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PARAMAGNETIC PALLADIUM(II) AND PLATINUM(II) COMPLEXES WITH STERICALLY DEMANDING ETHYLENEDIAMINES AND A STUDY OF THE COORDINATION CHEMISTRY OF 2,2'-BIS(PIPERIDINO)DIETHYLAMINE WITH DIVALENT TRANSITION METAL IONS.

The University of Oklahoma, Ph.D., 1976
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THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

PARAMAGNETIC PALLADIUM(II) AND PLATINUM(II) COMPLEXES WITH STERICALLY DEMANDING ETHYLENEDIAMINES

and

A STUDY OF THE COORDINATION CHEMISTRY OF 2,2'-BIS(PIPERIDINO)DIETHYLAMINE WITH DIVALENT TRANSITION METAL IONS

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

JOHN ROBERT HOOVER

Norman, Oklahoma

1976

PARAMAGNETIC PALLADIUM(II) AND PLATINUM(II) COMPLEXES

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DIVALENT TRANSITION METAL IONS

APPROVED BY

DISSERTATION COMMITTEE

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LIST OF ABBREVIATIONS

Abbreviation	Meaning
BHAE	bis(hexahydroazepino)ethane
bipy	bipyridine
BPEA	2,2'-bispiperidinodiethylamine
n-Buen	N-n-butylethylenediamine
c-C_6H_{11}	cyclohexyl
dien	diethylenetriamine
EDM	1,2-dimorpholinoethane
EDP	1,2-dipiperidinoethane
EDPy	1,2-dipyrrolidinoethane
en	ethylenediamine
Eten	N-ethylethylenediamine
N,N'-Et_2en	N,N'-diethylethylenediamine
Et_3en	N,N,N'-triethylethylenediamine
Et_4dien	N,N,N',N'-tetraethylethylenediamine
N-Meen	N-methylethylenediamine
Me_2en	N,N'-diamethylethylenediamine
Me_4en	N,N,N',N'-tetramethylethylenediamine
Me_4pn	N,N,N',N'-tetramethyl-1,2-propylenediamine
Me_4tn	N,N,N',N'-tetramethyltrimethylenediamine
Me_5dien	N,N,N',N'-tetramethyldiethylmethylamine
Ph, (ϕ)	phenyl

Abbreviation	Meaning
γ-pic	4-picoline
i-proen	N-i-propylethylenediamine
n-proen	N-n-propylethylenediamine
py	pyridine
TMEDM	2,2',6,6'-tetramethyl-1,2-dimorpholinoethane

PART I

PARAMAGNETIC PALLADIUM(II) AND PLATINUM(II) COMPLEXES WITH STERICALLY DEMANDING ETHYLENEDIAMINES

FOREWARD

The objective of this research was to synthesize palladium(II) and platinum(II) complexes with three related ligands and to study the effects of the ligands on the complexes. The ligands [1,2-dipyrrolidinoethane (EDPy); 1,2-dipiperidinoethane (EDP); and 1,2-bis(hexahydroazepino)ethane (BHAE)] were chosen for their ability to produce steric hindrance within the complexes along with having high base strengths.

All the complexes had the stoichiometry $M(L)X_2$, $M = Pd^{2+}, Pt^{2+}$; L = EDPy, EDP, BHAE; $X = Cl^-, Br^-, I^-, CNS^-$. $Pt(BHAE)I_2$ was not isolated. The complexes were non-electrolytes in CH_2Cl_2 at room temperature. Except for the thiocyanato complexes and $Pt(BHAE)Cl_2$, the complexes were paramagnetic. Temperature dependent susceptibility studies suggested an equilibrium between a singlet and triplet electronic ground state.

The bromo and iodo complexes of palladium showed variable magnetic moments. The moments were dependent upon sample preparation, age, and washing.

The magnetic moments of the complexes were explained by proposing an octahedral environment through halide bridging. The bridging was supported by far infrared spectral bands which were assigned as metal-bridging halide stretching frequencies.

Other possible causes of paramagnetism were not considered likely. A tetrahedral configuration would result in a paramagnetic species; however, tetrahedral complexes should absorb at lower energies than were observed. Furthermore, a crystal structure of paramagnetic $Pt(EDM)I_2$ where EDM is 1,2-dimorpholinoethane showed it to be square planar.

A third possible cause of paramagnetism in a four coordinate, d^8, complex is a weak ligand field strength for a square planar geometry. This also was not considered likely because of the observed spectrochemical order for the ligands used in this study. If indeed the paramagnetism is the result of a weak ligand field, then the paramagnetism should be greatest for the ligand that is lowest in the spectrochemical order. This order was not found.

The thiocyanato complexes were not paramagnetic, but did exhibit other interesting bonding features. Since the ligands were amines, the thiocyanate was expected to bond to the metal through the sulfur. All the complexes showed mixed bonding with both N and S bonded thiocyanate groups present. The mixed bonding modes of the thiocyanates were determined by C-N stretching frequencies and the CNS bending frequencies. The $Pt(EDP)(NCS)_2$ complex exhibited two linkage isomers, an all N-bonded species, and a complex with the thiocyanate bonding mixed. The unusual bonding occurs to lessen the steric hindrance present in the molecule.

PARAMAGNETIC PALLADIUM(II) AND PLATINUM(II) COMPLEXES WITH STERICALLY DEMANDING ETHYLENEDIAMINES

CHAPTER I

INTRODUCTION

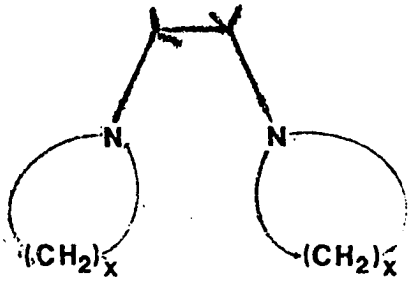
A. Statement of the Problem

The objectives of this research were to synthesize and characterize compounds of very sterically hindered bidentate nitrogen containing ligand systems and to relate their properties to similar known complexes. To realize these objectives, palladium(II) and platinum(II) were chosen due to their uniqueness in their inability to acquire geometries other than square planar. The ligands chosen were 1,2-dipyrrolidinoethane, 1,2-dipiperidinoethane, and 1,2-(bishexahydroazepino)-ethane. The ligands were chosen not only because of the large amount of steric hindrance, but also because of the greater base strength over the previously studied and similar ligand 1,2-dimorpholinoethane, (EDM). Therefore, the characterization of the complexes should show if the previously reported Pd(II) and Pt(II) EDM complexes were paramagnetic because of low base strength of the EDM or the large degree of steric hindrance, or a combination of both factors.

B. The Ligands

B.1. 1,2-dipyrrolidinoethane, 1,2-dipiperidinoethane, and 1,2-bis(hexihydroazepino)ethane

Three ditertiary amines which are related to N,N,N',N'-tetraalkylethlenediamine were used as chelating agents. The ligands, 1,2-dipyrrolidinoethane, (EDPy), 1,2-dipiperidinoethane, (EDP), and 1,2bis(hexahydroazepino)ethane, (BHAE), were selected because their only structural difference is in the size of the heterocyclic rings attached to the ethylene bridges, (I). The number of methylene groups, X in (I), is 4, 5, and 6, thereby giving ring sizes of 5, 6, and 7 for EDPy, EDP, and BHAE respectively.



(I)

All three ligands were expected to produce considerable steric demands on a complex; even more so than the very sterically demanding N,N,N',N'-tetraethylethylenediamine. This is due to the more rigid conformation of the rings as opposed to the free N-substituted alkyl groups. For the bonded ligands EDPy and EDP, the most stable ring conformations are the envelope and the chair respectively.[1] The seven-menbered ring ligand, BHAE, may or may not be as sterically demanding as the other two since it can "twist" into more possible conformations even though it is larger in size. The two possible conformations of the ethylene bridge are the equatorial and the axial with respect to the rings. The

equatorial conformation for EDP should be energetically favorable by about 1.5 kcal per ring.[2]

To further emphasize the steric requirements of the ligands, a spatial analogy can be made between EDP and 1,2-dimorpholinoethane, (EDM). The only difference in structure is that the ether linkage at the gamma position of the morpholine rings in EDM is replaced by a methylene group in EDP. Space filling molecular models show EDP and EDM to have virtually identical steric requirements. There have been x-ray crystal structures obtained for three different EDM complexes, $Co(EDM)Cl_2$,[3] $Cu(EDM)(NO_2)_2$,[4] and $Pt(EDM)I_2$.[5] The $Co(EDM)Cl_2$ complex has a pseudo-tetrahedral geometry with the ligand in a chair-chair equatorial-equatorial conformation. The structure showed severe interactions of the rings, through the beta methylene groups with the chlorides. The structures of the Cu and Pt complexes revealed pseudo-octahedral and planar geometries, respectively. The ligand in both these complexes was found to be in a chair-chair, axial-axial conformation. The platinum complex exhibited considerable steric interactions between the iodides and the alpha methylene groups within the ligand rings. Since EDM and EDP ligands are so similar in their spatial requirements, their steric demands on a complex should also be similar.

The ligands, EDPy, EDP, and BHAE have essentially the same base strengths. Gero has determined the pK_a values, in H_2O, for a variety of ditertiary ethylenediamines including EDPy, EDP, and EDM.[6] These are shown in Table I along with the pK_b.

The Pk_b value for BHAE was not determined by Gero; however, the pK_b is probably close to those values for EDPy and EDP based upon the pK_b of only the heterocyclic rings. The pK_b values of the heterocyclic

TABLE 1

BASE STRENGTHS OF SOME TERTIARY ETHYLENEDIAMINES

Complex	pK_a Values		pK_b Values	
EDPy	9.47	6.25	4.53	7.75
EDP	9.47	6.30	4.53	7.70
EDM	6.65	3.63	7.35	10.37

rings are 2.68, 2.80, 2.90, and 5.74 for pyrrolidine, piperidine, hexahydroazepine and morpholine respectively.[7] As a result, any major difference in the metal-amine bond strengths of the EDPy, EDP and BHAE complexes should depend upon the steric factors involved.

There are no complexes of the EDPy and BHAE ligands reported in the literature. For EDP, first row transition metal complex have been recently reported and characterized.[8,9] There it was shown that the ligand was sterically demanding by forcing the divalent metal ions into a pseudo-tetrahedral geometry.

The earliest report of EDP was in 1871 by Bruhl[10] when he prepared platinum(IV) salts with the ligand as diquaternary ammonium ions.

$$[EDPH_2]^{+2}[PtCl_6]^{-2} \qquad \text{(II)}$$

$$[EDP(CH_2CH_2)]^{+2}[PtCl_6]^{-2} \qquad \text{(III)}$$

B.2. The Effects of Ligands on Steric Requirements

There are two competing factors responsible for determining the coordinating ability of N-alkyl substituted ethylenediamines: (1) inductive effects and (2) steric effects.

The successive addition of an alkyl grouping to an amine generally leads to an increase in the base strength of the amine because

alkyl groups are slightly electron releasing.[11] For comparison, some K_b's for simple aliphatic amines are:[12] NH_3, $K_b = 1.8 \times 10^{-5}$; CH_3NH_2, $K_b = 4.4 \times 10^{-4}$; $CH_3CH_2NH_2$, $K_b = 5.6 \times 10^{-4}$; $(CH_3CH_2)_2NH$, $K_b = 9.6 \times 10^{-4}$. With this increase in base strength with increasing alkyl substitution, alkyl amines thus become potentially stronger coordinating agents than the unsubstituted amines.

Although increasing the number of alkyl groups leads to an increased base strength and better coordinating ability, the bulk or steric requirements of these alkyl groups is also of great importance in determining the stability of the complex and the number of ligands the metal ion can accommodate.

Pfieffer and Glasser undertook the first systematic investigation of N-alkyl substituted ethylenediamines in 1938.[13] A series of $Cu(ClO_4)_2$ complexes were prepared with ethylenediamine (en) and substituted ethylenediamines (N-Ren). The ligands are en, N-Meen; N,N'-Et_2en; N,N-Et_2en; N-Me,N'N'-Et_2en; and N,N,N'-Et_3en. The first four ligands listed produced complexes with the general formulation $Cu(diamine)_2(ClO_4)_2$, and the last two ligands formed complexes with a different formulation, $[Cu(OH)(diamine)][ClO_4]$. A binuclear bridged structure was assigned the last two substances. The alkyl groups apparently have sufficient bulk to prevent a second molecule of the amine from approaching close enough for coordination. These authors also attempted to prepare bisdiamine complexes of $Cu(ClO_4)_2$ with the ligands, N-Ph,N',N'-Et_2en and trisdiamine complexes of Co(III) and Cr(III) with N,N-Et_2en; however, all attempts to isolate characterizable complexes failed.

In 1952 Keller and Edwards[14] prepared complexes of Co(III) and Ni(II) with N-Meen, N-Eten, and N-n-Proen. The cobalt and nickel

complexes have the stoichiometry $Co(diamine)_3X_3$ and $Ni(diamine)_3X_2$; (X = Cl and Br). The complexes were not completely characterized but the authors observed that they were quite similar to trisethylenediamine complexes of Co(III) and Ni(II). Apparently, the addition of one alkyl group did not noticeably affect the nature of the compound formed.

Beginning in 1952, Basolo and Murmann[15,16] published a series of papers on the base strengths of various N and N,N'-alkyl substituted ethylenediamines and the stability of Cu(II) and Ni(II) complexes formed from the lignads. They found that the base strength of the diamine generally increased with the number of alkyl substituents and also the length of the alkyl group. The N-alkyl derivatives studied were en, N-Meen, N-Eten, N-n-Proen, N-i-Proen and N-n-Buen. The order of stability of the complexes decreased in the order: en > Meen > Eten > n-Buen > n-Proen > i-Proen. This order is the inverse of the ordering for the basicity of the ligands with the exception of n-Buen. The effects of the spatial demands of the ligands become evident since the complex stability and ligand basicity are inversely related. The position of the n-Buen complex in the series was attributed to the long chain being able to coil and fold back out of the way to relieve some of the steric strain.

Similar results were found with the N,N'-dialkyl series. The order of stability of the complexes decreased in the same manner as did the N-alkyl series. The dialkyl series were found to have appreciably more steric crowding than the monoalkyl series as was shown by the lower stability constants.

In 1965, Meek[17] synthesized Ni(II) perchlorate complexes with a series of ligands: en, N-Meen, N-Eten, N-n-Proen, N,N'-Me_2en, N-Me,N'-Eten, and N,N-Me_2en. All the complexes exhibited the stoichiometry,

$Ni(diamine)_3(ClO_4)_2$. From the optical spectra, the D_q value was found to decrease in order: en > N-Meen > N-Eten > N-n-Proen > N,N'-Me_2en > N-Meen,N'-Eten > N,N-Me_2en. The D_q values are a result of both inductive and steric factors. It can be seen that these results are in general agreement with those mentioned earlier for the stability constant measurements of Basolo and co-workers. Even though inductive effects are increasing the basicity of the ligands, the steric effects are increasing at an even more rapid rate and very soon become the dominant factor.

C. Related Chemical Literature

C.1. Palladium and Platinum Complexes of N-Substituted Ethylenediamines

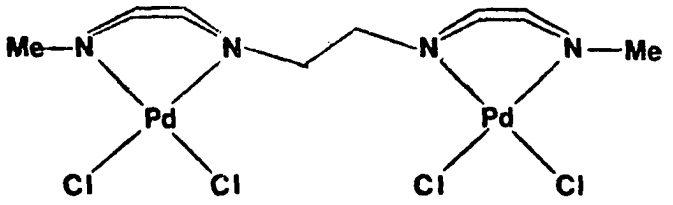
There have been relatively few studies reported in the literature concerning substituted ethylenediamine complexes of palladium(II) and platinum(II). These complexes are listed in Table II. In 1930, Bennett[18] reported the preparation of palladium(II) and platinum(II) chloride complexes of the following ligands: N,N'-diphenylethylenediamine, N,N'-dianisylethylenediamine, and N,N,N',N'-dimethyldiphenylethylenediamine. These complexes were found to be insoluble in all solvents except those that reacted with the complex and decomposed upon heating without melting. The complexes were not characterized beyond their stoichiometries: $M(ligand)Cl_2$.

Mann and Watson[19] prepared complexes of substituted ethylenediamines of the type $M(diamine)X_2$ (where M = Pd(II), Pt(II), and Ir(II); $X = Cl^-$ and Br^-; and diamine = Me_4en and 1,4-dimethylpiperazine). They also prepared a palladium chloride complex with the ligand, 1,2-di(4-methyl-1-piperazinyl)ethane which had the stoichiometry $Pd_2(tetramine)Cl_2$,

TABLE II

PALLADIUM(II) AND PLATINUM(II) COMPLEXES OF N-ALKYL SUBSTITUTED ETHYLENEDIAMINES

Complex	Reference
$Pd(N,N'\text{-}Me_2en)Cl_2$	20
$Pd(N,N,N',N'\text{-}Me_4en)Cl_2$	19, 20
Pd N,N'-bis(1-methylheptyl)en Cl_2	20
Pd $N,N'\text{-}Phen_2en)Cl_2$	18, 20
$[Pd(N,N'\text{-}Me_2en)_2]Cl_2$	20
$[Pd(N,N'\text{-}Me_2en)_2](NO_3)_2$	20
$[Pd(N,N,N',N'\text{-}Me_4en)_2](NO_3)_2$	20
Pd 1,2-di(4-methyl-1-piperazinyl)ethene Cl_2	19
$Pd(1,4\text{-dimethylpiperazine})Cl_2$	19
$Pd(EDM)X_2$ ($X = Cl^-$, Br^- and I^-)	21
$Pd(dianisylen)Cl_2$	18
$Pd(N,N\text{-}Me_2\text{-}N',N'\text{-}Phen_2en)Cl_2$	18
$Pt(N,N,N',N'\text{-}Me_4en)Cl_2$	19
Pt 1,2-di(4-methyl-1-piperazinyl)ethane Cl_2	19
$Pt(1,4\text{-dimethylpiperazine})Cl_2$	19
$Pt(N,N'\text{-}Phen_2en)Cl_2$	18
$Pt(dianisylen)Cl_2$	18
$Pt(N,N,N',N'\text{-}Phen_2Me_2en)Cl_2$	18
$Pt(EDM)X_2$ ($X = Cl^-$, Br^- and I^-)	5
$Pt(TMEDM)X_2$ ($X = Cl^-$ and Br^-)	5



(IV)

(IV). The reason the ligand did not behave as a tetradentate chelating agent was given to be the tetrahedral dispositions of the nitrogens not allowing all four nitrogens to bond to one metal ion. Furthermore, they were not able to prepare the bisdiamine complexes with either ligand. The bis complexes were thought to be too sterically encumbered to be stable. By contrast, Meek[20] prepared several N-substituted ethylenediamine palladium complexes. He, too, could not synthesize the palladium complex with two Me_4en ligands having chloride as the anion. However, using a poor coordinating anion, NO_3^-, the bis complex was isolated. The stability of $[Pd(Me_4en)_2](NO_3)_2$ was attributed to the greater ability of the amine to compete for coordination sites on the metal than nitrate.

In 1969, Lott and Rasmussen[21] reported the systhesis of palladium halide complexes with the ligand, EDM. The chloride and bromide complexes were insoluble, diamagnetic and were found to have the stoichiometry of $Pd(EDM)X_2$. A polymeric structure was proposed to explain the insolubility of the complexes. Polymerization was assumed to occur through ligand bridging <u>via</u> a trans square planar geometry. A diamagnetic iodide complex was isolated with the approximate stoichiometry $Pd(EDM)I_2$. Upon dissolving the iodide complex in acetone with a large excess of ligand, the solution became different in color and paramagnetic. When the red

iodide complex was dissolved in acetone, there was initially a light red colored solution. This solution darkened over a period of two hours. Upon addition of a large excess of EDM, the solution reverted to light red color and was paramagnetic. Kinetic studies showed that the dark red solution was an equilibrium mixture between two species. $Pd(EDM)I_2$ and $[Pd_2EDM_2I_2]I_2$ were postulated to be in equilibrium based upon the conductivity of the solution. The paramagnetism was attributed to the formation of $[Pd(EDM)_2]I_2$ which had acquired a tetrahedral geometry in solution. The square planar or octahedral geometries were ruled out because of the steric requirements of the ligands.

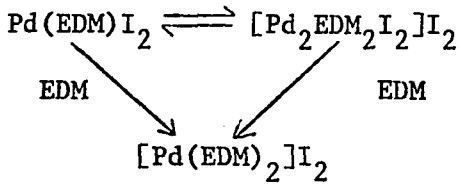
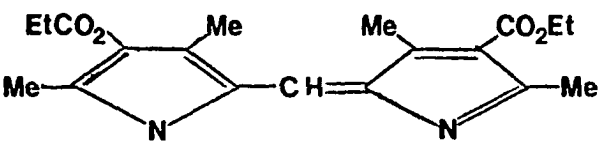


FIGURE 1. Reactions of $Pd(EDM)I_2$ in Acetone.

