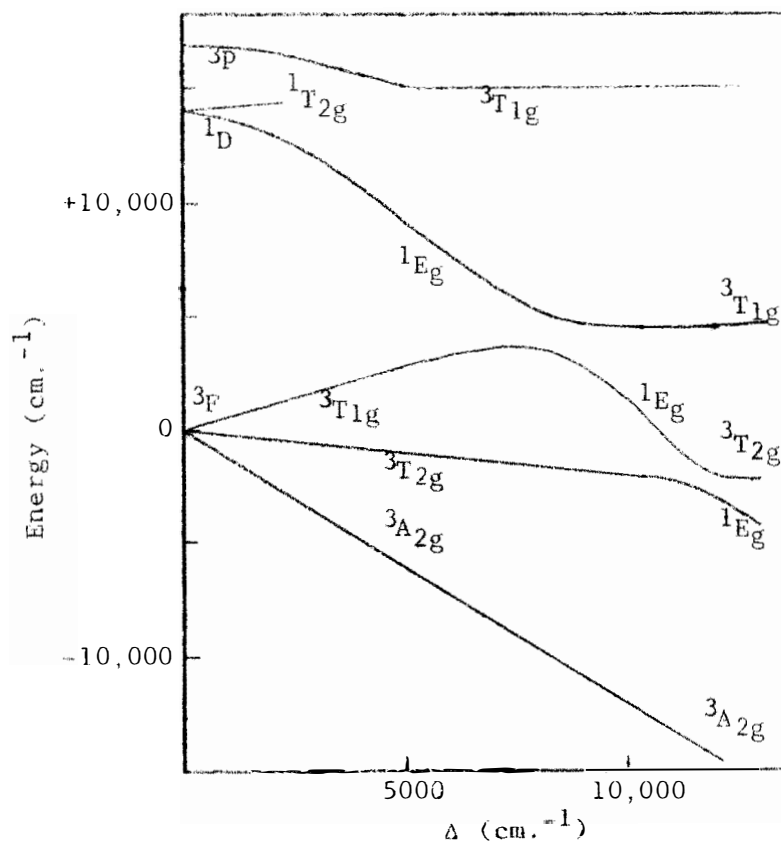


Figure 9. Energy levels of octahedral nickel(II) by Jørgensen,⁶ showing intermixing effects of singlet and triplet levels.

It can be seen that the diagram predicts a triplet-singlet transition at about $13,000 \text{ cm}^{-1}$ when Δ is assigned a value of $10,100 \text{ cm}^{-1}$, thus accounting for the $13,400 \text{ cm}^{-1}$ band observed in the spectra under consideration. This diagram predicts the three spin-allowed transitions to occur at $10,100$, $16,500$, and $27,000 \text{ cm}^{-1}$.

Liehr and Ballhausen⁵ have calculated a "complete" energy level diagram for nickel(II) in a cubic field. To do this, they included the spin-orbit coupling term $\sum (r_i) l_i \cdot s_i$ (l_i and s_i are orbital angular momentum and spin quantum numbers, respectively) in the Hamiltonian operator of the Schrodinger equation. (Previously, spin-orbit coupling has been neglected for 3d ions.) The Schrodinger equation was then solved in both weak-field and strong-field formalism for the energy matrices. The solutions in both cases were functions of the four quantities F_2 , F_4 , λ , and Dq . F_2 and F_4 are the well-known Slater functions, λ is the spin-orbit coupling constant, and Dq is a measure of the crystal field strength and is defined by $\Delta = 10 Dq$. All four quantities were treated as parameters and the matrices solved using an IBM 704 data processing machine. Figure 10 shows Liehr and Ballhausen's energy level diagram, with spin-orbit coupling included, for nickel(II). Values assigned to the parameters were $\lambda = -275 \text{ cm}^{-1}$, $F_4 = 90 \text{ cm}^{-1}$, and $F_2 = 14 F_4$.