The ethylenedimorpholine complexes of the platinum halides have also been prepared[5] and are unusual in that the bromide and iodide complexes are paramagnetic in the solid state. The paramagnetism exhibited by the two complexes was believed to be related to the large amount of steric hindrance of the ligand, EDM. Similar complexes, $Pt(TMEDM)X_2$ ($X = Cl^-$ and Br^-) were also prepared to test the idea of steric strain as the cause of paramagnetism. Both complexes were paramagnetic in the solid state. The authors believed that all the platinum complexes have a square planar geometry because as previously mentioned, the paramagnetic $Pt(EDM)I_2$ complex was found to be square planar by a crystal structure.

Although this section is devoted to N-substituted ethylenediamine complexes, the following discussion concerns similar complexes and is included to illustrate the difficulty with which palladium(II) and platinum(II) accept tetrahedral geometries.

Porter[22] has tried to isolate non-planar complexes of palladium(II) by using the ligand, ethyl-3,3',5,5'-tetramethylpyrromethene-4,4'-dicarboxylate, (V). Due to steric interactions between the methyl groups in



(V)

the 5 and 5' positions on adjacent chelating agents, a non-planar bis-(ethyl-3,3',5,5'-tetramethylpyrromethene-4,4'-dicarboxylate) palladium(II) complex was assumed. The analogous nickel(II) complex has, indeed, been found to have a distorted tetrahedral geometry.[23] However, a crystal structure has shown the palladium complex to have a definite planar geometry at the expense of ligand distortion.[24] A portion of the coordination sphere is shown in Figure 2 in order to illustrate the degree in which the ligand is distorted. The ligand distortion consists of folding of the ligand out of the PdN_4 plane by bending around the N(1) - N(11) vector. The pyrrole rings are also folded away from the plane of the chelate ring by folding along the N(1) - C(5) and N(11) - C(7) vectors.

Similar ligand distortions have been found in bis-N-t-butylsalicylaldiminatopalladium(II)[25] and bis(2,2'-bipyridyliminatopalladium(II)).[26]

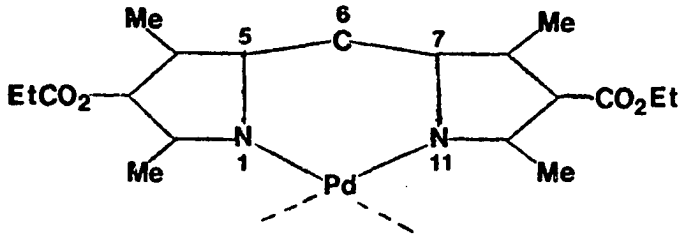
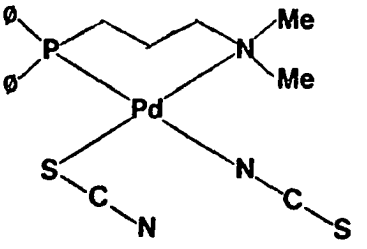


FIGURE 2. A portion of the Molecular Structure of bis-ethyl 3,3',5,5'-tetramethylpyrromethene-4,4'-dicarboxylate

C.2. Thiocyanate Complexes of Palladium(II) and Platinum(II)

The thyocyanate ion $:N\equiv C-\ddot{S}:^-$ readily undergoes linkage isomerism. Three types of bonding are known for the ion, thiocyanato, (M-SCN); isothiocyanato, (M-NCS); and briding, (M-SCN-M). There are several review articles that describe the large variety of compounds containing thiocyanate as a ligand or as an anion.[27-30] Here, however, the emphasis is on the different modes in which the thiocyanate group bonds to the palladium(II) and platinum(II). Turco and Pecile[31] found that for soft (class b) metals, the bonding mode of thiocyanate depends upon the nature of the other ligands present in the complex. Their arguments were based upon electronic factors. They pointed out that strong pi-bonding ligands enhanced M-NCS bonding while weak pi-bonding ligands promoted M-SCN bonding. They reasoned that the M-SCN bond gains additional stability over the M-NCS bond by backbonding of the non-bonding electrons in the d-orbitals of the metal into the anti-bonding pi-orbitals and the vacant d-orbitals of the sulfur. However, if a good pi-bonding ligand is present that competes with the sulfur for the available d-electrons in the metal, the additional stability of the M-SCN bond is lost and M-NCS becomes the more stable bonding mode. This is illustrated by the thiocyanate bonding in the complexes cis-$[P(Ph)_3]_2(NCS)_2$ and cis-$Pt(NH_3)_2(SCN)_2$.

Pearson[32] suggested that all class b metal ions, more often than not, exhibit antisymbiosis. That is, soft bases already bonded to a metal ion reduce the tendency of that metal ion to bond to an additional soft base. Pearson discussed antisymbiosis in terms of the trans effect. Invariably ligands with a strong trans effecting ability are soft bases. As a result, if two soft bases occupy a mutual trans position, then there will be a destabilization effect on both bases. Therefore, with the proper choice of ligands the metal ion can be made to form either the M-SCN bond or the M-NCS bond or even both modes. An example is PdL(NCS)(SCN), (VI) where L = 1-diphenylphosphino-3-dimethylaminopropane.[33] The structure of (VI) can be predicted from Pearson's discussion of antisympiosis. The thiocyanate trans to the soft phosphino group is N-bonded while the other thiocyanate, trans to the hard amino group, is S-bonded.



(VI)

A further example of electronic effects was provided by Basolo's and Burmeister's synthesis of the first linkage isomer of palladium(II) thiocyanato complexes.[34] They reasoned that by choosing a ligand that is intermediate in the hard-soft base concept, a complex with a small energy difference in the formation of the M-SCN and the M-NCS bonds could be synthesized. They succeeded in preparing $Pd(bipy)_2(SCN)_2$ and $Pd[As(C_6H_5)_3]_2(SCN)_2$ which upon heating at 156°C for 30 minutes isomerized to $Pd(bipy)_2(NCS)_2$ and $Pd[As(Ph)_3]_2(NCS)_2$.

The above "rules" do not cover every case. Obviously, steric factors are important. In 1964, Basolo, Baddley and Burmeister[35] prepared thiocyanato complexes of palladium which demonstrated the importance of the balance between electronic and steric factors in determining the mode of thiocyanato bonding. The importance of electronic factors were shown by the synthesis of two compounds with nearly identical ligand steric requirements, but having different electronic characteristics. Thus, two different modes of thiocyanato bonding were shown in the complexes, $Pd(\gamma\text{-pic})_2(SCN)_2$ and $Pd(py)_2(NCS)_2$. Steric factors were also shown to be major considerations for the mode in which the thiocyanate ion bonded to the palladium. The two compounds prepared were [Pd(dien)SCN]CNS and [Pd(Et_4dien)NCS]CNS. Based on electronic factors alone, the two complexes should exhibit M-SCN bonding. This was not observed. Through their work, the authors pointed out that electronic factors are important but that small differences are often all that are required to change the mode of CNS^- bonding. Furthermore, they suggested that with many phosphino complexes the steric requirements may be more important than the electronic factors. Later Burmeister, et al.[36] reported how delicate the balance of electronic and steric effects can be in the bonding of thiocyanate to the palladium(II) ion. Their study showed the effects of the counter ion in preparing the compound [Pd(Et_4dien)CNS]X. When the counter ion, X, was SCN^- or PF_6^-, the thiocyanate in the coordination sphere was N bonded; however, when $B(Ph)_4^-$ was used as the counter ion, the M-SCN bond was formed.

Recently, several palladium and platinum complexes having mixed thiocyanato bonding have been prepared and characterized (Table III). The bonding in these complexes can be explained on the basis of the

TABLE III

NON-BRIDGING MIXED THIOCYANATO COMPLEXES OF PALLADIUM(II) AND PLATINUM(II)

Complex	Reference
$Pd(NCS)(SCN)\ Ph_2P(CH_2)_3NMe_2$[a]	33, 39
$Pd(NCS)(SCN)\ Ph_2P(CH_2)_2PPh_2$[a]	40
$Pd(NCS)(SCN)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)$[a]	41
$Pt(NCS)(SCN)(Ph_2PC{\equiv}C\text{-}t\text{-}Bu)$[a]	42
$Pd(NCS)(SCN)\ Ph_2P(o\text{-}C_6H_4AsPh_2)$[b]	37
$Pd(NCS)(SCN)\ Ph_2P(CH_2)_2NMe$[b]	37
$Pd(NCS)(SCN)(Ph_2PC{\equiv}CPPh_2)$[b]	43
$Pt(NCS)(SCN)(Ph_2PC{\equiv}CPPh_2)$[b]	43
$Pt(NCS)(SCN)$4,4'-dimethylbipyridyl)[4]	44
cis-$Pt(NCS)(SCN)(Ph_2PC{\equiv}CEt)_2$[b]	45
cis-$Pt(NCS)(SCN)(Ph_2PC{\equiv}CPh)_2$[b]	45
cis-$Pt(NCS)(SCN)(Ph_2PC{\equiv}Ci\text{-}Pr)_2$[b]	45
cis-$Pd(NCS)(SCN)[P(OMe)_3]_2$[b]	45
cis-$Pt(NCS)(SCN)[P(OPh)_3]_2$[b]	45
cis-$Pt(NCS)(SCN)[P(OMe)_3]_2$[b]	45

[a] Structure determined by crystal structure.

[b] Infrared measurements indicate probable mixed bonding modes.

theories concerning the electronic and steric effects of the ligands. Many of the complexes have both hard and soft donors present in the ligands, thereby supporting the electronic theories by having both M-NCS and M-SCN bonding in the same complex (see compound VI). Other complexes listed show mixed bonding present for complexes which should exhibit only M-NCS bonding based upon electronic factors alone, and are explained by the steric requirements of the ligands forcing the mixed bonding. It has been argued that in complexes, such as cis$Pd(Ph_2PCH_2CH_2PPh_2)(SCN)(NCS)$, the formation of the M-SCN bond relieves steric hindrance in the molecule.[37] The argument is based upon the fact that the M-SCN group is non-linear and that by rotation the nitrogen end can be directed away from other ligands. This cannot occur with the linear M-NCS moiety which is fixed in space with respect to the rest of the molecule.

Recent work has raised doubt concerning the electronic theories in palladium thiocyanato complexes where phosphines are used as the ligands. Carty, et al.[38] have completed a crystal structure of $Pd(SCN)_2[P(OPh)_3]_2$. The existence of the Pd-SCN bonds rather than the Pd-NCS bonds is incompatible with the electronic or pi-bonding theories; however, the reduced steric hindrance of the phosphites favor Pd-SCN bonding. The authors suggested that the bonding mode in many phosphine thiocyanato complexes is dictated by steric effects as opposed to electronic factors or pi-acceptor ability of the ligands.

C.3. Paramagnetic Four-Coordinate d^8 Complexes

C.3.a. Paramagnetic Ni(II) Complexes

Coordination chemists have found the chemistry of Ni(II) complexes to be quite fascinating.[46] This fascination is due to the ability of the metal ion to readily form a variety of complexes with different

structures and coordination numbers together with the ability to undergo conformational isomerism. Four-coordinate complexes of the type $Ni(CN)_4^{2-}$ are square planar and diamagnetic while complexes like $Ni(Br)_4^{2-}$ are tetrahedral and paramagnetic.[47]

Considerable work has shown the coordination numbers and structures of Ni(II) complexes to be exceptionally sensitive to the steric requirements and the inductive properties of the ligands.[48] Tetracoordinate Ni(II) complexes that are square planar generally contain ligands of high field strength and low ligand-ligand repulsion interactions, whereas ligands of low field strength and high repulsion interactions tend to form tetrahedral Ni(II) complexes. This is primarily due to square planar, low spin systems producing a greater crystal field stabilization energy as opposed to the tetrahedral high spin systems. Ligands that are intermediate in the above factors have been shown to produce Ni(II) complexes having small energy differences between square planar and tetrahedral geometries. Complexes of this type are examples of conformational isomers in which one form is tetrahedral and paramagnetic and the other is square planar and diamagnetic.

Quite often only one structure is isolated in the solid state, but in solution both isomers are clearly shown to be present in rapid equilibrium. Because the two forms have distinctly different absorption spectra, examination can give an estimation of the amount of both species present.

It is generally accepted that many diamagnetic Ni(II) complexes dissolve to give paramagnetic solutions. Some complexes, when dissolved in good coordinating solvents such as pyridine, exhibit magnetic moments of about 3.3 B.M. These moment values are in the range of moments for

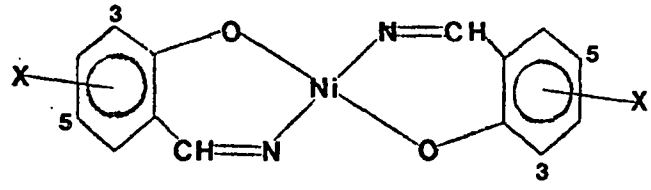
six-coordinate Ni(II) complexes. It has been definitely established that in these systems solvent molecules associate along the Z-axis of the metal ion to produce octahedral complexes.[49,50] Furthermore, certain diamagnetic Ni(II) complexes were found to have magnetic moments ranging between zero and about 3 B.M. in essentially non-coordinating solvents such as benzene. The suggested explanation was the formation of the paramagnetic tetrahedral species.[47-49] A later suggestion was that the paramagnetism in solution may be due to some type of axial interaction to generate a triplet ground state.[51-54] This possibility brought extensive reinvestigations of these systems. It was found that the paramagnetism was dependent upon the system in question. In many cases, the observed paramagnetism was a result of solute axial interactions, the formation of a tetrahedral species, or both.

Holm et al. have reported on numerous occasions excellent examples of Ni(II) complexes in which observed paramagnetism has been found to be a result of solute axial interactions and tetrahedral conformations. In 1960, Holm and McKinney published a paper[55] on N-alkyl-salicylaldimine Ni(II) complexes. They found that in benzene and chloroform solutions, a magnetic moment varying from 0.23 to 2.58 B.M. was obtained for the complexes by changing the N-substituent, R. When R was an ethyl group he found the magnetic moment to be 0.23 B.M. When R was sec-Butyl and cyclopentyl groups, the moments were 2.10 and 2.58 B.M. respectively. There was a direct correlation between the size of the R group and the observed magnetic moment when the concentrations of the different solutions were the same. The optical spectra of the compounds in both solution and the solid state were not related to spectra of tetrahedral Ni(II) complexes in most cases. Furthermore, they showed that complexes in

solution having the higher magnetic moments also exhibited an observed molecular weight 20-47% higher than that calculated for the monomer. Thus, Holm and McKinney attributed the paramagnetism in solution to intermolecular association of the solute and a pseudo-octahedral geometry.

In another paper by Holm[56] in 1961, a strong concentration dependence of the solution magnetic moment of bis-(N-methylsalicylaldimine)-nickel(II) in non-coordinating solvents of benzene and chloroform was shown. For benzene, the highest magnetic moment of 2.23 B.M. was observed at the limit of the complex's solubility. A saturated solution in chloroform produced a magnetic moment of 1.86 B.M. Lower concentrations in both types of solvents caused the magnetic moment to drop.

In the same paper, Holm examined a number of ring substituted N-methylsalicylaldimine nickel(II) complexes (VII). The Ni complexes



(VII)

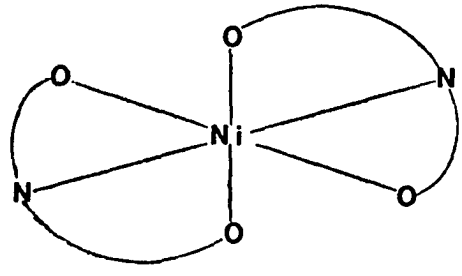
showed no paramagnetism in solution when the ring substituent, X, was in the 3-position (X = i-propyl and methyl). When the ring substituent was in the 5-position, solution paramagnetism was observed. Holm concluded that the paramagnetism of bis-(N-methylsalicylaldimine)-Ni(II) in inert solvents is predominantly, if not completely, a consequence of solute association. Furthermore, if ring substitution is made at the 3-position, then association is sterically inhibited.

In a continuation of this work, Holm and Swaminathan[57] increased the size of the N-substituted group, R, by the formation of bis-(N-arylsalicylaldimine)-Ni(II) complexes. By varying the nature of the aryl group appended to the imine nitrogen, they found that the Ni(II) complexes fell into three categories: (1) those with o-substituted groups were diamagnetic and monomeric; (2) those with p-substituted groups were strongly paramagnetic in solution (μ_{eff} = 2.8 B.M.), were associated and were either diamagnetic or paramagnetic solids; (3) those with m-substituted aryl groups had a solution μ_{eff} = 3.2 B.M., a greater degree of association than the p-substituted complexes and were always paramagnetic solids. The molecular association was determined in solution and the complexes in category two gave an observed molecular weight 1.5-2.0 times that calculated for the monomer, while those of category three ranged from 2 to 3 times the calculated value. For complexes of the second category, the magnetic and molecular weight data were interpreted in terms of a diamagnetic monomer-paramagnetic dimer equilibrium. The optical spectra for the complexes did not suggest that paramagnetism was due to the tetrahedral conformation in either solution or the solid state. The complexes in the third category were presumed to be associated solids. The degree of association in the solid state was not determined. As in the previous papers, there appeared a direct relation between three factors: (1) the steric hindrance produced by the imine nitrogen substituent; (2) the observed magnetic moment; and (3) the degree of intermolecular association.

In a fourth and final paper by Holm and Swaminathan[58] in 1962, on the series of N-substituted salicylaldime Ni(II) complexes, the nitrogen or N-substituents were sec-alkyl groups. These complexes were also

diamagnetic in the solid state and paramagnetic in solution. However, in inert solvents these complexes had a fundamentally different behavior than the N-methyl, -n-alkyl and -aryl complexes. Evidence was presented in the form of x-ray, molecular weight, spectral, and magnetic data to show that a conformational equilibrium existed between planar and tetrahedral isomers. The increased steric requirement of the sec-alkyl groups over the previous substituents was argued for the origin of the non-planar conformations.

In 1964, Holm et al.[59] published a report on a series of bis-(N-R-salicylaldimine)-nickel(II) complexes in which the R group was an ether linkage capable of coordination. The complexes in which the R group was a branched chain alkyl group with a terminal methoxy or hydroxyl group, were without exception paramagnetic and octahedral in conformations. In chloroform solutions below room temperature, the complexes were octahedral; however, with increasing temperature an equilibrium was set up between octahedral, square planar, and tetrahedral species. At high temperatures the equilibrium was displaced toward the tetrahedral forms. The spectra of the octahedral complexes were found to be quite similar to those of associated paramagnetic bis-(salicylaldimine) nickel(II) complexes, suggesting quasi-octahedral coordination in the latter, (VIII).



(VIII)

Bertini and co-workers[60-61] published two papers on an extensive investigation on N-substituted diamine complexes of several transition metals ions: Fe(II), Co(II), Ni(II), and Cu(II). The ligands used were Me_4en, Me_4pn, and Me_4tn. The bromide and iodide complexes were assigned a distorted tetrahedral geometry. The nickel chloride complexes were of a polymeric hexacoordinate nature with chloride bridges in the solid state. In solution the polymeric structure broke apart to give a mixture of octahedral and tetrahedral species with the equilibrium displaced toward the tetrahedral species as the temperature was increased.

The nickel nitrate and thiocyanate complexes were also found to be octahedral. The nitrate complexes were found to be monomeric octahedral units with two bidentate nitrate groups on the basis of their optical and infrared spectra and their molecular weights. The thiocyanate complexes were insoluble and of a polymeric nature which was achieved through bridging thiocyanate groups.

The authors concluded that tetrahedral complexes are still not as common as octahedral and planar complexes. The alkyldiamines and N- and C-substituted alkyldiamines generally give nickel(II) complexes with structures preferrably planar or octahedral. As the ligand becomes more and more bulky by successive substitutions, the planar diamagnetic configuration becomes more unstable. The tendency to form octahedral complexes increases with bulk and finally, with sufficient bulk, the tetrahedral conformation is achieved.

C.3.b. Paramagnetic Pd(II) and Pt(II) Compounds.

Although five and six coordinate compounds of palladium(II) and platinum(II) are known, the coordination chemistry of these two elements deal almost exclusively with four-coordinate square planar,

diamagnetic complexes. Whereas, nickel(II) can be forced into tetrahedral geometry by the use of sterically forcing ligands, the same is not true for the second and third row d^8 elements.