Using this diagram, the authors dispute Jørgensen's assignment of the $15,400 \text{ cm}^{-1}$ band in the hexaquaonickel(II) ion ($Dq = -850 \text{ cm}^{-1}$) to a triplet-singlet transition, but agree with his assignment of the

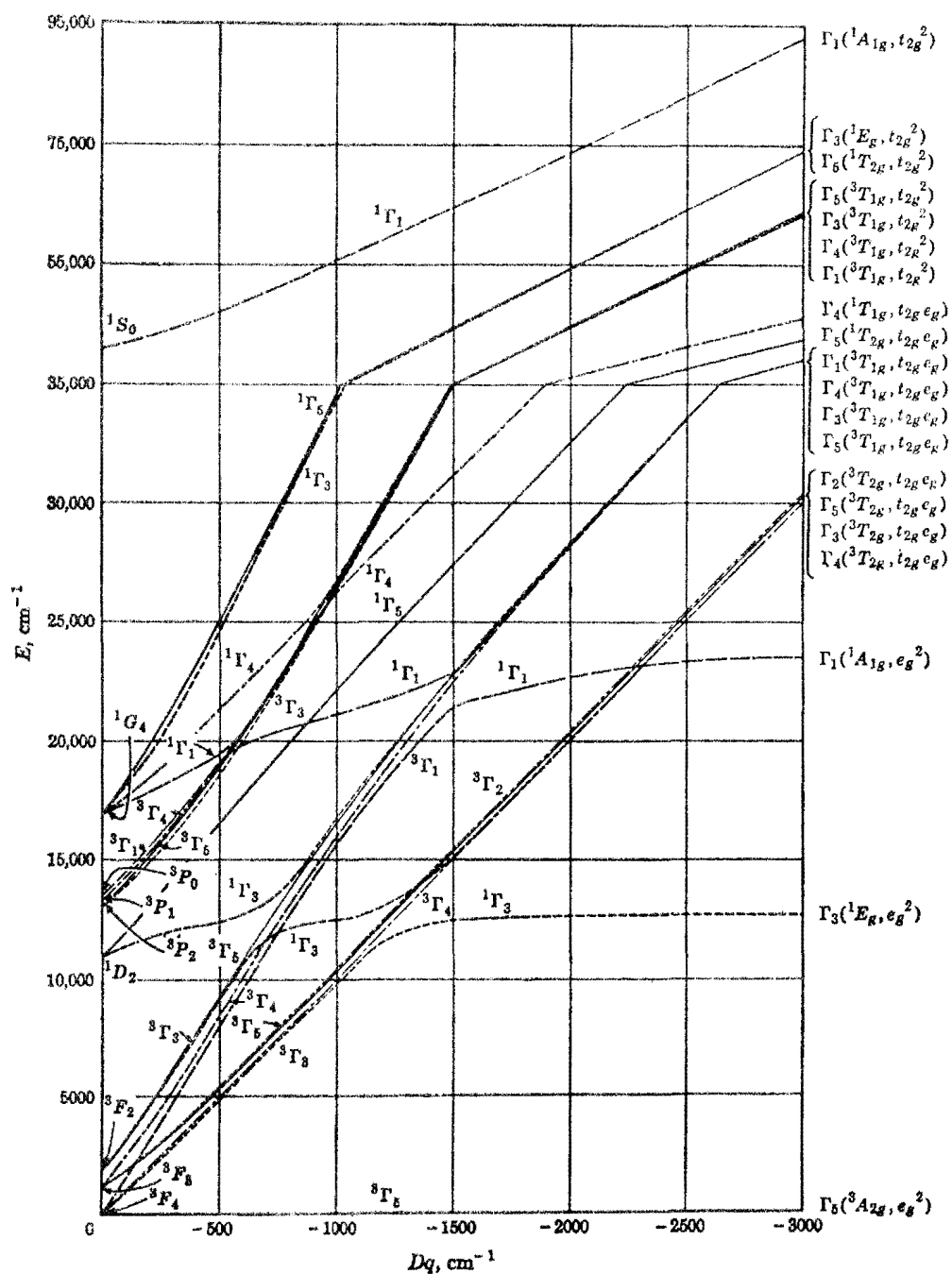


Figure 10. Energy-level diagram for $(3d)^8$ with spin-orbit coupling included. The labeling is that of the double group. The hole formalism has been used.