The only well confirmed examples of paramagnetic palladium(II) or platinum(II) compounds are found to have octahedral environments Bartlett, et al.[62,63] have found that $CsPdF_3$ and PdF_2 are paramagnetic with moments of 1.60 B.M., and 1.84 B.M. respectively. Crystal structure determinations have shown both compounds to be octahedral through fluoride bridging.

As mentioned in section B.1., several palladium(II) and platinum(II) complexes with substituted ethylenediamines as ligands are paramagnetic. The first of these was $Pd(EDM)I_2$[21] and was reported to have a tetrahedral geometry. The tetrahedral assignment was based, primarily, upon the old dogma of d^8 complexes that diamagnetic complexes are square planar while paramagnetic complexes are tetrahedral.

The paramagnetic complexes of $Pt(EDM)X_2$[5] ($X = Br^-$ and I^-) and $Pt(TMEDM)X_2$[64] ($X = Cl^-$ and Br^-) are all assumed to have square planar geometries. This conformation was assigned on the basis of the crystal structure of $Pt(EDM)I_2$ and the similarities of all their optical spectra. On the other hand, a quasi-octahedral environment for the Pt(II) ions may have been overlooked. Monomeric units of $Pt(EDM)I_2$ have been found to be rigorously planar by the structure determination; however, the possibility of Z-axial intermolecular association was not determined.[64] It is conceivable that the platinum complexes could approach an octahedral environment and a triplet ground state by halogen bridging and still retain the above stoichiometries. Furthermore, their low solubilities are indicative of a polymeric nature. The $Pt(EDM)Br_2$ complex was found

to be insoluble in all common organic solvents, while $Pt(EDM)I_2$ was the most soluble and only slightly so in chloroform and acetone.

TABLE IV

PARAMAGNETIC COMPOUNDS OF PALLADIUM(II) AND PLATINUM(II)

Compound	μ_{eff}	Reference
PdF_2	1.84	62
$CsPdF_3$	1.60	63
$[Pd(EDM)_2]I_2$ (Solution)	3.4	21
$Pt(EDM)Br_2$	2.97	5
$Pt(EDM)I_2$	2.76	5
$Pt(TMEDM)Cl_2$	3.02	64
$Pt(TMEDM)Br_2$	1.86	64
$Pd(TMEDM)Cl_2$	3.02	5
$Pd(TMEDM)Br_2$	1.86	5

CHAPTER II

EXPERIMENTAL

A. Instruments Used

A.1. Infrared Spectra

The infrared spectra were recorded on Beckman Instruments I.R.-8 and I.R.-10 recording spectrophotometers in the range 4000-600 cm^{-1}. The spectra were obtained as KBr disks or as Nujol mulls between NaCl plates. Infrared spectra were also recorded on a Beckman Instruments I.R.-12 recording spectrophotometer in the range 4000-400 cm^{-1}. Nujol mulls between CsI windows were used to 250 cm^{-1}. The absorption bands of polystyrene film at 2851.5 and 1601.8 cm^{-1} were used as reference standards.

Infrared data for the halide complexes are included in the discussion in chapters three and four along with representative spectra. Infrared data for the thiocyanate complexes are found in Table XII and representative spectra are in chapter six.

A.2. Absorption Spectra

Near infrared, visible and ultraviolet spectra were recorded on a Beckman Instruments Model DK-1 recording spectrophotometer in both the solid state and solution in the range 4000-40,000 K. A tungsten lamp was used as the light source from 4000-28,500 K, and a deuterium lamp was used from 28,500-40,000 K. The majority of the solution spectra were

recorded in the visible and ultraviolet regions on a Cary Model 118-C recording spectrophotometer in the range 12,500-28,500 K with a tungsten light source and in the range of 28,500-40,000 K with a deuterium light source.

Representative absorption spectra are included in chapters three, four and five with all the data listed in Tables VII, X, and XI.

A.2.a. Reflectance Spectra

Reflectance spectra were recorded using the reflectance attachment for the Beckman DK-1 Instrument; MgO was used as the reflective coating. The solid samples were prepared by triturating and then placing in an indention on a pyrex slide and covering with a thin pyrex cover-plate. The 0% and 100% absorbance scales of the instrument were adjusted with slides containing MgO in both the sample and reference beams, and a background spectrum recorded. The spectrum of the sample was then recorded against a reference of MgO.

A.2.b. Solution Spectra

Solution spectra were obtained in methylene chloride solution using two matched 1 cm quartz cells. One of the cells contained the sample dissolved in the solvent, and the other contained the solvent as a blank and placed in the reference beam. Prior to recording the spectra, the instrument was adjusted to a constant baseline with solvent in both cells.

The samples were weighed directly into a volumetric flask using a single pan analytical balance. The volumetric flask was made up to volume at ambient temperature. The sample cell was thoroughly rinsed with the solution whose spectrum was to be recorded.

A.3. Mass Spectra

Mass spectra of the complexes were obtained on a Hitachi-Perkin Elmer Model RMU-7E spectrometer. The samples were introduced by means of the direct introduction probe, and the spectra were calibrated with perfluorokerosine.

A.4. Magnetic Moments

Two different techniques were used to obtain magnetic moments.

A.4.a. Solution Magnetic Moments

Evans' method[65] for magnetic moments of solutions by Nuclear Magnetic Resonance was used with solvents of methylene chloride and chloroform. N.M.R. spectra were recorded on a Varian Associates Model T-60 spectrometer at the ambient temperature of the instrument (310°K). A 25 Hz. sweep width and a 50 sec. sweep time were used. The splitting of the methyl resonance of acetaldehyde, J = 2.85 Hz.,[66] was used to calibrate the sweep width. Samples were weighed directly into volumetric flasks using a single pan analytical balance and the flasks were made up to volume at ambient temperature.

Samples were placed in a thin-wall N.M.R. tube which had a 3 mm. O.D. pyrex tube, containing only solvent, mounted coaxially inside of it. The splitting between the proton peak of the pure solvent and the same peak of the solvent with the solute added was measured. The magnetic moment was calculated using equations 1 and 2.

$$\chi = \frac{3\Delta\nu}{2\pi\nu_m} + \chi_o + \frac{d_o - d_s}{M}\chi_o \qquad (1)$$

$$\mu_{eff} = 2.84\sqrt{\chi_m' T} \qquad (2)$$

The terms of the above equation have been defined elsewhere.[67] In

practice, the third term in equation (1) was ignored because of its small significance at the concentrations that were used.

A.4.b. Solid State Magnetic Moments

Magnetic susceptibilities for solid samples were determined by using a Faraday type balance which employed a quartz spring. The balance has been fully described elsewhere.[68,69]

The mass of the samples was determined by measuring the extension of the quartz spring. The force constant of the quartz spring had previously been calculated by suspending standard weights in the quartz bucket on the spring and measuring the extension with the cathetometer (±0.0005 cm). By using a series of standard weights and the method of least squares, the force constant was found to be 0.1965 cm/mg (±0.0005 cm/mg).

The magnetic susceptibilities of the samples were determined by raising and lowering the poles of the magnet past the quartz bucket containing the sample. By measuring the average deflection, i.e., the apparent change in weight of the sample and bucket in the field, the average deflection of the sample was compared to the deflection of standard samples. The standards used were solid $HgCo(NCS)_4$[70] and $(NH_4)_2SO_4 \cdot NiSO_4 \cdot 6H_2O$,[71] whose susceptibilities are well known. The gram susceptibility of an unknown sample was determined by equation (3).

$$\chi_{unk} = \frac{\Delta W_{unk}}{W_{unk}} \cdot \frac{W_{std}}{\Delta W_{std}} \chi_{std} \qquad (3)$$

The deflections of both the unknown sample and the standards were corrected for the diamagnetism of the bucket.

$$\Delta W(\text{Corrected}) = \Delta W(\text{Sample + bucket}) - \Delta W(\text{empty bucket}) \qquad (4)$$

The molar susceptibility was then found (equation 5) and corrected for the diamagnetism of the ligands and the closed electronic shells of the metal ion[72] (equation 6).

$$\chi_m = \chi_{unk} \cdot \text{formula weight} \tag{5}$$

$$\chi_m' = \chi_m - \sum \chi_{diamag} \tag{6}$$

From the corrected molar susceptibility, the effective magnetic moment was calculated as follows:

$$\mu_{eff} = 2.828(\chi_m' \cdot T)^{1/2} \tag{7}$$

The procedure for determining the susceptibilities of the samples was to initially triturate the dry sample and place 15-30 mg in the balance's quartz bucket. The magnet was then raised and lowered until ten deflections were measured. The measured deflection for the sample is one-half the difference of the average upward and downward maximum deflection as the magnet passes the sample. For each determination, at least two different samples of the unknown and often more than two at room temperature were used and the results were averaged. The errors in the reported magnetic moments are 1-5% with the greatest error occuring for the samples with moments less than 1.5 B.M.

Magnetic susceptibilities were determined twice for each sample at three different temperatures other than room temperature. For samples showing unique behavior, a determination at a fifth temperature was recorded. For the three temperatures below room temperature, the balance containing the sample was slowly evacuated of air. After evacuation, dry nitrogen was allowed to enter the balance to a pressure of 200-300 torr to allow thermal conductivity between the sample and the

coolant. The coolants, liquid nitrogen (-196°), dry-ice acetone (-78°), and carbon tetrachloride slush (-23°) were held in a dewar flask suspended around the part of the balance containing the sample. The fifth temperature determination for some samples was obtained by pumping heated water through a pyrex jacket surrounding the sample tube portion of the balance.

A.5. Conductivity Measurements

The conductivity of each of the complexes was determined using methylene chloride as a solvent. The measurements were made with an Industrial Instruments Model RC-16B2 conductivity bridge. The conductivity cell was equipped with platinized platinum electrodes and was calibrated with a standard aqueous potassium chloride solution. The solutions were prepared by weighing the samples directly in volumetric flasks on a single pan analytical balance. The volumetric flasks were then filled to volume at ambient room temperature. The cell and flasks containing the solutions were thoroughly cleaned and dried before each determination.

The conductivity data are included in the tables with the electronic absorption data.

A.6. X-ray Powder Patterns

X-ray powder patterns were used to check for isomorphism for some of the complexes. The powder patterns were taken with a Norelco Type 12045 diffractometer employing $Cu_{K\alpha}$ radiation. The data are found in Table VII.

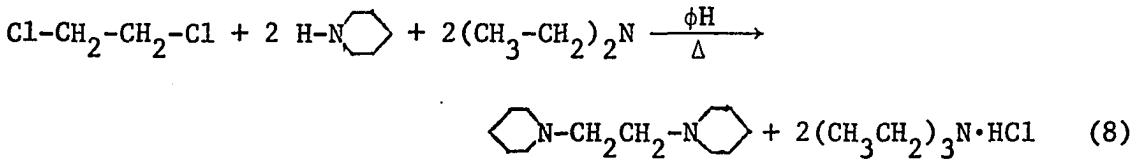
A.7. Elemental Analysis

Elemental analysis for carbon and hydrogen were done by Galbraith Laboratories, Inc., Knoxville, Tennessee. In addition to carbon and

hydrogen analyses, nitrogen analysis was obtained for the complexes containing the thiocyanate ligand.

B. Reagents

The ligands, EDPy, EDP and BHAE were not available commercially. All three were prepared in a similar manner by refluxing the amine, pyrrolidine piperidine or hexahydroazepine, with 1,2-dichloroethane (obtained from Eastman).[6,73] The reagents were placed in a 250 ml round bottom flask: 10 ml (125 mmol) of 1,2-dichloroethane; 275 mmol of the appropriate amine; 36 ml (260 mmol) of triethylamine and 70 ml of benzene. The benzene was added to dilute the reactants since the reaction is very exothermic. After mixing the reactants, the mixture was allowed to digest for 10 hr. after which time it cooled to room temperature. The reaction mixture was then refluxed for 70 hr.



(8)

The triethylaminehydrochloride was filtered from the mixture and the volatile starting materials removed on a rotary evaporator. The ligands were purified by vacuum distillation through a 10 cm Vigreaux column. At about 10^{-3} torr, EDPy was collected at 49-50°, EDP at 55-57°, and BHAE at 92-94°C. The ligands were confirmed by N.M.R., i.r., and mass spectra. Since amines of the type similar to the ligands are quite hydroscopic, they were stored over sodium hydroxide.

The salt K_2PdCl_4 was obtained from Alfa Inorganics, Inc. The other palladium and platinum halide starting materials were obtained from K and K Laboratories as MX_2.

Some of the solvents were treated to remove water and other impurities. Benzene was distilled and stored over sodium. Acetonitrile was distilled and stored over CaH_2. Acetone was distilled prior to use through a 60 cm Vigreaux column and stored over anhydrous $MgSO_4$. Both methylene chloride and chloroform were distilled over P_4O_{10} and stored over anhydrous $CaCl_2$.

C. Preparation of Complexes

C.1. Preparation of dichloro-1,2-dipyrrolidinoethanepalladium(II), $PdCl_2EDP$

The complex was prepared by dissolving 0.50 mmol (160 mg) of K_2PdCl_4 in a mixture of 20 ml of 1,2-dimethoxyethane and 10 ml of H_2O. To the stirred solution, 1.5 mmol (3.0 ml) of EDPy was added dropwise. Precipitation of the product began before the ligand addition was complete. The reaction mixture was stirred for an additional 20 min. and then filtered. The product was washed with two 25 ml portions of acetone, three 25 ml portions of anhydrous ether, and then air dried.

Analysis of $PdCl_2EDPy$:

Calculated: Carbon, 34.76%; Hydrogen, 5.83%.

Found: Carbon, 34.59%; Hydrogen, 5.91%.

C.2. Preparation of dichloro-1,2-dipiperidinoethanepalladium(II), $PdCl_2EDP$

The complex was prepared in an analogous fashion to the dichloro-1,2-dipyrrolidinoethanepalladium(II) complex.

Analysis of $PdCl_2EDP$:

Calculated: Carbon, 38.56%; Hydrogen, 6.47%.

Found: Carbon, 38.30%; Hydrogen, 6.60%.

C.3. Preparation of dichloro-1,2-bis(hexahydroazepino)ethanepalladium(II), $PdCl_2BHAE$

The complex was prepared in an analogous manner to the dichloro-1,2-dipyrrolidinoethanepalladium(II).

Analysis of $PdCl_2BHAE$:

Calculated: Carbon, 44.99%; Hydrogen, 7.57%.

Found: Carbon, 44.68%; Hydrogen, 7.00%

C.4. Preparation of dibromo-1,2-dipyrrolidinoethanepalladium(II), $PdBr_2EDPy$

The complex was prepared by two different procedures.

C.4.a. Method One.

Palladium(II) bromide, 0.5 mmol (230 mg), and 2.5 mmol (280 mg) of potassium bromide were stirred together in 40 ml of acetone at room temperature for 12 hours. After the palladium salt had gone into solution, the reaction mixture was filtered to remove any excess potassium bromide and any other insolubles. To the resulting K_2PdBr_4 solution 1.5 mmol (3.0 ml) of EDPy was added dropwise. Precipitation of the complex occurred almost immediately after the addition of the ligand was completed. The reaction mixture was then stirred for an additional hour. The product was filtered and washed, as follows: two 25 ml portions of a 1:1 mixture of ethanol and H_2O, three 25 ml portions of absolute ethanol, three 25 ml portions of anhydrous ether. The product was air dried. Although it was not found necessary, the product can be recrystallized by Soxhlet extraction with chloroform.

Analysis of $PdBr_2EDPy$:

Calculated: Carbon, 27.64%; Hydrogen, 4.64%.

Found: Carbon, 27.80%; Hydrogen, 4.74%.

C.4.b. Method Two

A solution of K_2PdBr_4 was prepared by stirring 0.2 mmol (10 mg) of palladium(II) bromide with 1.0 mmol (120 mg) of potassium bromide in 16 ml of acetone until all of the palladium salt had gone into solution. The solution was filtered to remove any insoluble material. The filtrate was added, dropwise, to a solution of 10 mmol of EDPy dissolved in 8 ml of absolute ethanol. The orange colored product began to precipitate from solution after 5 ml of the K_2PdBr_4 acetone solution had been added to the ligand solution. The reaction mixture was stirred for 15 minutes after the addition of the Pd solution was completed. The product was filtered and washed as in C.4.a.

C.5. Preparation of Dibromo-1,2-dipiperidinoethanepalladium(II), $PdBr_2$EDP

The complex was prepared in three ways.

C.5.a. Method One

The complex was synthesized using the method reported for dibromo-1,2-dipyrrolidinoethane palladium(II) in section C.4.a.

C.5.b. Method Two

The complex was prepared with the method reported in section C.4.b for dibromo-1,2-dipyrrolidinoethanepalladium(II).

C.5.c. Method Three

A neat solution of $PdBr_2(\phi C{\equiv}N)_2$ was prepared according to the method reported by Kharasch et al.,[74,75] by dissolving 0.37 mmol (170 mg) of $PdBr_2$ in 10 ml of benzonitrite at 100°C. After the solution cooled to room temperature, 1.5 mmol of 1,2-dipiperidinoethane was added dropwise to the stirred benzonitrite solution. The product precipitated immediately after the ligand addition was completed. The reaction mixture was stirred for an hour and was filtered and washed as in C.5.a.

Analysis of $PdBr_2$(EDP):

Calculated: Carbon, 31.16%; Hydrogen, 5.23%.

Found: Carbon, 31.01%; Hydrogen, 5.30%.

C.6. Preparation of dibormo-1,2-bis(hexahydroazepino)ethanepalladium(II), $PdBr_2$BHAE

The complex was prepared by two different procedures.

C.6.a. Method One

The complex was prepared by the method reported in section C.4.a.

C.6.b Method Two

The complex was prepared using the method reported in section C.4.b.

Analysis of $PdBr_2$(BHAE):

Calculated: Carbon, 36.34%; Hydrogen, 6.11%.

Found: Carbon, 35.45%; Hydrogen, 5.84%.

C.7. Preparation of diiodo-1,2-dipyrrolidinoethanepalladium(II), PdI_2EDPy

The complex was prepared by two different methods.

C.7.a Method One

The complex was prepared by the procedure reported in section C.4.a.

C.7.b Method Two

The complex was prepared by the method reported in section C.4.b.

Analysis of PdI_2EDPy:

Calculated: Carbon, 22.73%; Hydrogen, 3.81%.

Found: Carbon, 22.51%; Hydrogen, 3.86%.

C.8. The Preparation of diiodo-1,2-dipiperidinoethanepalladium(II), PdI_2EDP

The complex was synthesized by two different methods.

C.8.a. Method One

The complex was prepared by the method reported in section C.4.a.

Analysis of PdI_2EDP:

Calculated: Carbon, 25.88%; Hydrogen, 4.35%.

Found: Carbon, 25.10%; Hydrogen, 4.40%.

C.8.b. Method Two

The complex was synthesized by the method reported in section C.4.b.

Analysis of PdI_2EDP:

Calculated: Carbon, 25.88%; Hydrogen, 4.35%.

Found: Carbon, 25.77%; Hydrogen, 4.26%.

C.9. The Preparation of diiodo-1,2-bis(hexahydroazepino)ethanepalladium(II), PdI_2BHAE

The complex was prepared by two different methods.

C.9.a. Method One

The complex was prepared by the method reported in section C.4.a.

C.9.b. Method Two

The complex was prepared by the method reported in section C.4.b.

Analysis of PdI_2BHAE:

Calculated: Carbon, 28.76%; Hydrogen, 4.84%.

Found: Carbon, 28.81%; Hydrogen, 4.81%.

C.10. The Preparation of dichloro-1,2-dipyrrolidinoethaneplatinum(II), $PtCl_2EDPy$

$PtCl_2(\phi CN)_2$[74,75] 0.40 mmol (180 mg) was dissolved in 35 ml of 1,2-dimethoxyethane under an atmosphere of dry nitrogen. To the stirred solution, 2.4 mmol of EDPy was added dropwise while the reaction system was continually flushed with N_2. After 24 hours the solution was filtered and washed with 10 ml of ether. The yield was 15 mg.

Analysis of $PtCl_2EDPy$:

Calculated: Carbon, 27.66%; Hydrogen, 4.64%.

Found: Carbon, 27.81%; Hydrogen, 4.58%.

C.11. The Preparation of dichloro-1,2-dipiperidinoethaneplatinun(II), $PtCl_2EDP$

The complex was prepared by the method reported in section C.10. There was one difference and that was the reaction mixture containing the ligand was stirred at 40°C for one hour after the ligand addition.

Analysis of $PtCl_2EDP$:

Calculated: Carbon, 31.15%; Hydrogen, 5.24%.

Found: Carbon, 31.07%; Hydrogen, 5.20%.

C.12. The Preparation of dichloro-1,2-bis(hexahydroazepino)ethaneplatinum(II), $PtCl_2BHAE$

The complex was prepared by the method reported in section C.10.

Analysis of $PtCl_2BHAE$:

Calculated: Carbon, 34.30%; Hydrogen, 5.77%.

Found: Carbon, 34.00%; Hydrogen, 5.63%.

C.13. The Preparation of dibromo-1,2-dipyrrolidinoethaneplatinum(II), $PtBr_2EDPy$

The dibromo bis-benzonitrile Platinum(II) complex was first prepared in an analogous fashion to the preparation of $PtCl_2(\phi CN)_2$ reported in section C.10. A solution of 0.23 mmol (130 mg) of $PtBr_2(\phi CN)_2$ in 30 mls of acetone was prepared. The ligand, EDPy, was added dropwise to the stirred acetone solution until 2 mmol had been added. After three hours a yellow precipitate had formed. The reaction mixture was filtered after 18 hours and washed with three 20 ml portions of absolute ethanol followed by three 20 ml portions of anhydrous ether to yield 70 mg of product.

Analysis of $PtBr_2EDPy$:

Calculated: Carbon, 22.96%; Hydrogen, 3.83%.

Found: Carbon, 23.16%; Hydrogen, 3.90%.

C.14. The Preparation of dibromo-1,2-dipiperidinoethaneplatinum(II), $PtBr_2EDP$

$PtBr_2$, 0.57 mmol (200 mg), was added to 70 ml of acetone solution containing 1.50 mmol (180 mg) of KBr. The solution was stirred at 40°C for 48 hours, and then filtered. To the filtrate, 0.25 ml (1.25 mmol) of EDP was added dropwise. After 24 hours the reaction mixture was filtered and washed in an analogous fashion to the washing in section C.13. The yield was 200 mg.

Analysis of $PtBr_2EDP$:

Calculated: Carbon, 26.15%; Hydrogen, 4.39%.

Found: Carbon, 26.30%; Hydrogen, 4.26%.

C.15. The Preparation of dibromo-1,2-bis(hexahydroazepino)ethaneplatinum(II), $PtBr_2BHAE$

The complex was synthesized by the method reported in section C.5.c.

Analysis of $PtBr_2BHAE$:

Calculated: Carbon, 29.02%; Hydrogen, 4.88%.

Found: Carbon, 29.18%; Hydrogen, 4.99%.

C.16. The Preparation of diiodo-1,2-dipyrrolidinoethaneplatinum(II), PtI_2EDPy

The complex was prepared by the method reported in section C.14. The product was recrystallized from $CHCl_3$ by soxhlet continuous extraction. The reaction time was 40 hours.

Analysis of PtI_2EDPy:

Calculated: Carbon, 19.45%; Hydrogen, 3.27%.

Found: Carbon, 19.58%; Hydorgen, 3.33%.

C.17. The Preparation of diiodo-1,2-dipiperidinoethaneplatinum(II), PtI_2EDP

The complex was prepared by the method reported in section C.14. The product was recrystallized by continuous extraction from $CHCl_3$. The reaction time was 48 hours.

Analysis of PtI_2EDP:

Calculated: Carbon, 22.34%; Hydrogen, 3.75%.

Found: Carbon, 22.50%; Hydrogen, 3.70%.

C.18. The Attempted Preparation of diiodo-1,2-bis(hexahydroazepino)-ethaneplatinum(II), PtI_2BHAE

The synthesis of PtI_2BHAE was attempted by several methods of which none were successful. All attempts ended in the recovery of starting materials or reduction of the platinum(II) salts to the metal.

C.18.a. Method One

The preparation of the complex was attempted by a method analogous to C.5.c. After 72 hours, only $PtI_2(\phi CN)_2$ and the ligand BHAE were recovered.

C.18.b. Method Two

The preparation of PtI_2BHAE was attempted by a method analogous to the method reported in section C.10. After 30 hours, the appearance of metallic platinum was noted in the reaction vessel. No recoverable amount of the desired product was formed.

C.18.c Method Three

The synthesis of PtI_2BHAE was attempted by a method analogous

to that reported in section C.14. After 72 hours, metallic platinum was noted in the reaction mixture with no formation of the product.

C.19. The Preparation of dichlorobenzamido-1,2-dipyrrolidinoethane-platinum(II), $Pt(\phi CONH_2)(EDPy)Cl_2$

$PtCl_2(phCN)_2$, 0.6 mmol (270 mg), was dissolved in 30 ml of acetone and 2 mmol of EDPy was then added dropwise to the stirred solution in a nitrogen atmosphere.

Analysis of $Pt(\phi CONH_2)(EDPy)Cl_2$:

Calculated: Carbon, 36.76%; Hydrogen, 4.90%.

Found: Carbon, 37.34%; Hydrogen, 5.19%.

C.20. Preparation of isothiocyanatothiocyanato-1,2-dipiperidinoethane-palladium(II), Pd(NCS)(SCN)EDP

A solution of $K_2Pd(SCN)_4$ was prepared by dissolving 2 mmol of $PdCl_2$ (360 mg) in 150 ml of acetone which contained 15 mmol of KCNS. The solution was stirred at 50°C for 24 hours. The mixture was then filtered to remove solid KCNS and KCl. The solvent was evaporated to reduce the volume to 30 ml. The solution was then cooled to -78°C and filtered to remove excess KCNS and KCl. To the filtrate, 0.5 ml (2.5 mmol) of EDP was added dropwise and was stirred at room temperature for 24 hours. The product gradually precipitated from the solution to yield a yellow solid. The solid was filtered out of solution and washed with 15 ml of ether. The product was recrystallized from acetone by continuous extraction to yield 290 mg of product.

Analysis of Pd(NCS)(SCN)EDP:

Calculated: Carbon; 40.14%; Hydrogen, 5.78%; Nitrogen, 13.37%.

Found: Carbon, 40.01%; Hydrogen, 5.65%; Nitrogen, 13.41%.

C.21. Preparation of isothiocyanatothiocyanato-1,2-dipyrrolidinoethane-palladium(II), Pd(NCS)(SCN)EDPy.

The complex was prepared by the method reported in section C.20. However, in this preparation, 1 mmol (190 mg) of $PdCl_2$ and 8 mmol (800 mg) of KCNS in 100 ml of acetone were used to prepare the $K_2Pd(SCN)_4$ solution. The amount of ligand added was 0.30 ml (1.5 mmol) of EDPy. Product began to precipitate from the reaction mixture in 45 minutes.

Analysis of Pd(SCN)(NCS)EDPy:

Calculated: Carbon, 36.87%; Hydrogen, 5.17%; Nitrogen, 14.34%.

Found: Carbon, 36.69%; Hydrogen, 5.06%; Nitrogen, 14.45%.

C.22. Preparation of isothiocyanatothiocyanato-1,2-bis(hexahydroazepino)-ethanepalladium(II), Pd(NCS)(SCN)BHAE

The complex was synthesized by the method reported in section C.21. The only difference is that this reaction took considerably longer; the mixture was stirred 48 hours.

Analysis of Pd(NCS)(SCN)BHAE:

Calculated: Carbon, 42.99%; Hydrogen, 6.33%; Nitrogen, 12.54%.

Found: Carbon, 42.81%; Hydrogen, 6.25%; Nitrogen, 12.75%.

C.23. Preparation of isothiocyanatothiocyanato-1,2-dipyrrolidinoethane-Platinum(II), Pt(NCS)(SCN)EDPy

In the preparation, 0.75 mmol (310 mg) fo K_2PtCl_4 and 7.5 mmol (750 mg) of KCNS were stirred together in 50 ml of H_2O. After 4 hours the water was removed on a rotary evaporator. The yellow solid was dissolved in 20 ml of acetone and cooled to -78°C and the excess KCNS and KCl was filtered out. The filtrate was warmed to room temperature and 3.0 mmol (0.60 ml) of EDPy was added dropwise. After the solution had stirred for four days at room temperature, the solvent was removed

on a rotary evaporator. The solid was washed with ethanol which left a cream colored product. The product was recrystallized from acetonitrile.

Analysis for Pt(NCS)(SCN)EDPy:

Calculated: Carbon, 30.05%; Hydrogen, 4.21%; Nitrogen, 11.68%.

Found: Carbon, 30.15%; Hydrogen, 4.32%; Nitrogen, 12.39%.

C.24. Preparation of isothiocyanatothiocyanato-1,2-dipiperidinoethaneplatinum(II), Pt(NCS)(SCN)EDP

The complex was prepared by the method reported in section C.23. In the experiment, the product began to precipitate out of solution after 5 days. After the reaction mixture had been stirred for 7 days, the solid was filtered and recrystallized from acetonitrile.

Analysis of Pt(NCS)(SCN)EDP:

Calculated: Carbon, 33.12%; Hydrogen, 4.78%; Nitrogen, 11.04%.

Found: Carbon, 33.01%; Hydrogen, 4.70%; Nitrogen, 11.08%.

C.25. Preparation of diisothiocyanato-1,2-dipiperidinoethaneplatinum(II), $Pt(NCS)_2EDP$

The preparation of the all N-bonded isomer of this complex was accomplished in the same manner as the above mixed isomer except that the reaction mixture was refluxed for 4 days in acetone to give the product as a white precipitate. The solid was filtered from the solution, washed with two 25 ml portions of anhydrous ether and recrystallized from acetonitrile.

Analysis of $Pt(NSC)_2EDP$:

Calculated: Carbon, 33.12%; Hydrogen, 4.78%; Nitrogen, 11.04%.

Found: Carbon, 33.05%; Hydrogen, 4.95%; Nitrogen, 10.81%.

C.26. Preparation of isothiocyanatothiocyanato-1,2-bis(hexahydroazepino)-ethaneplatinum(II), Pt(NCS)(SCN)BHAE

The preparation and purification of this complex was an identical method as that reported in section C.23 for preparation of Pt(NCS)-(SCN)EDPy.

Analysis of Pt(NCS)(SCN)BHAE:

Calculated: Carbon, 35.87%; Hydrogen, 5.28%; Nitrogen, 10.46%.

Found: Carbon, 35.78%; Hydrogen, 5.32%; Nitrogen, 10.55%.

CHAPTER III

THE PALLADIUM HALIDE COMPLEXES

A. Results

The complexes [$Pd(L)X_2$; L = EDPy, EDP, BHAE; X = Cl, Br, I] have very low solubilities in the solvents acetone, chloroform and methylene chloride. The greatest solubilities are exhibited in CH_2Cl_2 and range in magnitude from 10^{-4} mol/ℓ for the chlorides to a little less than 10^{-3} mol/ℓ for the iodide complexes. The complexes are air and water stable.

A variation in the magnetic moments was observed for some of the complexes. The data reported in Table V is the highest moment for a given complex if variation is present. All the data are for the solid state since magnetic moment values in solution could not be obtained due to the low solubilities of the complexes. For the iodide complexes, solutions sufficiently concentrated to observe solution moments of 2.0 to 2.5 B.M. were prepared; however, no splitting of the solvent resonance was observed even though moments that high were observed in the solid state.

Variable magnetic behaviour is exhibited by $Pd(EDPy)Br_2$, $Pd(EDP)Br_2$ and all of the iodide complexes. By varying the method of preparation of these species a large range in the effective magnetic moments can be obtained as shown in Table VI. By using the method of

TABLE V

Effective Magnetic Moments for $PdLX_2$ Complexes

μ_{eff}^{a} ($\chi_m \times 10^6$)[b]

	77°K	195°K	250°K	297°K	331°K
$Pd(EDP)Cl_2$	1.25 (2,548)	1.99 (2,533)	2.20 (2,430)	2.39 (2,399)	
$Pd(EDP)Br_2$	2.58 (10,785)	4.05 (10,545)	4.50 (10,135)	4.87 (9,994)	5.06 (9,677)
$Pd(EDP)I_2$	1.81 (5,307)	2.85 (5,215)	3.19 (5,100)	3.44 (4,979)	
$Pd(EDPy)Cl_2$	0.83 (1,116)	1.30 (1,081)	1.45 (1,048)	1.56 (1,028)	
$Pd(EDPy)Br_2$	1.70 (4,717)	2.65 (4,514)	2.99 (4,472)	3.22 (4,366)	
$Pd(EDPy)I_2$	1.42 (3,273)	2.23 (3,187)	2.51 (3,140)	2.68 (3,032)	
$Pd(BHAE)Cl_2$	0.92 (1,354)	1.39 (1,238)	1.55 (1,206)	1.69 (1,191)	
$Pd(BHAE)Br_2$	0.85 (1,162)	1.31 (1,097)	1.44 (1,034)	1.54 (1,006)	
$Pd(BHAE)I_2$	1.32 (2,833)	2.06 (2,740)	(2.31) (2,675)	2.47 (2,570)	

[a] μ_{eff} expressed in units of Bohr Magnetons

[b] The molar susceptibility with diamagnetic correction expressed in cgs units

TABLE VI

The Range in Values for Complexes Showing

Variation in Magnetic Moments

Complex	Lowest μ_{eff}	Highest μ_{eff}
$Pd(EDP)Br_2$	1.33	4.87
$Pd(EDPy)Br_2$	1.20	3.22
$Pd(BHAE)Br_2$	1.21	1.54
$Pd(EDP)I_2$	1.50	3.44
$Pd(EDPy)I_2$	1.45	2.68
$Pd(BHAE)I_2$	1.53	2.47

preparation labeled (a) in the experimental chapter, low magnetic moment complexes are obtained. By using preparation (b), complexes having higher magnetic moments are formed. An individual sample of one of these complexes generally, but not always, shows an increase in magnetic moment with time. The time required to reach a constant value ranges from 2 days to several months, depending upon the particular sample. Samples of identical preparations generally require differing amounts of time to reach a constant value.

By continuous extraction with chloroform, a sample with a magnetic moment in the high portion of the range for the complex may be recrystallized to give a lower magnetic moment. Samples with high and low moments were compared by elemental analysis, x-ray powder patters, infrared and solid state reflectance spectra. In all cases the measurements were identical within experimental error, with the exception of the powder patterns for $PdBr_2EDP$ shown in Table VII. The greatest variation in magnetic moments was exhibited by the $Pd(EDP)Br_2$ complex with 1.33 B.M. for the low moment form and 4.87 by the high moment form of the complex. Both forms of the complex gave essentially the same d spacings with different intensity measurements being the major difference.

While instrumental methods generally yielded no difference in the high and low magnetic moment forms, a difference in solubilities, or rate of dissolution, was noted. The low moment form of a given complex dissolves more readily than does the high moment form.

The electronic spectral data and conductivity data are shown in Table VIII. The conductivities suggest that all the complexes are nonelectrolytes in CH_2Cl_2 solution.

TABLE VII

Powder Pattern Data for Two Samples of $PdBr_2EDP$

With Different Magnetic Moments

Data reported in d-spacings, $(\lambda/\sin\theta)$[a]

Sample 1 μ_{eff} = 4.87 B.M.	Sample 2 μ_{eff} = 1.33 B.M.	Sample 1 μ_{eff} = 4.87 B.M.	Sample 2 μ_{eff} = 1.33 B.M.
9.36	9.51		2.38
7.53	7.56		2.32
5.05	5.04	2.25	2.25
4.96	4.94		2.23
	4.86	2.21	2.21
4.45	4.42	2.19	2.19
4.19	4.17		2.12
4.09	4.09		2.08
3.91	3.90	2.02	2.01
3.74	3.74		2.00
	3.52		1.94
3.41	3.41	1.91	1.90
3.21	3.20	1.87	1.87
3.09		1.86	1.85
3.07	3.06		
2.99	2.99		
2.95	2.94		
2.82	2.81		
2.61	2.61		
	2.57		
	2.51		
2.47	2.46		
	2.44		
	2.39		

[a]Wavelength of Cu K_α radiation = 1.54178 Å.

TABLE VIII

Conductivity and Electronic Spectral Data

for the Palladium Halide Complexes

Compound	Solution[a] kK	(ε)	Reflectance kK	Λ^b
$Pd(EDPy)Cl_2$	25.58	(339)	20.62sh	< 0.127
	34.01	(1056)	25.64	
$Pd(EDP)Cl_2$	25.32	(500)	20.20sh	< 0.132
	33.90	(1412)	25.00	
$Pd(BHAE)Cl_2$	24.88	(484)	20.00sh	0.0921
	33.33	(1570)	25.00	
$Pd(EDPy)Br_2$	23.81sh	(303)	20.00sh	0.157
	27.93	(1010)	24.10	
			27.78	
$Pd(EDP)Br_2$	23.53sh	(509)	19.61sh	0.386
	27.40	(1226)	23.53	
			27.62	
$Pd(BHAE)Br_2$	22.99sh	(298)	19.23sh	0.0156
	26.95	(1097)	22.99	
			26.67sh	
$Pd(EDPy)I_2$	20.37	(1293)	20.28	0.0662
	23.53sh	(362)	23.26sh	
$Pd(EDP)I_2$	20.12	(1924)	20.20	< 0.0757
	22.99sh	(278)	28.17sh	
$Pd(BHAE)I_2$	19.72	(1821)	19.80	0.224
	22.47	(275)		

[a]Methylene chloride solution.

[b]Conductivity of 1×10^{-4} molar solution in methylene chloride at ambient temperature (about 298°K). A typical value for 1:1 electrolyte is 20. The conductivity values have the units: $ohm^{-1}cm^2moles^{-1}$.

sh: shoulder

B. Discussion

Using existing models, paramagnetism of four coordinate d^8 complexes may be attributed to any of three factors:[76] (1) The complex has a tetrahedral geometry; (2) Interactions of solvent or solute molecules along an axis normal to the square planar complex may affect the complex to produce an octahedral of pseudo-octahedral species; (3) Ligands of a square planar complex may have insufficient strength to cause electron pairing. The data in this work indicates the second factor exists.

It seems unlikely that these Pd(II) complexes have a tetrahedral geometry. A tetrahedral coordination geometry should give rise to absorptions at lower energies than those observed in the electronic spectra. Also, there has been no unambiguous report of any tetrahedral Pd(II) compounds in the literature. Complete paramagnetism, or full occupation of the $^3T_{1g}$ ground state, would be expected for a tetrahedral species, but this is not the case. Less than spin only μ_{eff} values are found for all the complexes at low temperatures. Room temperature μ_{eff} values below the spin-only values are also found for the low moment forms of the complexes. Even though the high magnetic moment forms for the complexes are above spin-only μ_{eff} values, other differences in the high and low moment forms are subtle. These differences, as previously mentioned, are too subtle to suggest conformational isomerism between tetrahedral and planar geometries. Furthermore, even the high magnetic moment forms for the complexes do not show Curie-Weiss behavior. Temperature dependent studies suggest that all the complexes exist in a singlet-triplet equilibrium ground state, i.e. the energy separation between the singlet and triplet state is approximately equal to kT. A tetrahedral geometry requires no temperature dependence of the magnetic moment.

Arguments against using the in-plane, weak field ligand model can be made by considering the spectrochemical series for the ligands. Since bonding of amines to transition metals is primarily sigma in nature, increasing the base strength will strengthen the amine bond, providing other factors such as steric demands do not change. The pK_a's for pyrrolidine, piperidine, and hexahydroazepine are 11.32, 11.20, and 11.10, respectively.[7] These are values for the free amines, but the relative base strengths should carry over to the condensed ligand.[6] The base strengths of the amines correlate with the observed electronic absorptions for the complexes. The relative ligand field strengths for the ligands are EDPy > EDP > BHAE.

If the paramagnetism is, indeed, the result of weak intrinsic ligand field strength of the ligands, then the BHAE complexes should show the largest degree of paramagnetism. By comparing the electronic spectra in either solution or the solid state, it is found that the d → d transitions are the same for all three ligands with a particular palladium halide. The only difference in a series is a slight shift in wavelength in accordance with the ligand spectrochemical order. For example, all the palladium bromide complexes exhibit the same peaks with a slight shift to lower energies in the order: $PdBr_2EDPy > PdBr_2EDP > PdBr_2BHAE$. Therefore, based solely on the weak in-plane ligand field model, the order of magnetic moments for the complexes should be $PdBr_2BHAE > PdBr_2EDP > PdBr_2EDPy$. This is not the observed order for the paramagnetism of the palladium complexes. The order of magnetic moment values has been found to be $PdBr_2EDP > PdBr_2EDPy > PdBr_2BHAE$.