13,150 cm^{-1} band in the hexamminenickel(II) ion ($Dq = -1075 \text{ cm}^{-1}$) to a spin-forbidden transition. They invoke the splitting at intermediate field strengths of the components of the ${}^3T_{1g}$ level to explain the 13,500 and 15,400 cm^{-1} bands of the hexaquaonickel(II) ion.

For the three pyridine complexes of current interest, having Dq values of -1010 cm^{-1} , Liehr and Ballhausen's energy level diagram is seen to predict spin-allowed transitions at 10,100, 16,100, 16,700, and 27,000 cm^{-1} . A spin-forbidden transition is predicted at 12,500 cm^{-1} . It seems likely that the splitting of the ${}^3T_{1g}$ levels is not resolved in the spectra of these pyridine complexes and that the observed 16,600 cm^{-1} bands correspond to the ${}^3A_{2g} \rightarrow {}^3T_{1g}$ transitions. Thus, in analogy with the hexamminenickel(II) spectrum, the weak 13,400 cm^{-1} bands in the spectra of the pyridine complexes are assigned to the spin-forbidden ${}^3A_{2g} \rightarrow {}^1E_g$ transition. Since all bands have been satisfactorily assigned for regular octahedral symmetry, the complex species in solution is thought to be $[\text{Ni}(\text{X-py})_6]^{+2}$. This latter conclusion is supported by the conductivity measurements which indicate the presence of ions in the solutions.

Turning attention now to the spectra of the remaining three compounds listed in Table X, it is seen that there is an apparent splitting of the low energy absorption band of these complexes into two components (see Figure 11). This splitting, as mentioned in Chapter I, is an indication of slight tetragonal distortion in octahedral complexes. (It will be recalled that the conductances of these three solutions were found to

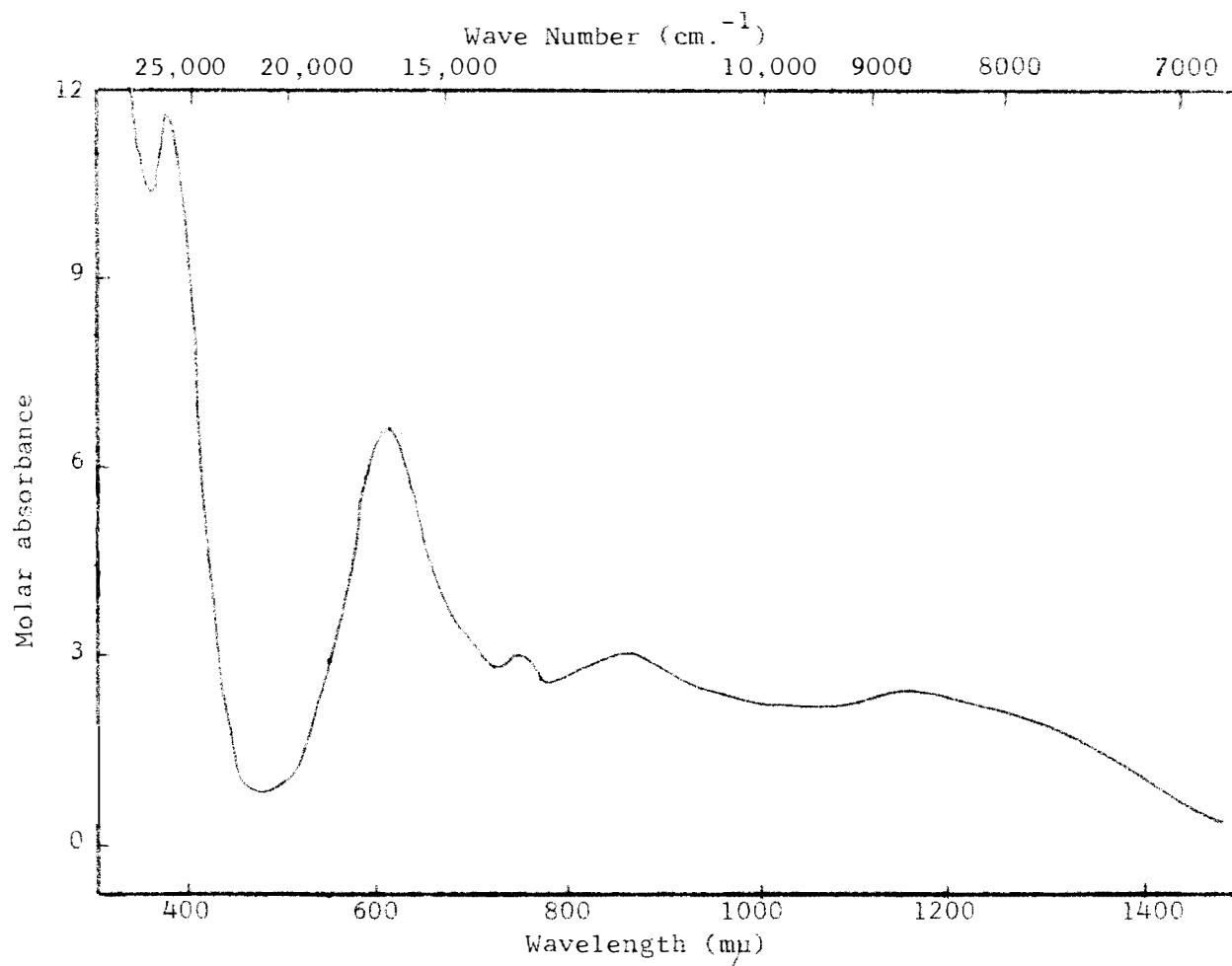


Figure 11. Visible and near-infrared absorption spectrum of $[\text{Ni}(\text{3-Brpy})_4(\text{ClO}_4)_2]$ in 3-bromopyridine solution.

be considerably smaller than the conductances of the solutions already discussed. This indication that the perchlorate ion may still be coordinated in these solutions also supports the proposal of a tetragonal species in solution.)

In going from regular octahedral (O_h) symmetry to tetragonally distorted octahedral (D_{4h}) symmetry, the energy states for a d^8 system are split according to the correlations shown in Table XIII. The two ${}^3T_{1g}$ states, the ${}^3T_{2g}$ state and the ${}^3A_{2g}$ state of O_h symmetry are split into a total of seven triplet states in D_{4h} symmetry. Hence with weak tetragonality the spectrum should show six spin-allowed transitions from the ground state (${}^3B_{2g}$), provided no transitions are accidentally degenerate and all occur in the observed spectral region. Calculation of the energies for transitions in D_{4h} symmetry is more complicated than in O_h , but some theoretical work has been reported.^{24,46-51} The reader is referred to the work by Maki, whose results will be used here for the assignment of bands in D_{4h} symmetry.

For an octahedral nickel(II) complex in D_{4h} symmetry, Maki calculated the electronic energy states as functions of four parameters. The parameters were the in-plane point dipole strength μ , the nickel-dipole distance R , the axial point charge p , and the nickel-axial point charge distance Z . She then plotted energies of the electronic states as functions of μ at fixed values of p , Z , and R . In the reported energy level diagram, the parameters were assigned values $p = 1$, $Z = 2.1 \text{ \AA}$, and $R = 1.5 \text{ \AA}$. The diagram gives the correct qualitative prediction

TABLE XIII
CORRELATION TABLE FOR O_h AND D_{4h}

O_h	D_{4h}
A_{1g}	A_{1g}
T_{1g}	$A_{2g} + E_g$
T_{2g}	$B_{1g} + E_g$
A_{2g}	B_{2g}
E_g	$A_{1g} + B_{2g}$

of spectra of the distorted octahedral complexes at a μ -value of about 0.6 (Maki indicated μ in atomic units, where 1 au = 2.54 debye). Table XIV gives the assignments, based on Maki's diagram, for the spectra of the $[\text{Ni}(\text{X-py})_4(\text{ClO}_4)_2]$ complexes in X-py solutions, where X are the 3-bromo, 4-ethyl, and 4-isopropyl groups. Also, the corresponding approximate predictions for these transitions are given based on Maki's diagram. Further adjustment of the parameters from the fixed values reported should make the predicted values fit the observed spectra more closely (since Maki chose parameters to best fit the spectrum of a complex having chloride ions in the axial positions, these same parameters should not be expected to fit exactly the complexes under consideration).