Further comparisons between the palladium halide EDM complexes[77] and the palladium halide EDP complexes argue against model (3), i.e. the

weak ligand field strength of in-plane ligands. Space filling models show that the ligands, EDM and EDP, have virtually identical spatial requirements, but EDP is a considerably stronger base. EDP has a K_b about 10^3 times that of EDM.[6] As a result, EDP should be a stronger field ligand; this has been found to be correct.[6,77] If the paramagnetism of the complexes depends inversely upon the strength of the in-plane ligand field, then the PdX_2EDM complexes should show higher magnetic moments than the EDP complexes. On the contrary, only the PdI_2EDM complex of the Cl^-, Br^-, I^- series was found to be paramagnetic and that was in solution with a large excess of ligand present.[21,77]

Model (2) describing paramagnetic, four coordinate, d^8 systems best explains the palladium complexes. There is evidence suggesting that these palladium complexes exist as associated species in the solid state. The low solubilities of the complexes implies such associations since the low magnetic moment form of a complex is considerably more soluble than the high magnetic moment form.

More conclusive information is given by the far infrared spectra. All of the complexes were studied in the infrared out to the limit of CsI windows, about 250 cm^{-1}. The spectra were compared to eliminate ligand vibrations. Strong Pd-Cl stretches were observed for $PdCl_2EDPy$, $PdCl_2(EDP)$, and $PdCl_2BHAE$ at 323, 320, and 318 cm^{-1} respectively. In addition to the band at 320 cm^{-1} for $PdCl_2EDP$, there is a strong absorption at 293 cm^{-1} which is not observed in the other spectra. The band at 293 cm^{-1} is assigned as a bridging chloride-metal stretch. Allen, et al.,[78] have assigned terminal Pd-Cl stretching frequencies to the range of 370-340 cm^{-1} for a variety of Pd(II) complexes. For trans bridging chlorides, ν(M-Cl-M) was reported to be in the range 335-300 cm^{-1} while the cis

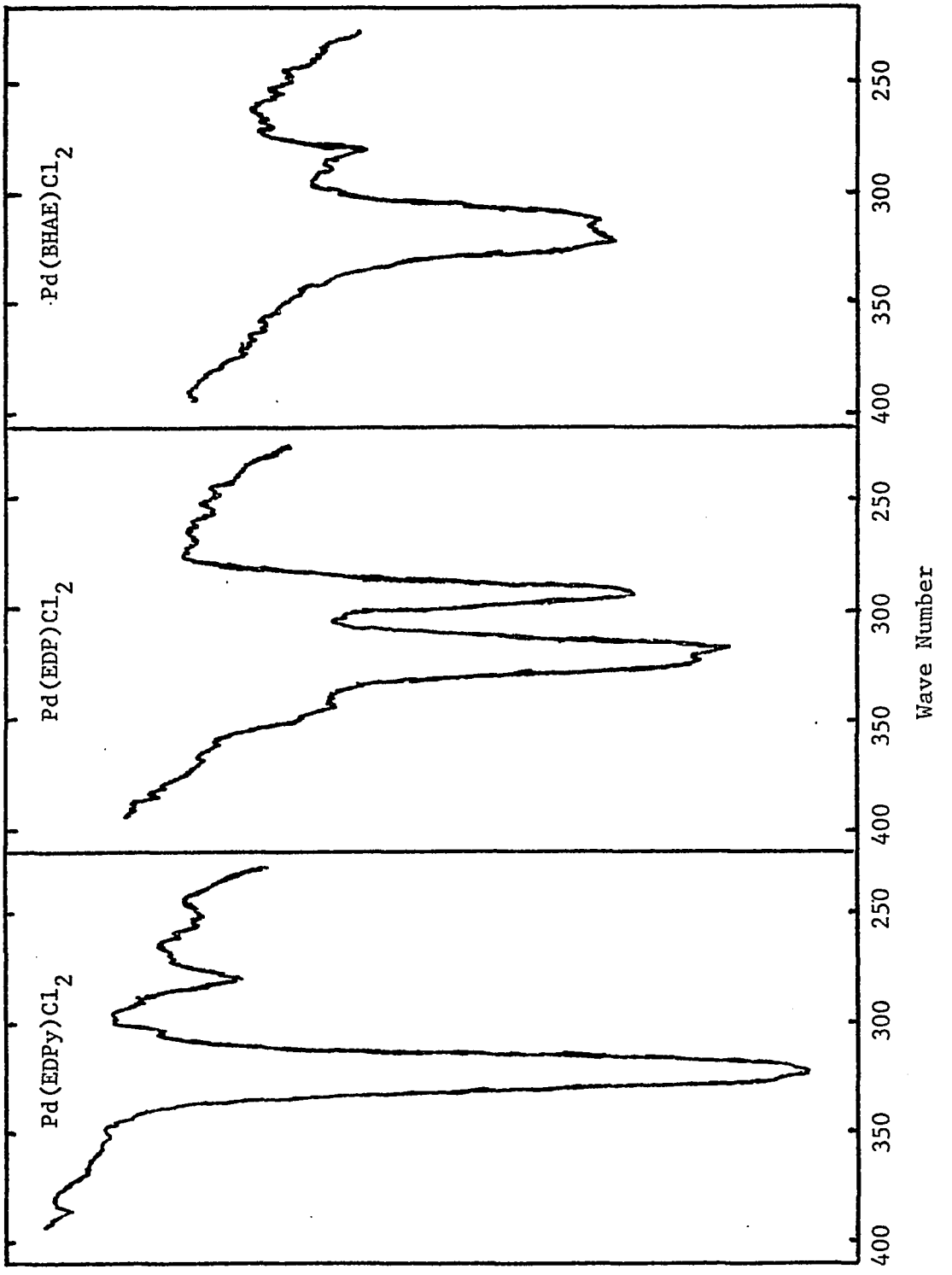
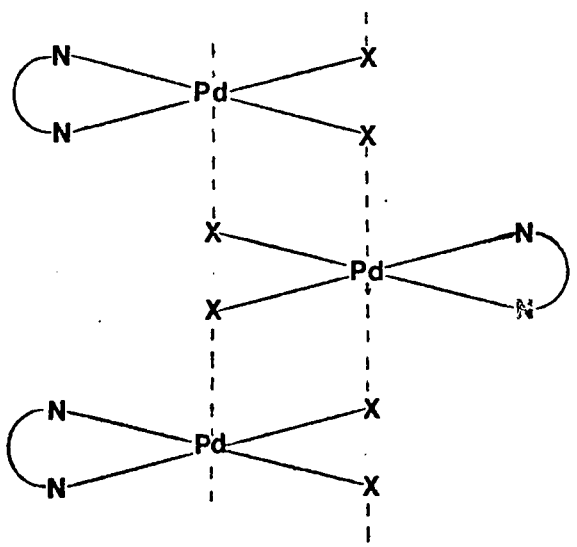


FIGURE III. The Far-Infrared Spectra for $Pd(EDPy)Cl_2$, $Pd(EDP)Cl_2$ and $Pd(BHAE)Cl_2$

ν(M-Cl-M) range was 295-250 cm^{-1}. Adams and coworkers[79-81] report similar ranges for complexes of the type, $Pd_2Cl_4L_2$, with ν(term)(M-Cl) = 370-345 cm^{-1} and ν(bridging)(M-Cl-M), <u>trans</u> = 310-300 and <u>cis</u> = 280-250 cm^{-1}. Weak bands were observed at 282 and 280 cm^{-1} for $PdCl_2$BHAE and $PdCl_2$EDPy respectively, but could not be assigned with certainty. Bridging for the bromide and iodide complexes could not be determined due to the limitations of the CsI windows. The Pd-Br stretching vibrations for bridging bromides are in the region 220-185 cm^{-1} and 200-165 cm^{-1} for <u>trans</u> and <u>cis</u> bridging respectively.

Assuming the amine ligands are bidentate and not bridging, the following axial interactions may be envisioned for planar complexes having the stoichiometry PdX_2L, (IX).



(IX)

Thus, there are axial components producing an octahedral environment on the complex which permit occupation of the low energy triplet state. This argument is supported by the strong bridging chloride band observed for $PdCl_2$EDP and the weak bands observed for $PdCl_2$EDPy and $PdCl_2$BHAE along with their respective magnetic moments of 2.39, 1.56 and 1.69 B.M.

The variation in the magnetic moment of the bromide and iodide complexes (Table VI) is likely due to the extent of the intermolecular interactions within the crystals. Evidence to support this is the relatively higher solubilities of the low magnetic moment forms of the complexes. By washing a sample of intermediate magnetic moment, e.g., $PdBr_2EDP$ with μ_{eff} = 2.5 B.M., with CH_2Cl_2, a portion of the sample will dissolve. The portion that did not dissolve will always exhibit a higher magnetic moment than the sample before washing with no evidence of any other property changing. Upon recrystallization of the dissolved portion, the magnetic moment may or may not be lower than the original sample. Apparently, during crystallization of the complexes, delicate equilibrium conditions exist in a manner that dictate the extent of interactions that take place within the crystals.

As mentioned in the introduction, similar variable magnetic behaviour has been found for square planar Ni(II) complexes, in solution and the solid state. Holm et al. have done considerable work with bis-(N-substituted-salicylaldimine)-nickel(II) complexes.[55-59] Their work has shown a direct correlation between the degree of steric hindrance produced by the N-alkyl substituents in the salicylaldimine moiety and the extent of intermolecular association.

In considering the bromide and iodide complexes as monomeric planar species with few interactions vs. extensively interacting octahedral ones, one should expect a difference in the electronic spectra of the two forms. This difference is not evident. However, evidence of the change may be hidden under the broad absorption bands in the solid state spectra. Also, since no pure diamagnetic species has been isolated in the solid state, there exists a non-equilibrium mixture of associated

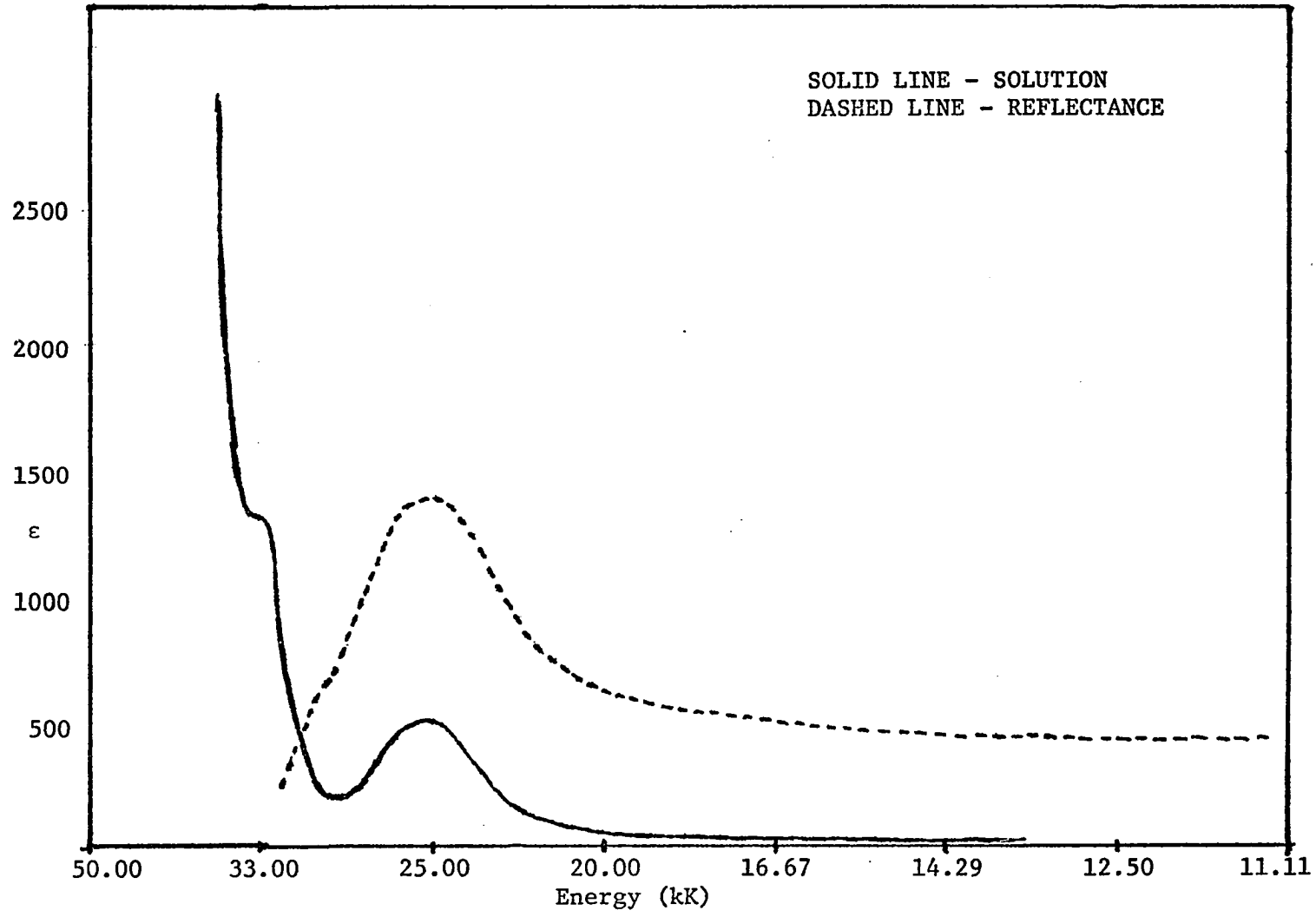


FIGURE IV. Electronic Spectra of $Pd(EDP)Cl_2$

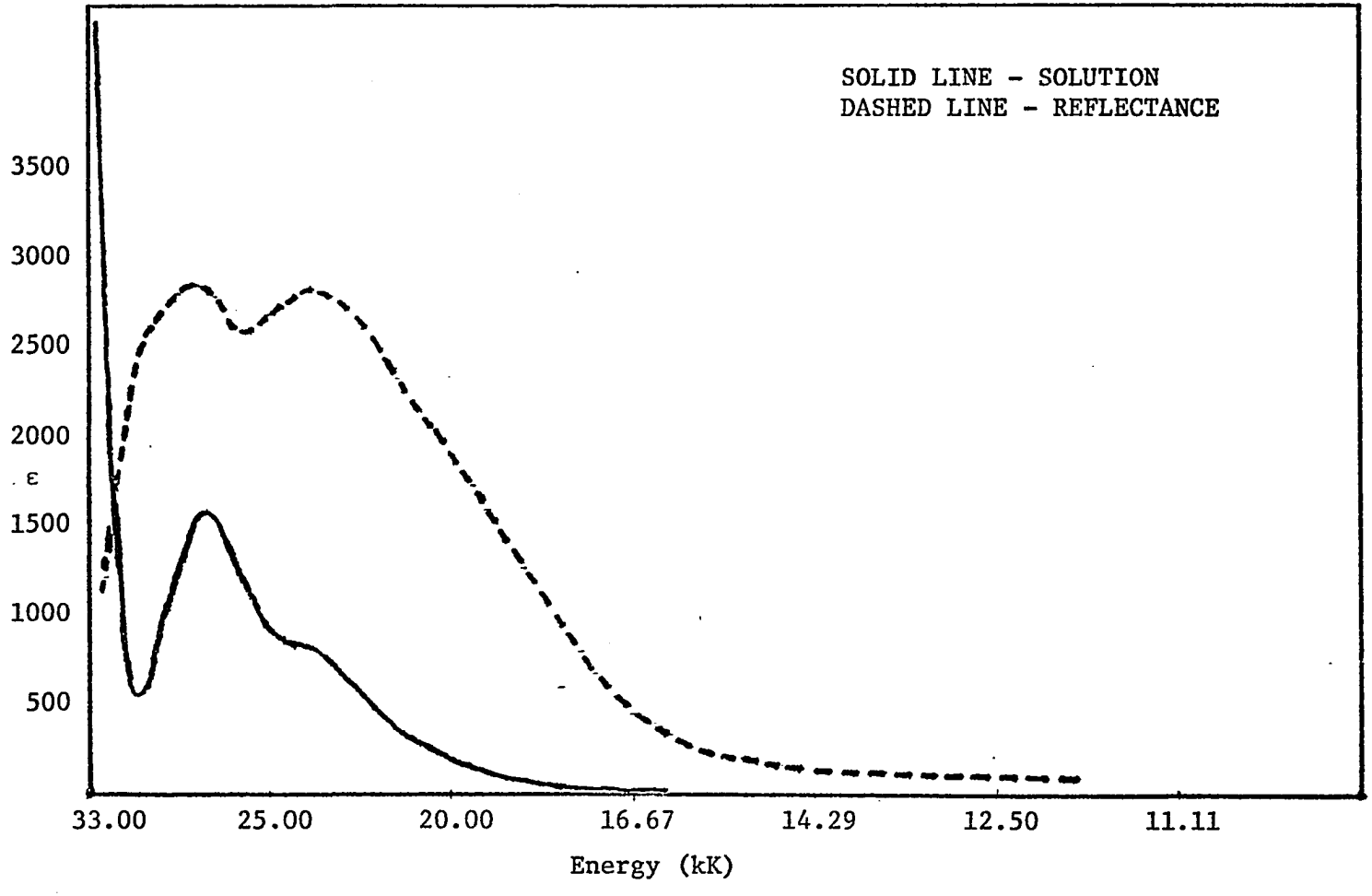


FIGURE V. Electronic Spectra of $Pd(EDP)Br_2$

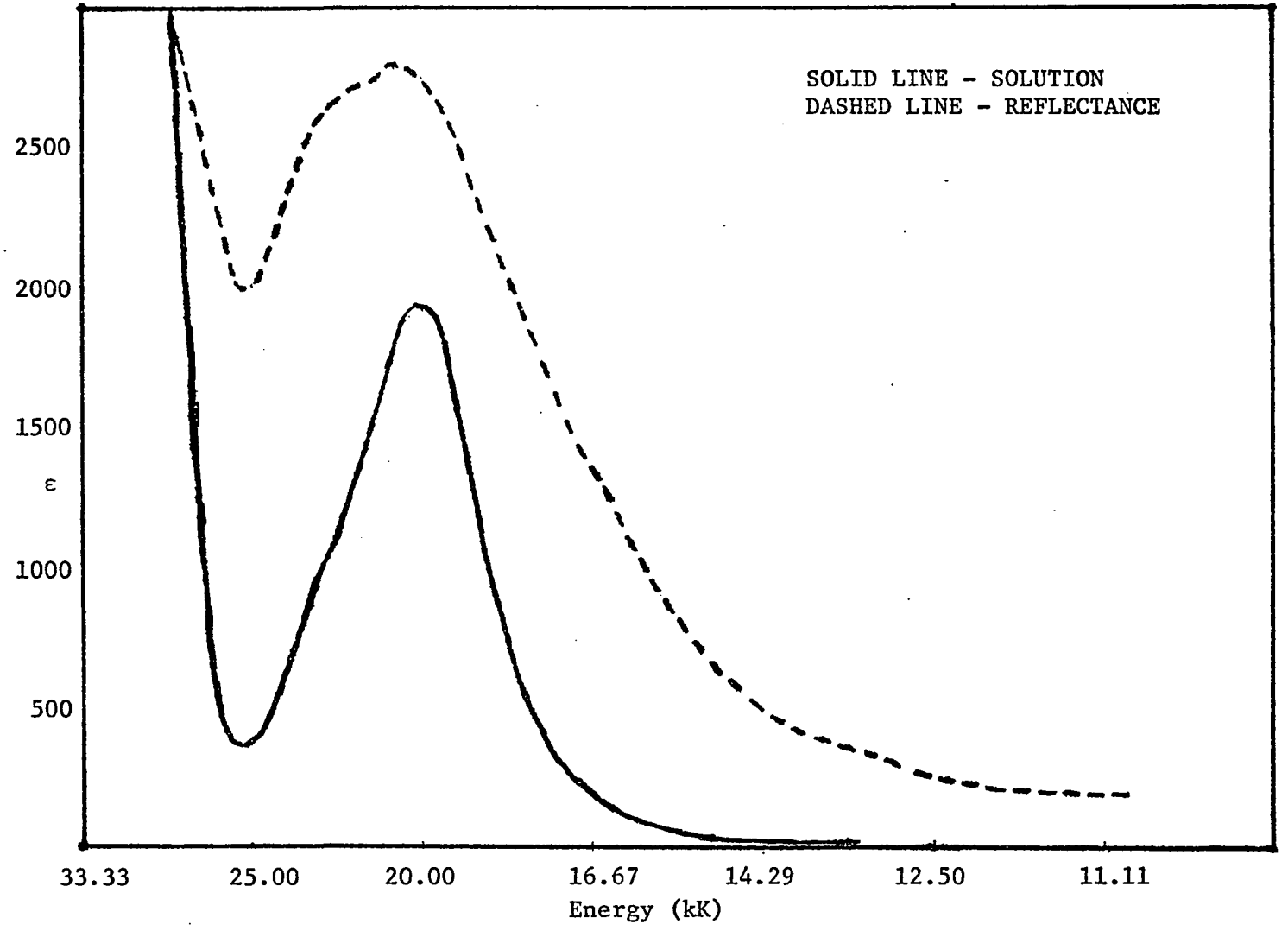


FIGURE VI. Electronic Spectra of $Pd(EDP)I_2$

and nonassociated species. This would result in the differences of the spectra of high and low moment forms being mainly in the intensities of absorption peaks.