b. Complexes in acetone solutions. The visible and near-infrared absorption bands for acetone solutions of the complexes are listed in Table XV. Since these solutions are electrolytes, and since the spectra have the features characteristic of regular octahedral nickel(II) complexes, it is thought that the absorbing species in solution is probably $[\text{Ni}(\text{X-py})_4(\text{acetone})_2]^{+2}$. Since both acetone and the pyridine bases are neutral molecules, the tetragonal distortion in the complexes is apparently not great enough to cause splitting of the first band. Instead, the nickel "sees" an averaged crystal field. The assignments of the bands, also listed in Table XV, are therefore those of octahedral nickel(II) complexes. Definite assignments have not been made for the bands appearing in the 22,000-24,000 cm^{-1} region of two of the spectra.

TABLE XIV
ASSIGNMENT OF TETRAGONAL BANDS

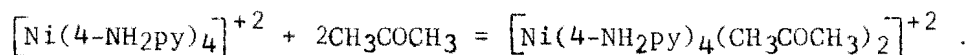
3-Brpy	Observed Cm. ⁻¹ x 10 ⁻³		Assignment 3B _{2g} →	Predicted Cm. ⁻¹ x 10 ⁻³
	4-etpy	4-ippy		
8.8	8.8	9.9	3E _g (F)	8
11.6	11.4	10.4	3A _{2g} (F)	13
13.4	13.1	13.4	3B _{1g} (F)	14
16.4	16.5	16.5	3E _g (P)	18
26.9	26.7	27.0	3A _{2g} (P)	28

TABLE XV

VISIBLE AND NEAR-INFRARED BANDS OF COMPLEXES IN ACETONE SOLUTIONS

Compound	Concen- tration mole/l.	Band Maximum (Absorbancy Index) cm. ⁻¹ x 10 ⁻³ (l./mole cm.)				
		Assignment ${}^3A_{2g}(F) \longrightarrow$	${}^3T_{2g}(F)$	${}^1E_g(D)$	${}^3T_{1g}(F)$	${}^3T_{1g}(P)$
[Ni py ₄ (ClO ₄) ₂]	0.0147		9.9 (3.9)	13.7 sh	16.2 (6.3)	26.6 (13.2)
[Ni(4-pic) ₄](ClO ₄) ₂	0.0215		10.1 (3.8)	13.7 sh	16.4 (6.9)	26.7 (15.1)
[Ni(3-pic) ₄](ClO ₄) ₂	0.0100		9.9 (4.0)	13.7 sh	16.1 (6.2)	26.5 (14.0)
[Ni(3-pic) ₄](ClO ₄) ₂	0.0121		9.9 (3.9)	13.7 sh	16.1 (6.1)	26.5 (11.9)
[Ni(3-Brpy) ₄](ClO ₄) ₂	0.0175		9.5 (4.4)	13.7 sh	15.7 (5.7)	26.1 (11.8)
[Ni(3,5-lut) ₄](ClO ₄) ₂	0.00897		10.0 (3.9)	13.7 sh	16.1 (6.2)	27.2 (12.2)
[Ni(4-etpy) ₄](ClO ₄) ₂	0.0153		10.0 (3.1)	13.7 sh	16.2 (5.3)	26.6 (11.3)
[Ni(4-ippy) ₄](ClO ₄) ₂	0.0145		10.0 (3.8)	13.7 sh	16.2 (6.5)	26.7 (15.3)
[Ni(bipy) ₂](ClO ₄) ₂	0.0141		11.0 (11.3)	12.9 sh	17.9 (8.4)	23.5 sh
[Ni(4-NH ₂ py) ₄](ClO ₄) ₂	0.00594		10.0 sh (5)		16.1 (12.2)	22.1 (27.5)
						26.4 (38.8)

The weak shoulder at $23,400\text{ cm}^{-1}$ in the spectrum of the bipyridine complex is probably a spin-forbidden transition. The band at $22,100\text{ cm}^{-1}$ in the spectrum of the 4-aminopyridine complex is, however, too intense and broad for a spin-forbidden band. The shape and position of this band are similar to that of the single bands appearing in the spectra of the solid square-planar complexes. Hence this band probably arises from a square-planar species in solution due to an equilibrium of the type



Since a Δ value for acetone apparently has not been reported, it is appropriate to use the averaged field approximation⁵² to calculate it from the spectral data now available. According to the averaged field approximation, the crystal field strength for a complex of the type postulated above should be given by

$$\Delta_{\text{avg.}} = (1/6)(4\Delta_{\text{py}} + 2\Delta_{\text{act.}}).$$

Using the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ transition energies of the first three compounds in Table XV as values of $\Delta_{\text{avg.}}$ and the corresponding energies from Table X as values of Δ_{py} , three values of $\Delta_{\text{act.}}$ were calculated to give an average of 9600 ± 400 for the Δ value of acetone.

c. Powders in Nujol. The visible and near-infrared spectral bands of the solid $\text{Ni}(\text{X-py})_4(\text{ClO}_4)_2$ complexes in Nujol mulls are listed in Table XVI. The yellow complexes exhibit single, rather intense bands at $22,000\text{-}24,000\text{ cm}^{-1}$. The assignment of these bands is uncertain. However, the spectra are typical of square-planar nickel(II) complexes.

TABLE XVI

VISIBLE AND NEAR-INFRARED BANDS OF SOLID COMPLEXES AND CLATHRATES

Compound	Band Maximum (cm. ⁻¹ x 10 ⁻³)						Other
Assignment	$^3B_{2g} \longrightarrow$	$^3E_g(F)$	$^3A_{2g}(F)$	$^3B_{1g}(F)$	$^3E_g(P)$	$^3A_{2g}(P)$	
[Ni py ₄ (ClO ₄) ₂]		7.0	12.3	13.4	16.7	27.2	24.0 sh
[Ni py ₄ (ClO ₄) ₂]·xC ₆ H ₆			12.1	13.4	16.7	27.1	23.9 sh
[Ni(bipy) ₂ (ClO ₄) ₂]			10.6		17.8	23.4	
[Ni(3-Brpy) ₄ (ClO ₄) ₂]			12	13.3	16.2	26.9	
[Ni(4-NH ₂ py) ₄](ClO ₄) ₂							23.6
[Ni(3-pic) ₄](ClO ₄) ₂							22.6
[Ni(3-pic) ₄ (ClO ₄) ₂]			12.3	13.4	16.8	27.1	
[Ni(4-pic) ₄](ClO ₄) ₂							22.9
[Ni(4-etpy) ₄ (ClO ₄) ₂]			12.2	13.5	16.6	26.9	
[Ni(3,5-lut) ₄ (ClO ₄) ₂]			12.4	13.4	16.7	27.2	
[Ni(4-ippy) ₄ (ClO ₄) ₂]			12.1	13.3	16.3	27.0	
[Ni(4-ippy) ₄](ClO ₄) ₂ ·xCH ₃ C ₆ H ₅							22.2

The spectra of the blue powders may be seen, by comparison of Tables XVI and XIV, to be similar to the spectra of those complexes which have been assigned a tetragonally distorted octahedral configuration in their pyridine base solutions. The maxima of the broad weak bands in the $6500\text{--}8500\text{ cm.}^{-1}$ region could not be accurately located in the powder spectra because of the low signal-to-noise ratio of the instrument and the interfering absorption of the pyridine bases in this region. However, the bands in Table XVI were assigned in analogy to the assignments in Table XIV. The infrared spectra confirm the coordination of perchlorate, and hence the assignment of distorted octahedral symmetry (D_{4h}), in these blue powders. The similarity of the spectra of the powders in the $10,000\text{--}30,000\text{ cm.}^{-1}$ region to that of the solutions listed in Table XIV lends additional support to the six-coordinate D_{4h} species postulated in the solutions.

C. Substituent Effects

The existence of a substituent effect in complexes of the empirical formula $\text{Ni}(\text{X-py})_4(\text{ClO}_4)_2$ is quite obvious since the complexes fall into either a blue series of compounds containing coordinated perchlorate or a yellow series of compounds containing ionic perchlorate, depending merely on the remote ring substituent. The manner by which the substituent determines the nature of the complex is, however, not so obvious. In seeking an explanation, it is appropriate to look at the roles of inductive effects, steric effects, and the resonance effects since these

have often been successfully invoked by organic chemists for explaining chemical properties of aromatic rings.