The absence of magnetic moments from solution determinations suggest that intermolecular interactions that occur in the solid state are removed in solution. Therefore, the solution spectra of a complex showing variable magnetic moments in the solid phase should be the same, regardless of what its moment is in the solid state. This is observed for solution spectra in chloroform or methylene chloride.

CHAPTER IV

THE PLATINUM HALIDE COMPLEXES

A. Results

The platinum halide complexes of EDPy, EDP and BHAE are similar to the palladium complexes. All of the complexes have the stoichiometry PtX_2L (X = Cl, Br, I; L = EDPy, EDP, BHAE). Of the series, only the PtI_2BHAE complex was not isolated. The complexes have very low solubilities in acetone, chloroform, and methylene chloride. The greatest solubility is in CH_2Cl_2 and ranges between 10^{-4} mol/ℓ and 10^{-3} mol/ℓ in the order $PtI_2L > PtBr_2L > PtCl_2L$. All the complexes are air and water stable.

The magnetic susceptibility data are given in Table IX. All the data are for the solid state since magnetic moment values in solution could not be obtained due to the low solubilities of the complexes. The magnetic moments of the complexes with the exception of $PtCl_2$BHAE were found to be temperature dependent. $PtCl_2$BHAE is diamagnetic.

Variable magnetic behaviour from different preparations as shown by some of the palladium complexes was not found for the platinum complexes. Although different methods of preparation gave the same moments, a change in magnetic moments would occur by rapid crystallization achieved by stripping a solvent with a rotary evaporator. This generally produced a lower moment for the recrystallized sample than what was originally found. Washing a sample with chloroform or methylene chloride generally

TABLE IX

Effective Magnetic Moments for $Pt(L)X_2$ Complexes

μ_{eff}^{a} $(\chi_m' \times 10^6)^b$

	77°K	195°K	250°K	297°K
$PtCl_2EDP$	1.10 (1975)	1.71 (1877)	1.87 (1747)	2.01 (1701)
$PtBr_2EDP$	1.04 (1761)	1.61 (1663)	1.79 (1610)	1.93 (1571)
PtI_2EDP	1.07 (1859)	1.65 (1736)	1.83 (1683)	1.96 (1618)
$PtCl_2EDPy$	2.32 (8762)	3.66 (8610)	4.13 (8533)	4.36 (8023)
$PtBr_2EDPy$	1.22 (2410)	1.92 (2358)	2.15 (2322)	2.33 (2300)
PtI_2EDPy	0.79 (1004)	1.19 (910)	1.33 (890)	1.42 (855)
$PtCl_2BHAE$	diamagnetic			
$PtBr_2BHAE$	1.15 (2664)	1.79 (2051)	1.98 (1955)	2.09 (1842)

[a] μ_{eff} expressed in units of Bohr Magnetons

[b] The molar susceptibility with diamagnetic correction expressed in cgs units

left the undissolved portion of the sample with a magnetic moment higher than that before washing.

The electronic spectral data and conductivity data are shown in Table X. The spectra for each complex in a given halide series are similar; the major difference is a slight shift to lower energy in the order of the ligands: EDPy > EDP > BHAE. This order agrees with the base strength of the ligands and what is found in the palladium system. Since the complexes have the greatest solubility in CH_2Cl_2, this solvent was used for conductivity determinations. The conductivities suggest that all the complexes are nonelectrolytes in solution.

B. Discussion

The solubility behaviour and far infrared data suggest that the observed paramagnetism is the result of intermolecular association giving the complexes an octahedral environment. All of the complexes were studied out to the limit of CsI windows, about 250 cm^{-1}. The spectra were compared to eliminate ligand vibrations. Strong Pt-Cl stretches were observed for $PtCl_2$EDPy, $PtCl_2$EDP, and $PtCl_2$BHAE at 325, 320, and 320 cm^{-1}, respectively. In addition to the band at 325 cm^{-1} for $PtCl_2$EDPy there is a moderate absorption at 244 cm^{-1} which is not observed in the other spectra. The band at 244 cm^{-1} is assigned as a bridging chloride-metal stretch. Adams and Chandler[79,80] have assigned terminal Pt-Cl stretching frequencies to the range 365-334 cm^{-1} for a variety of Pt(II) compounds. For bridging chloride-platinum stretches, the ranges 335-310 cm^{-1} and 295-250 cm^{-1} were reported for *trans* and *cis* bridging respectively. The weak band at 244 cm^{-1} which is assigned as a bridging M-Cl-M stretch, is low for the range reported by Adams and Chandler.[80]

TABLE X

Electronic Spectral and Conductivity Data
for the Platinum Halide Complexes

Compound	Solution[a] kK	(ε)	Reflectance kK	Λ^b
$Pt(EDPy)Cl_2$	20.77sh	(380)	30.30	2.30
	37.04sh	(760)		
$Pt(EDP)Cl_2$	30.77sh	(382)	28.99	2.01
	36.36sh	(907)		
$Pt(BHAE)Cl_2$	30.77sh	(452)	26.32sh	2.79
	35.71sh	(852)	29.85	
$Pt(EDPy)Br_2$	24.39	(67)	24.69	0.910
	29.67	(254)	28.99	
	36.10sh	(1060)		
	36.90	(1134)		
	37.45sh	(1060)		
$Pt(EDP)Br_2$	24.39sh	(99)	24.69	0.815
	28.65sh	(345)	28.99	
	35.71sh	(884)		
	36.36	(920)		
	37.04	(884)		
$Pt(BHAE)Br_2$	23.53	(57)	23.81	0.597
	28.57	(219)	27.93	
	35.34sh	(1027)		
	35.97	(1132)		
	36.76sh	(1027)		
$Pt(EDPy)I_2$	26.18	(1496)	26.46	0.453
	30.58	(1072)	29.85	
$Pt(EDP)I_2$	25.77	(1092)	22.22sh	0.590
	29.94	(689)	25.64	
$Pt(EDPy)-(\phi CONH_2)Cl_2$	28.17	(225)	28.99sh	0.831
	39.06	(7604)		

[a]Methylene chloride solution.

[b]Conductivity of 1×10^{-4} molar solution in methylene chloride at ambient temperature (about 298°K). A typical value for 1:1 electrolyte is 20. The conductivity values have the units: $ohm^{-1}cm^2moles^{-1}$.

sh: shoulder.

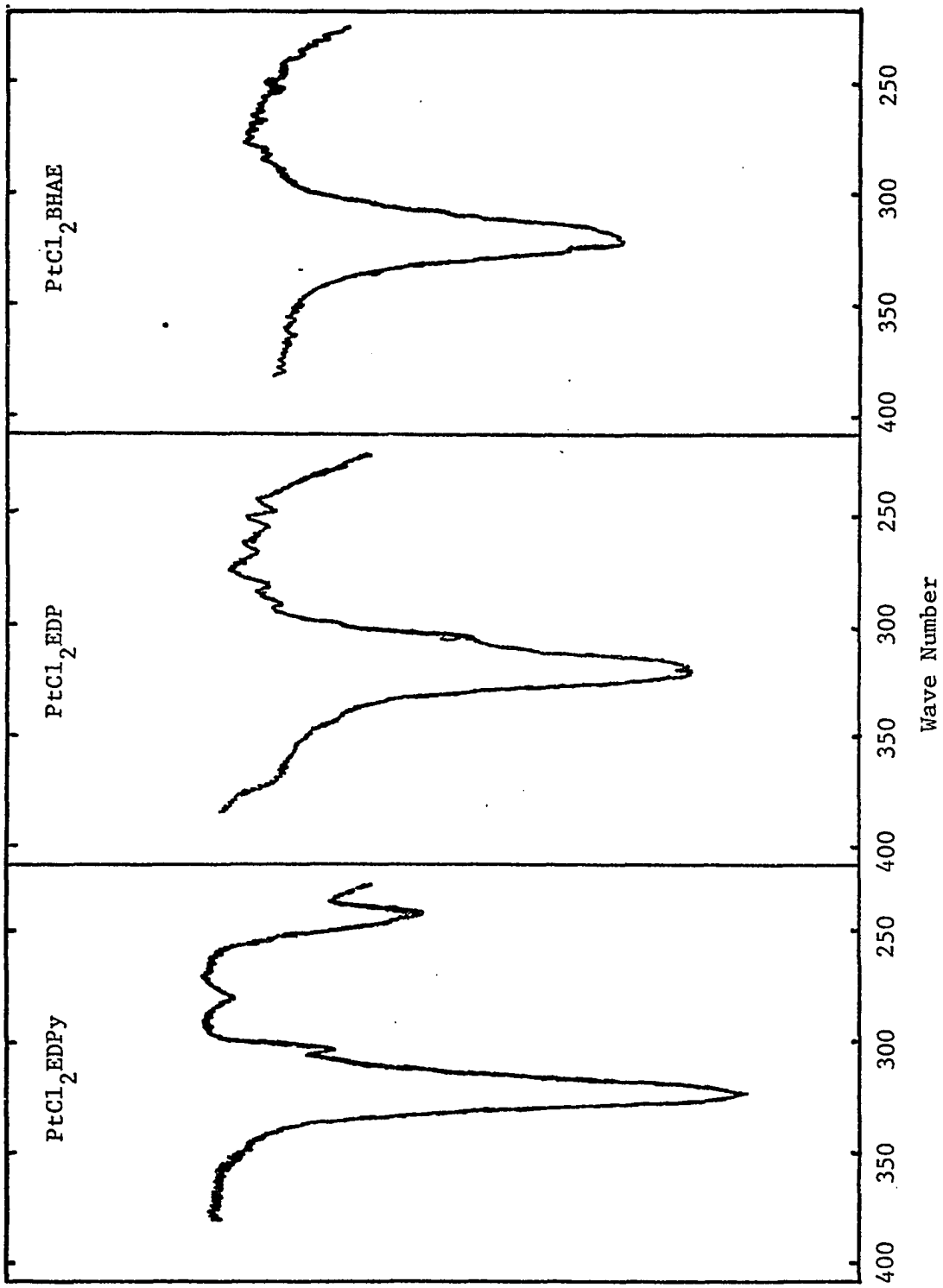


FIGURE VII. Far-Infrared Spectra of
Platinum Chloride Complexes

This may be explained by assuming there is not complete bridging, but rather a weak association of the chloride of one molecule with the metal of another molecule. There was no other band in the far infrared region for $PtCl_2BHAE$; only the terminal metal-chloride band at 320 cm^{-1}. The bridging halide bands found for the chloride complexes agree quite well with the magnetic moments. $PtCl_2EDPy$, $PtCl_2EDP$ and $PtCl_2BHAE$ have effective magnetic moments of 4.36, 2.01, and diamagnetic, respectively.

The arguments for the associated platinum complexes are the same as those made for the palladium complexes in chapter three. The low solubilities of the complexes suggest intermolecular association. Furthermore, washing a sample with a suitable solvent generally produces a higher magnetic moment form. This implies that in an equilibrium mixture of the high and low magnetic moment forms of a complex, the more soluble low moment form which is the nonassociated species, can be removed, but not isolated. When the solvent is removed, association is again present.

Since the observed order of paramagnetism for the platinum halide complexes are not in the order of $PtX_2BHAE > PtX_2EDP > PtX_2EDPy$, it is not likely the paramagnetism is due to monomeric square planar complexes with weak field ligands. Also, the electronic spectra do not suggest tetrahedral geometries for the complexes. Therefore, it is probable, especially in light of the far infrared data, that these complexes approach an octahedral environment, and this is the cause of the paramagnetism.

A unique reaction was found when a standard method for preparing the complexes was used to synthesize $PtCl_2EDPy$. By starting with $PtCl_2(\phi C{\equiv}N)_2$ and adding the ligand, EDPy, the product $PtCl_2(EDPy)(\phi CONH_2)$ was formed using acetone as a solvent. Suspecting a water reaction with