The inductive effect is a relay of electron polarization through a chain of sigma bonds. According to Fieser and Fieser,⁵³ the direction and magnitude of the inductive effects of different groups can be inferred from dipole moment data. Substituent groups which are more powerful electron attractors than the hydrogen atom are said to exhibit negative inductive effects (-I), whereas those which are poorer electron attractors than hydrogen display positive inductive effects (+I). Alkyl groups are considered +I groups; the bromo and amino groups are -I groups. The dipole moments of the substituted pyridines⁵⁴ are given in Table XVII as an indication of the relative inductive effects of their substituents. Since the 3-methylpyridine complex exhibits both blue and yellow forms, one would expect pyridine bases having more positive inductive effects to give only yellow complexes and ones having less positive inductive effects to give only blue complexes if only the inductive effect were the determining factor. The use of dipole moment data is, of course, an over-simplification since the inductive effect is transmitted only short distances through sigma bonds (hence a 3-methyl group, being closer to the ring nitrogen, should give a larger effect than a 4-methyl group). But even with this consideration, one cannot rationalize the blue 3,5-dimethylpyridine complex, or the blue 4-ethyl- and 4-isopropylpyridine complexes, which would seemingly have greater +I effects than the 3-methyl- and 4-methylpyridine complexes,

TABLE XVII
DIPOLE MOMENTS OF PYRIDINE DERIVATIVES AT 25°

Substituent	Dipole Moment
H-	2.3
Electron releasing (+I)	
3-CH ₃ -	2.4
4-CH ₃ -	2.6
3,5-(CH ₃) ₂ -	2.6
4-C ₂ H ₅ -	2.6
4- <u>i</u> -C ₃ H ₇ -	2.7
Electron attracting (-I)	
3-Br-	2.0
4-NH ₂ -	3.9

respectively. The yellow 4-amino pyridine complex is also not explained by the inductive effect.

Steric effects in the usual sense can be ruled out since none of the substituents are ortho to the ring nitrogen. The more subtle effects of the size and position of the substituent on the lattice energy of the crystal and its influence on the stereochemistry of the complex are not known. One can only observe that clathration, a sensitive indication of lattice structure, occurs with both the smallest (H-) and largest (i-C₃H₇-) substituents.

The resonance effect seems to hold the most promise of explaining the differences in the blue and yellow complexes. However, it does not give a completely satisfying explanation. When a disturbance of pi-electron density at one atom in a conjugated system becomes distributed over the pi-electron cloud associated with the entire system, affecting those atoms far from the source of the disturbance just as much as the atoms close to it, the effect is known as a resonance effect. Substituent groups which supply electron density to conjugated pi-systems are designated as +R in character. These include the alkyl groups, the amino group, and the bromo group. Groups having the opposite effect are designated as -R in character. No -R groups occurred among the complexes prepared in this study. The explanation of the blue and yellow complexes therefore rests, most probably, on the magnitude of the +R effect in these complexes.

It is thought that in the complexes the possibility of d- π back bonding (synergic bonding) is the critical factor which governs the nature of the complex. Thus, perchlorate might become coordinated to the nickel only if synergic bonding is effective in reducing the concentration of negative charge on the nickel which would result from the donation of six pairs of electrons from the ligands. The π cloud of unsubstituted pyridine is apparently an effective "electron sink" into which electrons from the d_{xz} - and d_{yz} -orbitals of the nickel can be delocalized by the formation of d- π bonds. But in the case of the substituted pyridines, it is the substituent group which governs the efficiency of this electron sink by the extent of its donation of electrons into the π cloud, i.e., by the magnitude of its +R effect.

Since the +R effect influences the π -electron density only at positions on the ring which are ortho or para to the substituent, +R groups located in the meta positions of the pyridine ring should have no effect on the π -electron cloud density at the nitrogen atom. Meta-substituted pyridines, therefore, should form blue complexes similar to the unsubstituted pyridine complex. This was indeed the case except for 3-methylpyridine which formed both blue and yellow complexes.