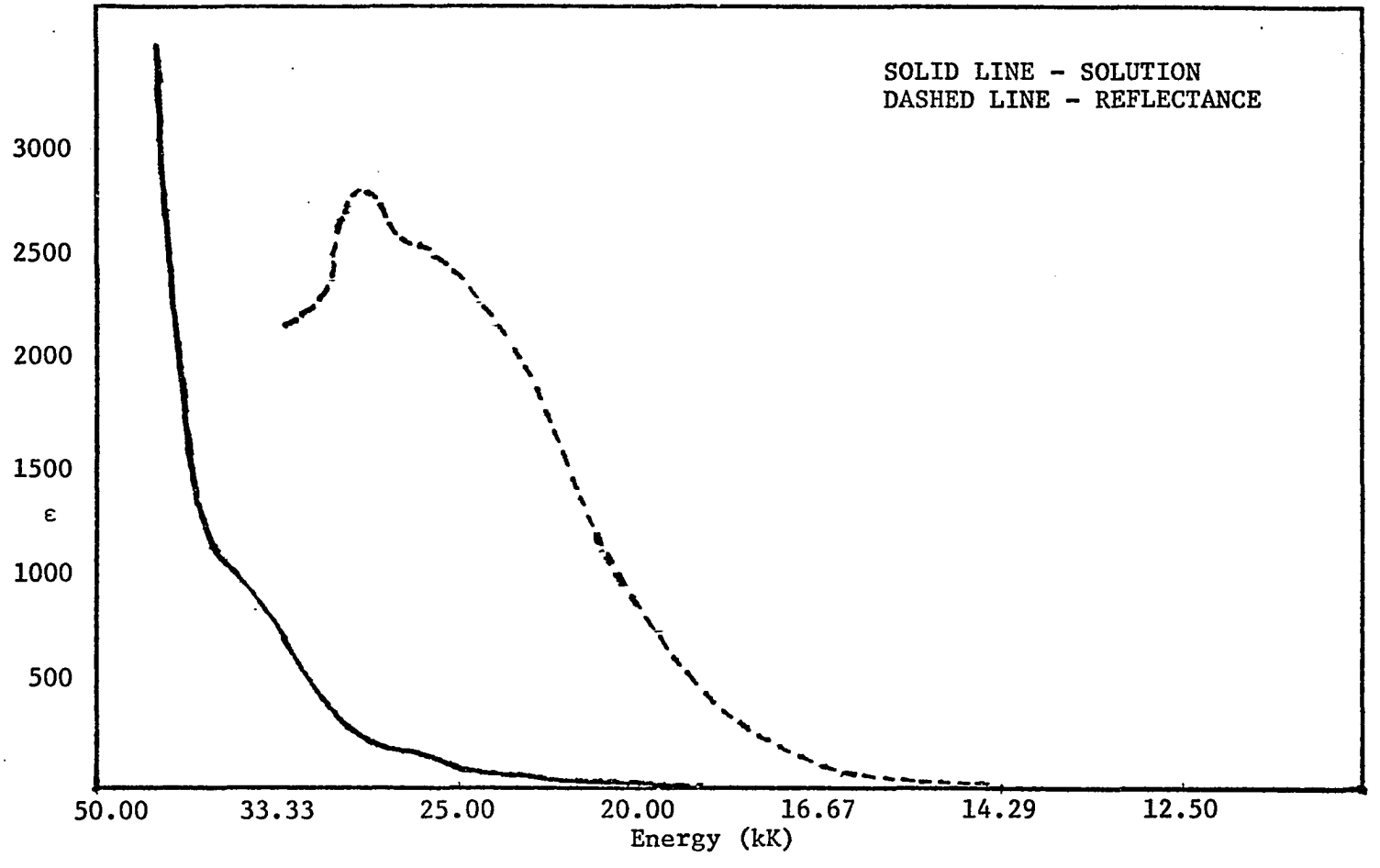


FIGURE VIII. Electronic Spectra of $Pt(EDP)Cl_2$

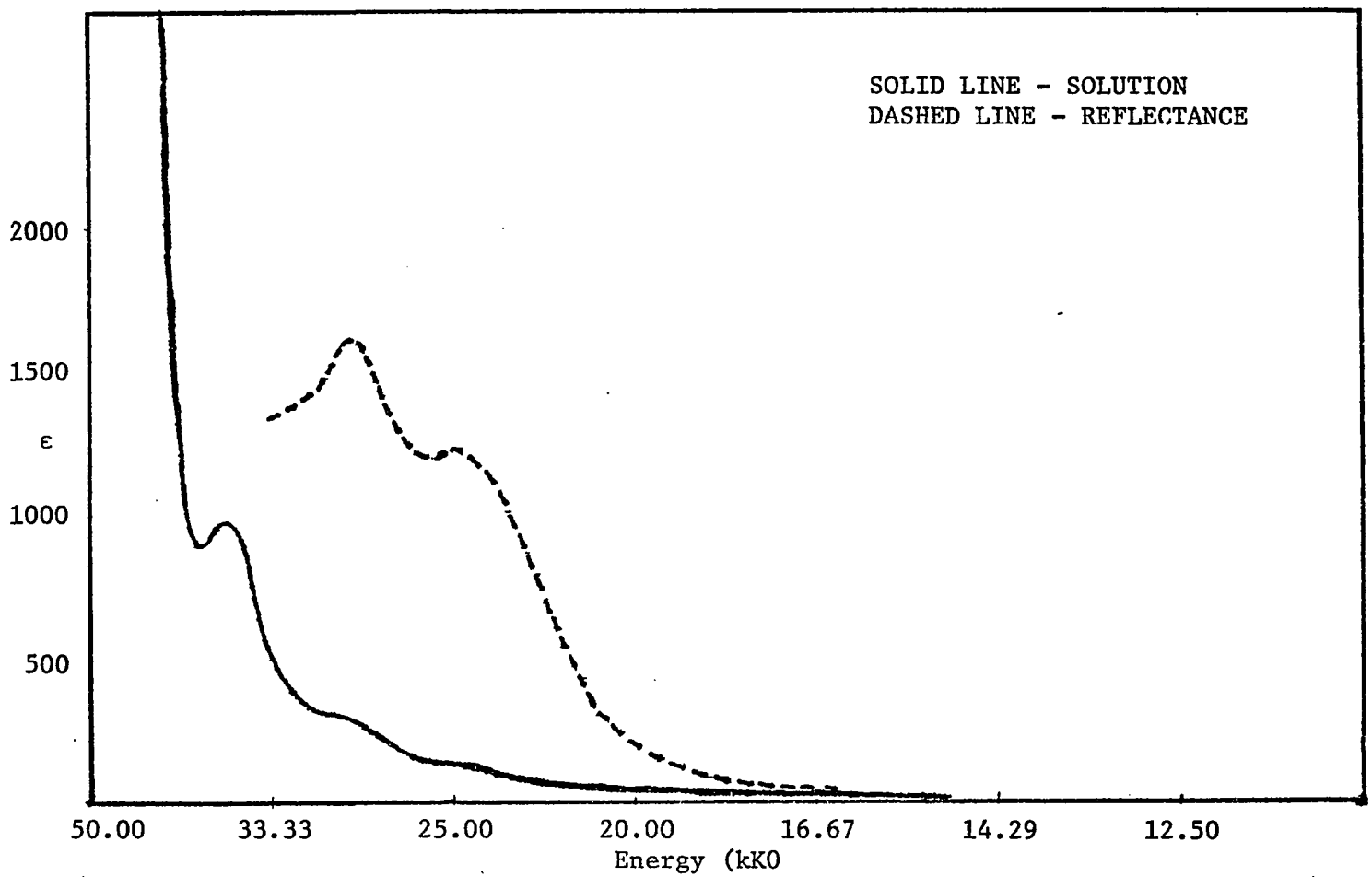


FIGURE IX. Electronic Spectra of $Pt(EDP)Br_2$

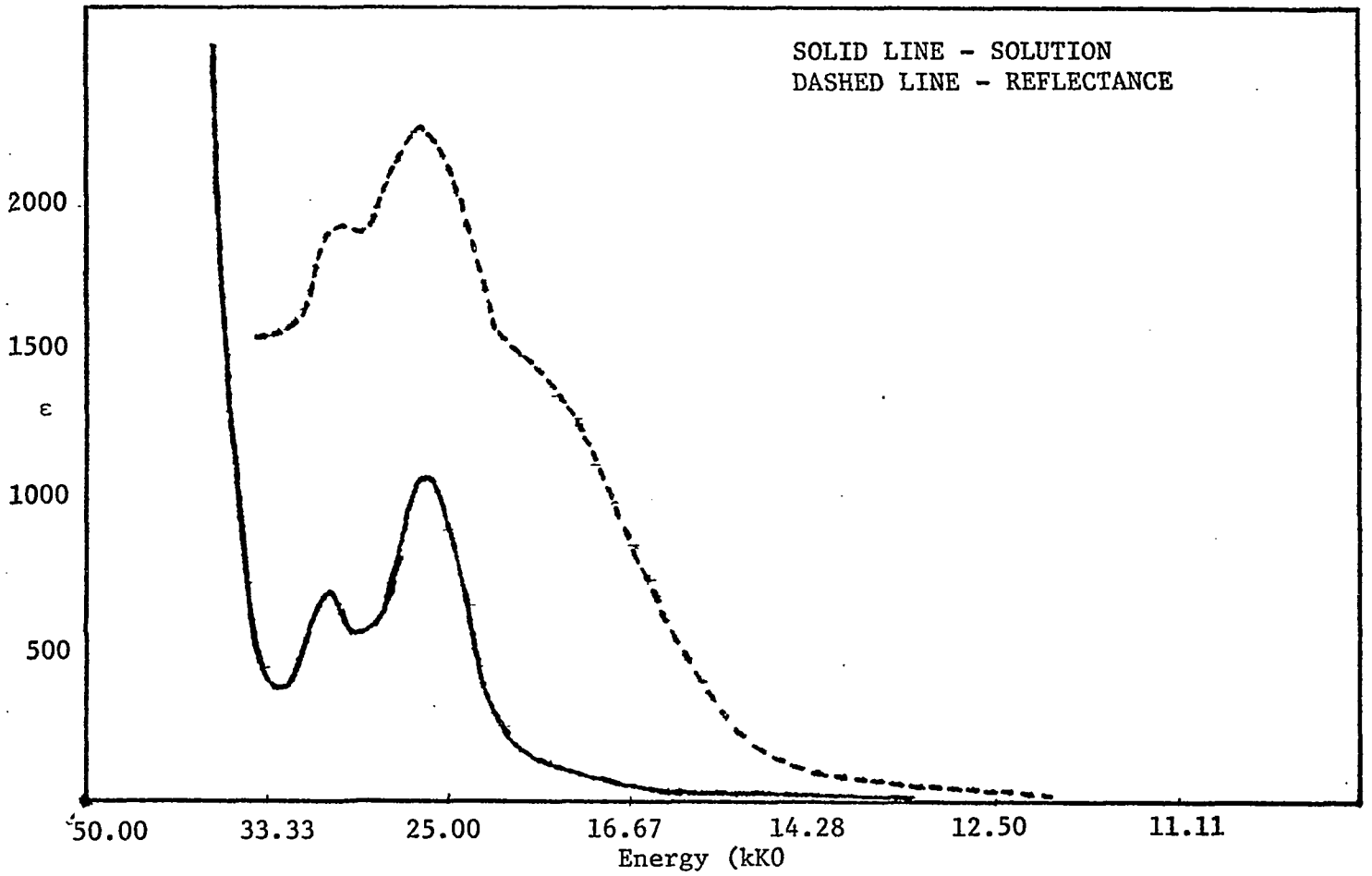


FIGURE X. Electronic Spectra of $Pt(EDP)I_2$

the nitrile, care was used to ensure all the reagents were dry and the reaction was carried out in a nitrogen atmosphere. Formation of the amide still occurred. Different solvents were tried and by using 1,2-dimethoxyethane of which the i.r. spectrum showed considerable H_2O, no hydrolysis of the nitrile occurred. The product isolated was $PtCl_2EDPy$.

To verify the benzamide complex, infrared and mass spectral data were used. The i.r. spectrum showed the benzamide to be coordinated by the shift of the carbonyl absorption band to 1600 cm^{-1}. Mass spectral data exhibited peaks for the ligand and benzamide. The mass spectrum was compared to a spectrum of EDPy to ascertain the benzamide peaks and then checked against a literature reference for benzamide.[82] To further verify the presence of benzamide the complex was decomposed in a sublimation apparatus at 200°C. The sublimed benzamide was verified by its melting point,[83] N.M.R.[84] and i.r. spectra.[85]

A proposed mechanism for the formation of benzamide complex is shown in Figure XI. It is probable that coordination occurs through the oxygen rather than the nitrogen. According to Drago, et al.[86,87] oxygen has invariably been found to be the principal donor site in the coordination of amides. This is attributed to delocalization of the nonbonding electron pair on the nitrogen into a π-molecular orbital involving oxygen, carbon, and nitrogen.

Hydrolysis of nitriles to amides is well known for catalysts other than Pt^{+2}. Ni and Cu and the oxides of the two metals in H_2O have been shown to catalyze the formation of amides from nitriles.[88,89] Also, a benzonitrile solution in CH_2Cl_2 with manganese(IV) oxide has produced a 72% yield of benzamide.[90] It is interesting to note that palladium did not catalyze the formation of benzamide under the same reaction conditions.

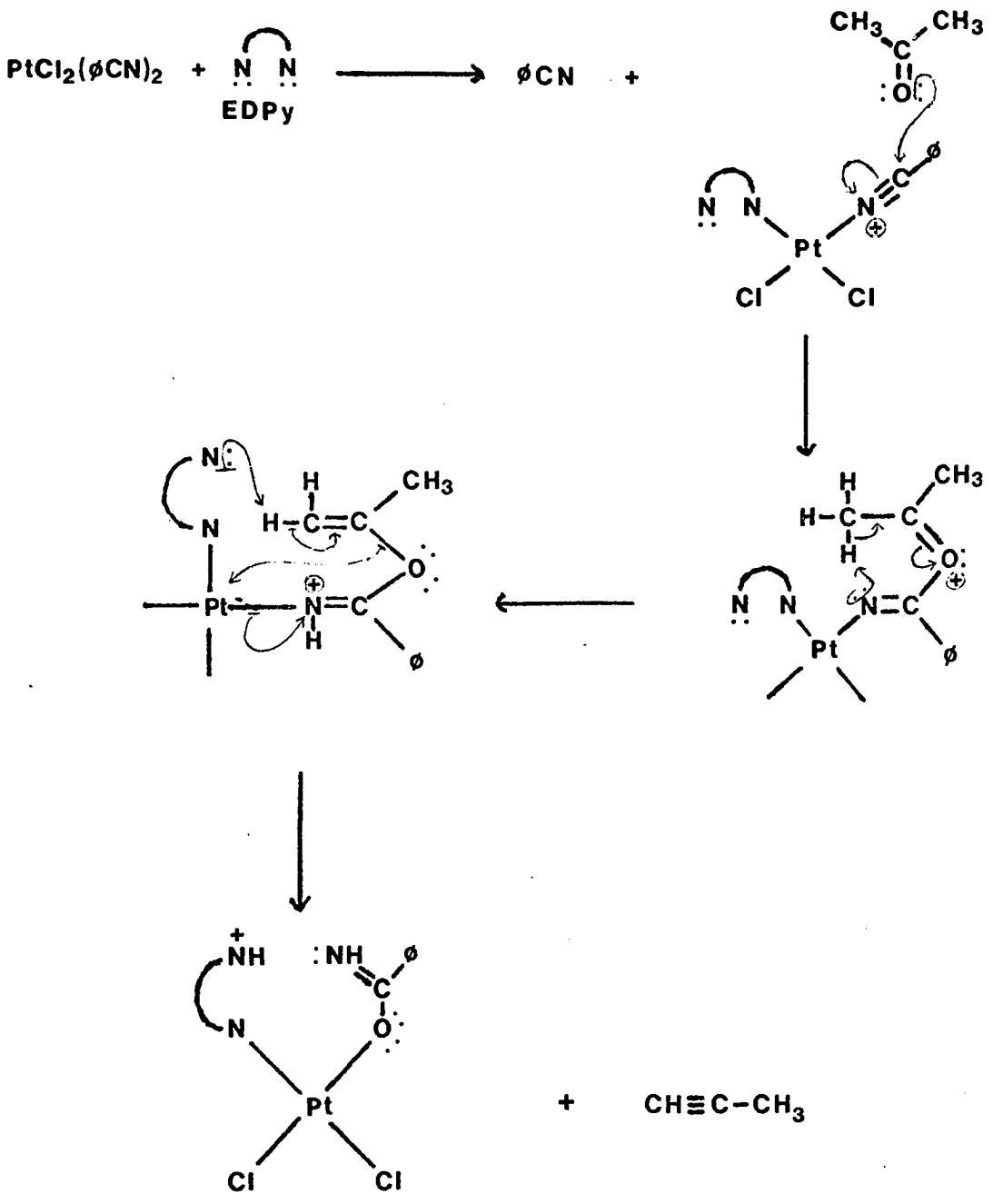


FIGURE XI. A Mechanism for the Formation of $Pt(\phi CONH_2)(EDPy)Cl_2$

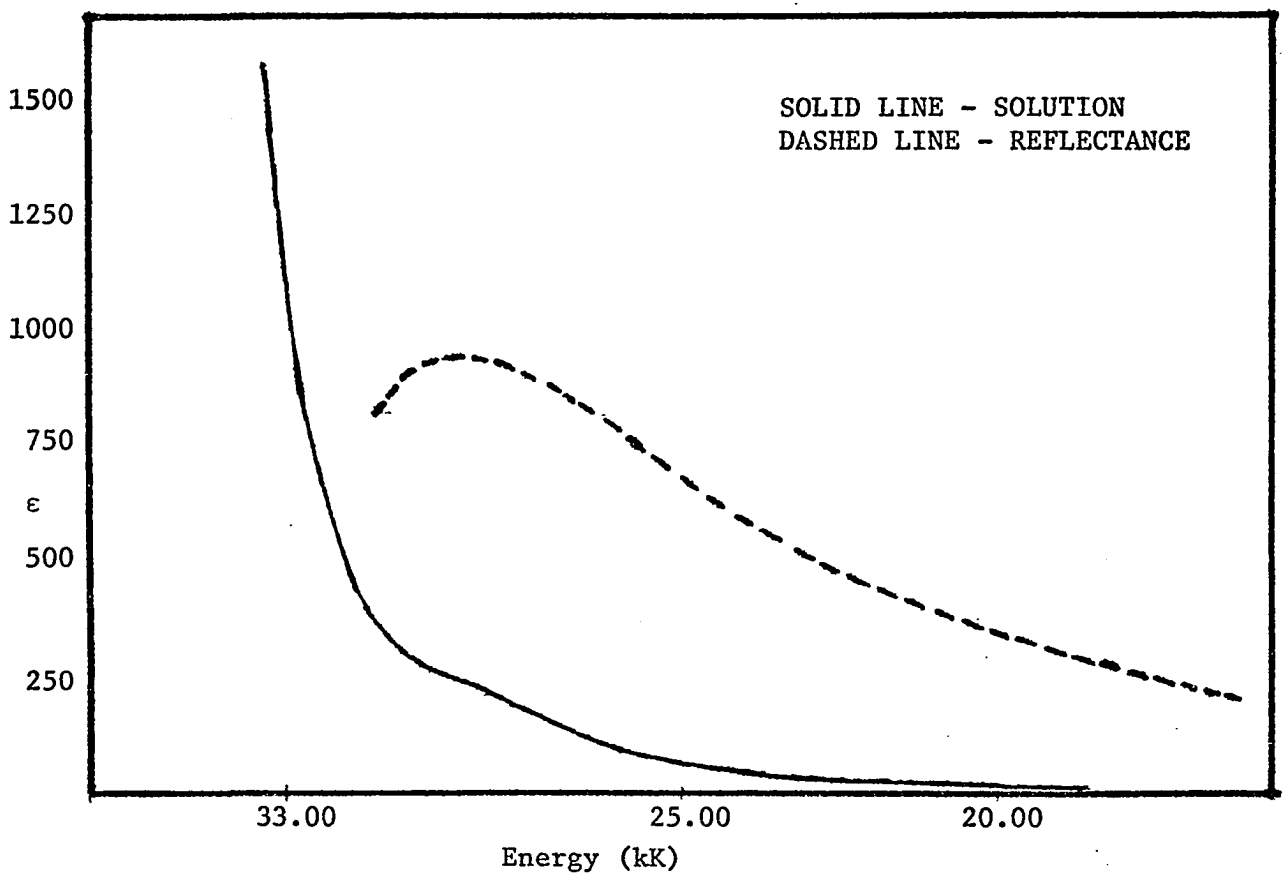


FIGURE XII. Electronic Spectra of $Pt(\phi CONH_2)(EDPy)Cl_2$

CHAPTER V

PALLADIUM(II) AND PLATINUM(II) THIOCYANATE COMPLEXES

The analytical data show that all the complexes have the stoichiometry, $M(CNS)_2L$ (M = Pd, Pt; L = EDPy, EDP, BHAE). Two different complexes with the stoichiometry $Pt(CNS)_2EDP$ were isolated. All the complexes are diamagnetic in the solid state and are non-electrolytes in methylene chloride solution. The conductivities along with the electronic spectral data are given in Table XI.

Many of the arguments presented in this chapter are based upon infrared data. Considerable infrared data is available in the literature regarding CNS^- complexes.[91-95] The three major vibrational modes, $\nu(C\equiv N)$, $\nu(C-S)$, and $\delta(CNS)$ lie in the ranges > 2100 cm^{-1} (sharp), 690-720 cm^{-1}, and 400-440 cm^{-1} for S-bonded CNS while for N-bonded species the absorptions lie at < 2100 cm^{-1} (broad), 780-860 cm^{-1}, and 450-490 cm^{-1}, respectively. Bertini and Sabatini,[95] however, have pointed out that the first harmonic of $\delta(CNS)$ mode for S-bonded species falls in the region 800-880 cm^{-1} with an intensity similar to $\nu(C-S)$. As a result, erroneous interpretations of CNS spectra are possible unless all three modes are considered simultaneously.

To determine the $\nu(C-S)$ and $\delta(CNS)$ modes of the complexes discussed herein, a comparison of the spectra with those of the corresponding

TABLE XI

Conductivities and Electronic Spectral Data for the

Palladium and Platinum Thiocyanate Complexes

Complex	Solution Spectra[b] kK (ε)	Solid State Spectra kK	Λ^c
Pd(EDPy)(NCS)(SCN)	sh28.57 (2620)	28.6	< 0.149
Pd(EDP)(NCS)(SCN)	sh28.57 (2925)	28.6	< 0.114
Pd(BHAE)(NCS)(SCN)	sh28.57 (2700)	28.2	0.154
Pt(EDPy)(NCS)(SCN)	sh35.71 (1737)	(a)	0.067
Pt(EDP)(NCS)(SCN)	sh35.71 (1730)	(a)	< 0.142
$Pt(EDP)(NCS)_2$	sh37.74 (3515)	(a)	< 0.186
Pt(BHAE)(NCS)(SCN)	sh35.59 (1340)	(a)	0.234

sh: shoulder

(a): no solid state electronic spectra were obtained because of the limitation of the reflectance attachment in the ultraviolet region.

[b]Methylene chloride solution.

[c]Conductivity of 1×10^{-4} molar solution in methylene chloride at ambient temperature (about 298°K). A typical value for 1:1 electrolyte is 20. The conductivity values have the units: $ohm^{-1}cm^2moles^{-1}$.

halide complexes were made. The $\nu(C\equiv N)$, $\nu(C-S)$, and the $\delta(CNS)$ absorptions are presented in Table XII.

The $\nu(C\equiv N)$ absorptions of the Pd(EDPy), Pd(EDP), and one of the two Pt(EDP) complexes clearly show the presence of both N- and S-bonded CNS^-. The other Pt(EDP) complex will be discussed later. The $\nu(C\equiv N)$ bands for Pt(EDPy) and the two BHAE complexes do not show clearly the distinct S-bonding absorptions, but do exhibit shoulders that correspond to peaks in the more definitive spectra of the EDP complexes. Mixed thiocyanate bonding for all the complexes was confirmed by the $\nu(C-S)$ and $\delta(CNS^-)$ absorptions. Even though the $\nu(C-S)$ assignments may be in error due to the previously mentioned overtone, $\delta(CNS)$, the presence of N-bonding in all the complexes is shown by the broad $\nu(C\equiv N)$ absorption below 2100 cm^{-1}. It is unlikely that the mixed mode bonding is the result of bridging CNS^- moieties as is found for the Pt(II) and Pd(II) halide complexes. Assuming the organic ligands to be bidentate, bridging CNS^-'s would require the expansion of the coordination sphere of the metal from 4 to 6. With such an octahedral coordination geometry, paramagnetic species would have been expected.

Good evidence for assigning an M(NCS)(SCN)L structure to the complexes as opposed to a mixture of all S- and all N-bonded species comes from the electronic spectra. For Pd(II) and Pt(II) the spectrochemical series is (NCS) > Cl > (NCS)(SCN) > Br > (SCN).[94] The platinum complexes all absorb at about 35.7 kK which is intermediate between the corresponding chlorides and bromides which absorb at 36.0 and 35.3 kK respectively. The same is found for the palladium species. They all have their major absorption in the vicinity of 28.6 kK while the chloride and bromide absorptions fall in the ranges 33.3 and 27.4 kK, respectively. If a mixture

TABLE XII

Infrared Absorption Data for the Thiocyanato Complexes

Complex	ν(C≡N)				ν(C-S)		δ(CNS)	
$Pt(EDPy)(CNS)_2$ [b]	2125sh	2120sp	2110sh	2080sh	840	(a)	417	(w)
$Pd(EDPy)(CNS)_2$ [b]	2120sp	2103sp	2076br	2060sh	735	(a)	471	(w)
$Pt(EDP)(SCN)_2$	2123sp	2113sp	2105sh	2075sh	843	(a)	413	(w)
$Pt(EDP)(NCS)_2$	2123br		2108br		848	853	463	(w)
$Pd(EDP)CNS)_2$ [b]	2120sp	2096	2086sh	2054	834	870w	412	(w)
$Pt(BHAE)(CNS)_2$ [b]	2125sh	2121sp	2106sh	2080sh	833	(a)	418	(w)
$Pd(BHAE)(CNS)_2$ [b]	2115sh		2092br	2052sh	835	(a)	416	(w)

(a) ν(C-S) for SCN^- bonding is masked by ligand absorptions.