Substituents of +R character in the 4-position of the pyridine ring should increase the π -electron density at the nitrogen atom. If the increase is great enough, synergic bonding from the metal to the π cloud at the nitrogen is prevented. Since electrons on the metal are then not efficiently delocalized, the metal cannot accommodate two additional ligands and the perchlorate ions are not coordinated.

The largest +R effects occur with substituents having unshared electron pairs on the atom attached to the ring.⁵⁵ For alkyl groups, +R effects are rather small, resulting from hyperconjugation of α -hydrogens with the pi-cloud of the ring. Among alkyl groups, therefore, the magnitude of the +R effect should decrease as the number of α -hydrogens decreases. From these considerations, the 4-substituents in this study may be ranked in order of increasing +R effects as follows: $i\text{-C}_3\text{H}_7-$ < C_2H_5- < CH_3- < NH_2- . The two substituents having the greatest +R effects were observed to result in yellow complexes having ionic perchlorate, while the remaining two substituents resulted in blue complexes having coordinated perchlorate. The difference in the complexes thus seems to depend on the subtle difference in resonance energy between a methyl group and an ethyl group. This slight difference and the anomaly of the yellow 3-methylpyridine complex constitute the major shortcomings of the resonance effect explanation.

Although the substituent on the pyridine ring does seem to determine the nature of the complex, it is interesting to note that, in general, the substituent, when located in the 3- or 4-position of the ring, has little, if any, effect on the Δ value of the pyridine. For comparison purposes, the most complete set of Δ values are the averaged field Δ values for the complexes in acetone solutions. They correspond to the energies of the first transitions in Table XV. From a study of these values, it can be seen that, of the monodentate pyridine derivatives, all except 3-bromopyridine have Δ_{avg} values of about 10,000 cm^{-1} .

D. Further Aspects

Although several complexes of nickel(II) perchlorate with pyridine derivatives have been synthesized and their compositions and stereochemistries established, the study is, in a sense, incomplete, for several questions have been raised and left unanswered. The nature of the slightly paramagnetic $[\text{Ni}(\text{3-pic})_4](\text{ClO}_4)_2$ complex could be further clarified by studies of variations in the visible and near-infrared absorption spectrum and in the magnetic moment as functions of temperature. Visible absorption spectra, using plane polarized light, of oriented single crystals of the complexes would be valuable in confirming the assignments of tetragonal bands in the powder spectra of the complexes. Single-crystal x-ray diffraction studies and further investigation of clathration properties of the complexes would also be desirable. The preparation of additional complexes, especially ones having non-alkyl substituted pyridines, should be possible, and their characterization should allow a more complete interpretation of the substituent effect.

CHAPTER IV

SUMMARY

Blue paramagnetic ($\mu = \sim 3.2$ B. M.) complexes having formulas $[\text{Ni}(\text{X-py})_4(\text{ClO}_4)_2]$, where X is H, 3-CH₃, 3-Br, 4-C₂H₅, 3,5-(CH₃)₂, and 4-i-C₃H₇, were prepared. Also, yellow diamagnetic $[\text{Ni}(\text{X-py})_4](\text{ClO}_4)_2$ complexes, where X is 4-CH₃ and 4-NH₂, and the slightly paramagnetic yellow $[\text{Ni}(3\text{-pic})_4](\text{ClO}_4)_2$ complex were prepared. Characterization of the complexes included studies of the infrared, near-infrared, and visible spectra of the solid complexes and their solutions in the component pyridine base and in acetone.

Near-infrared and visible absorption bands were assigned in agreement with either regular or distorted octahedral stereochemistries for the blue complexes and solutions and in agreement with square-planar stereochemistry for the yellow complexes. The coordination of the perchlorate ion to the nickel ion in the blue complexes was confirmed from the splitting of the degenerate modes and the activation of the symmetric modes of the perchlorate ion in the infrared spectrum. The ability of two of the complexes to form clathrates with aromatic guests was observed. Inductive, steric, and resonance effects of the substituents were considered as possible explanations of the observed substituent effects. The influence of the resonance effect on the possibility of synergic bonding between the nickel and the pyridine base was considered

to be the most important factor in determining the stereochemistries of the complexes. The value of Dq for the 3- and 4-substituted pyridines was judged relatively insensitive to the substituent group.

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