(b) mixed bonding modes present for thiocyanate

sp sharp

sh shoulder

br broad

w weak

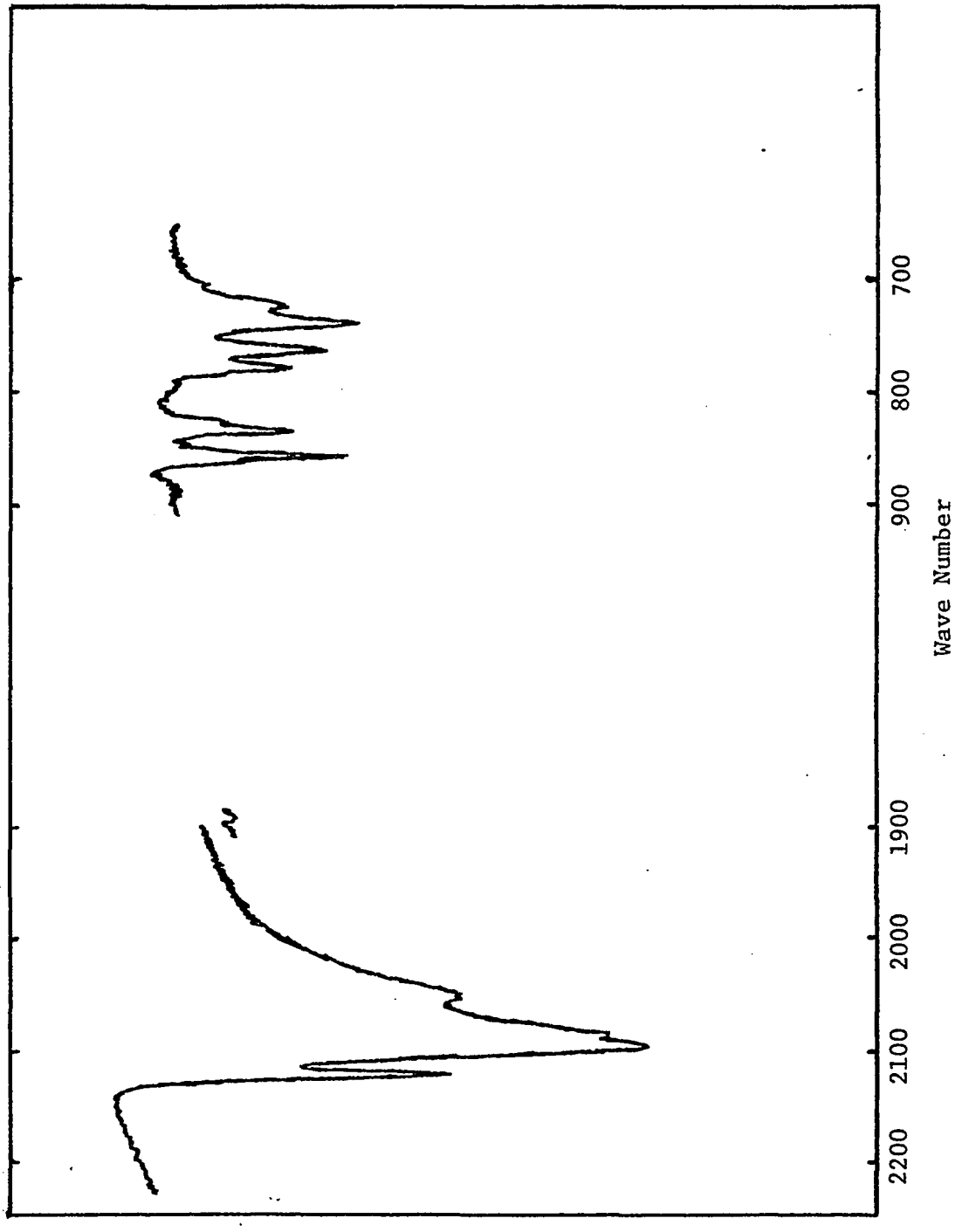


FIGURE XIII. Infrared Spectrum of Pd(EDP)(NCS)(SCN)

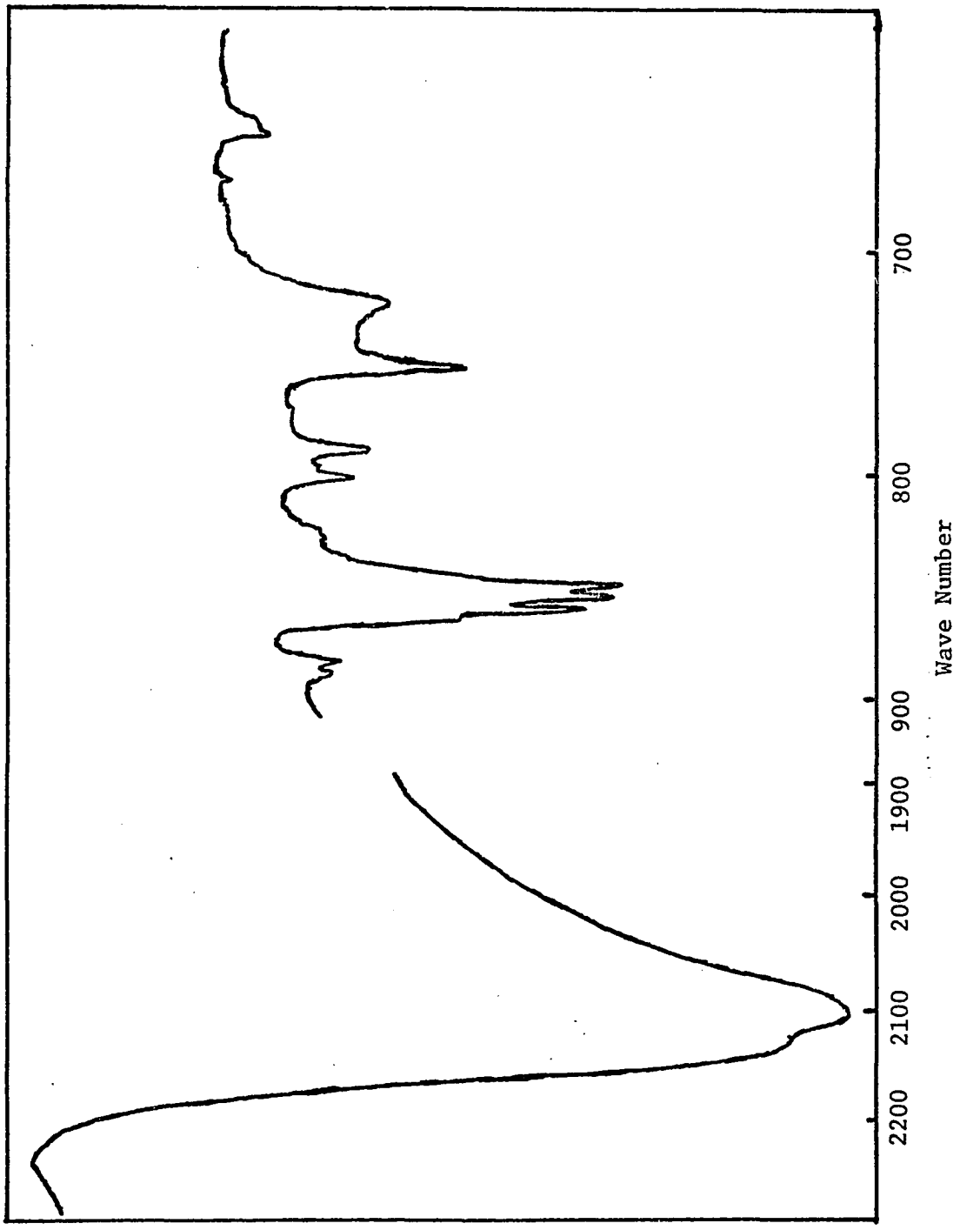


FIGURE XIV. Infrared Spectrum of $Pt(EDP)(NCS)_2$

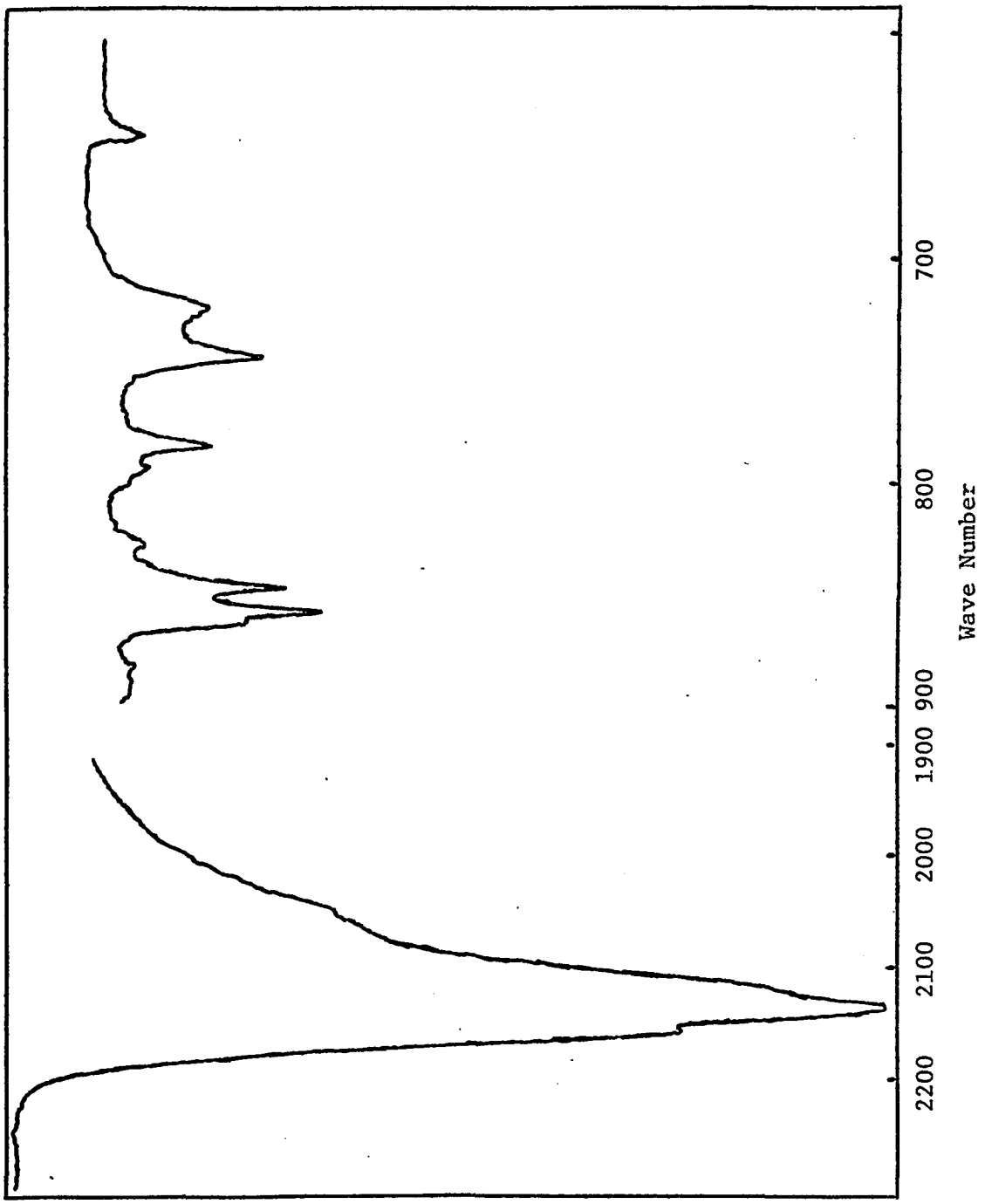


FIGURE XV. Infrared Spectrum of Pt(EDP)(NCS)(SCN)

of N- and S-bonded isomers were present, multiple absorptions would have been observed. Furthermore, if an equilibrium mixture of all N- and all S-bonded isomers were present, recrystallization from different solvents would be expected to alter the ratio of isomers. This would be easily detectable in the electronic spectra. Samples recrystallized from acetone, acetonitrile, and methylene chloride show identical spectra. Finally, no separation was noted upon thin-layer chromatography on silica gel with a variety of solvents.

The mixed bonding mode exhibited by the complexes must be the result of both electronic and steric factors. As previously mentioned, based only on electronic factors the complexes would be expected to have only S-bonded CNS^- moieties. An insight into the factors responsible for this mixed bonding can be gained from the results of the x-ray analysis of a related complex, $PtI_2(EDM)$.[64] EDM differs from EDP only in that the ether groups in the gamma positions of the heterocyclic rings in EDM are replaced by methylene moieties in EDP. EDM and EDP, as shown by space filling molecular models, have virtually identical steric requirements. In the $PtI_2(EDM)$ complex there are severe intramolecular interactions between the alpha carbons of the rings and the iodides. Non-bonded interactions of up to 0.68 Å less than the sum of the van der Waals radii were observed. Therefore, the smaller the anion the smaller will be the unfavorable steric interactions. Nitrogen is much smaller than sulfur so steric factors favor N-bonded over S-bonded thiocyanate and the steric and electronic factors balance each other.

With platinum and EDP as the organic ligand, it is possible to isolate a second complex with the stoichiometry $Pt(CNS)_2(EDP)$. Its infrared spectrum indicates it to be the all N-bonded isomer. Further evidence

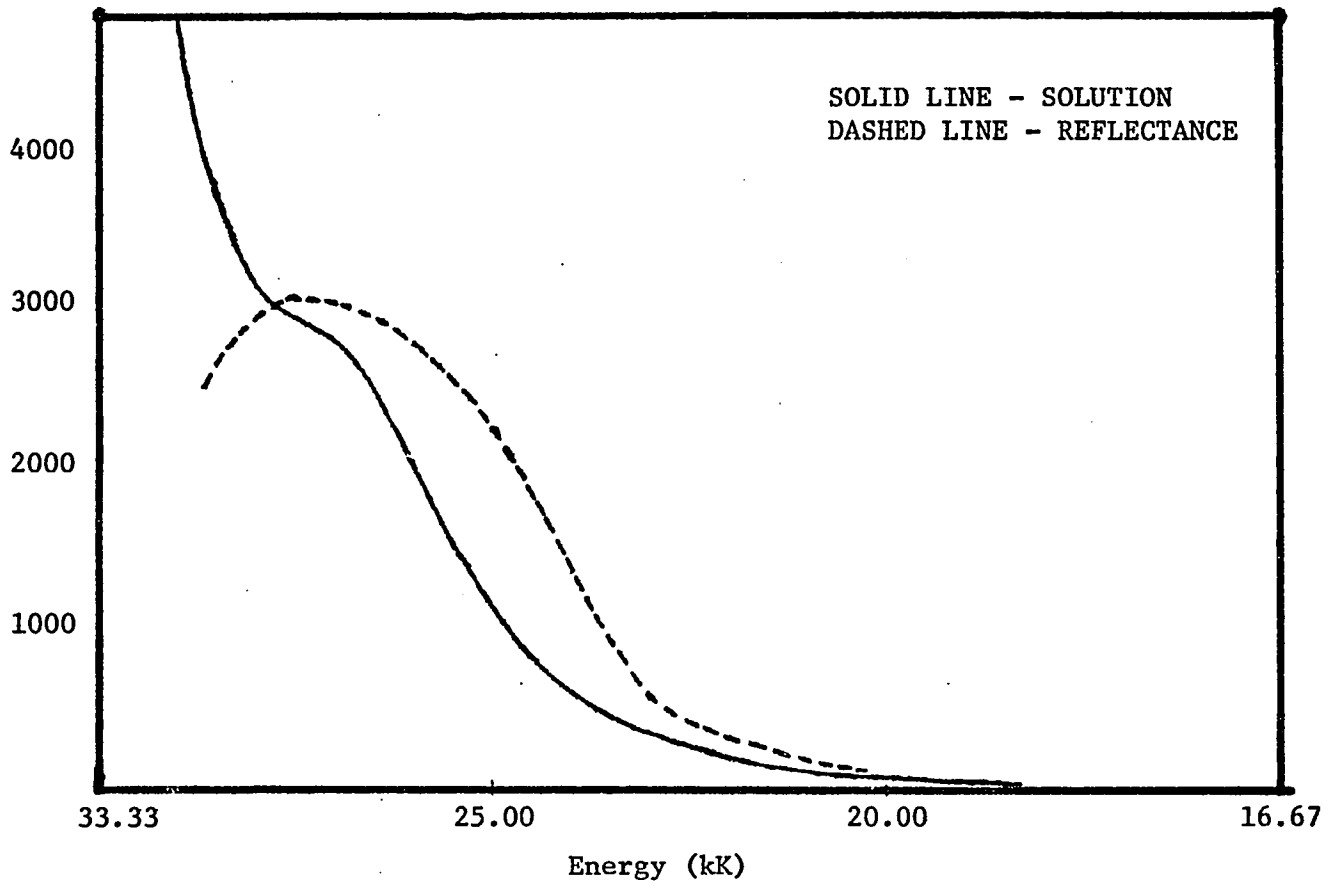


FIGURE XVI. Electronic Spectra of Pd(EDP)(NCS)(SCN)

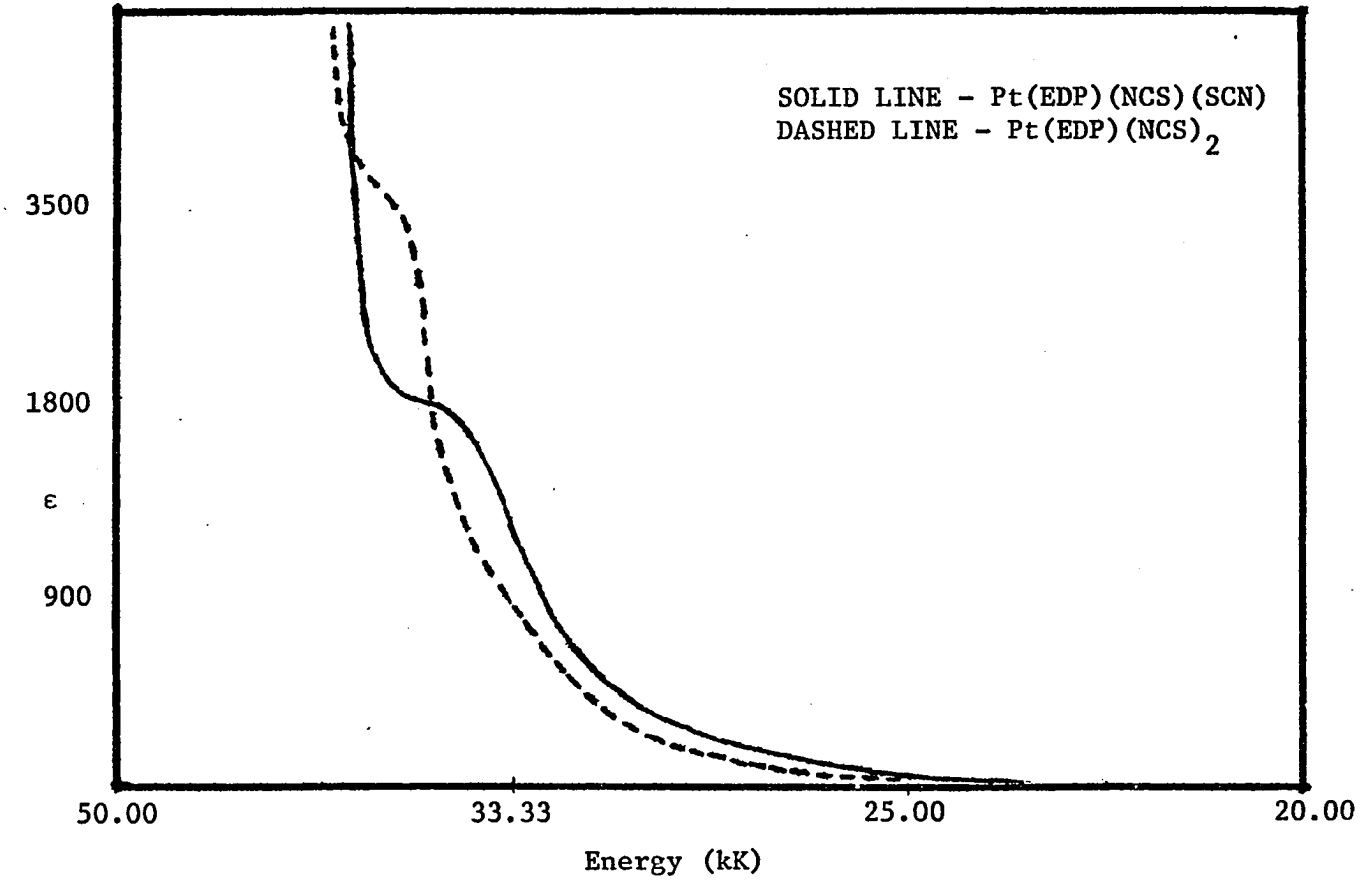


FIGURE XVII. Electronic Solution Spectra of $Pt(EDP)(NCS)_2$ and Pt(EDP)(NCS)(SCN)

for this comes from the electronic spectrum. The complex absorbs at 38.5 kK which is higher in energy than the corresponding chloride complexes (36.7-37.0 kK).

The fact that an all N-bonded complex is obtainable only with the Pt-EDP system and only after prolonged reaction times is interesting. The "effective" ionic radius of Pt(II) is slightly (3%) less than that of Pd(II).[96] This implies that in the platinum complexes there should be slightly greater steric interactions between the anions and the alpha carbons of the rings. Also, EDP appears to produce the greatest steric demands since the other ligands did not give all N-bonded isomers. This is not unreasonable considering the smaller ring size of EDPy and the ability of BHAE rings to "twist" into a number of conformations to relieve steric hindrance. These increased steric interactions in the case of the Pt-EDP system appear to be enough to swing the balance to the side of the steric requirements of the ligand as opposed to the electronic factors that favor sulfur bonding.

CHAPTER VI

CONCLUSIONS

The paramagnetism exhibited by the present palladium and platinum halide complexes is the result of an octahedral or a pseudo-octahedral environment around the metal ions. The thiocyanate complexes are diamagnetic and square planar. The extent to which an octahedral environment, as opposed to a square planar environment, is achieved in these complexes depends upon the degree of steric hindrance produced by the ligands. This dependence is well documented for square planar Ni(II) complexes.[55-60] The nickel complexes are octahedral in solution or in the solid state through ligand bridging.

Based upon the size of the rings in the ligands, the steric hindrance produced by the ligands in the Pd and Pt systems is expected to be BHAE > EDP > EDPy. As a result, the order of paramagnetism found in the complexes may be expected to follow the above trend according to ring size. The general trends observed for the magnetic moments of the palladium and platinum halide complexes are not those of the above order. For the palladium complexes the general trend is PdX_2EDP > PdX_2EDPy > PdX_2BHAE and the trend for the platinum complexes is PtX_2EDPy > PtX_2EDP > PtX_2BHAE. These observed trends can be explained by considering the chelate ring and the relative sizes of the heterocyclic rings in the ligands. The five membered chelate ring formed by the ethylene bridge,

the two nitrogen donors and the metal ion is "puckered,"[97] rather than planar. This causes the heterocyclic rings on the ligands to be directed out of the nitrogen-halide-metal plane. Therefore, if the heterocyclic rings become too large, the rings will sterically interfere with the intermolecular association. This steric interference to association has also been shown by salicylaldimine complexes of Ni(II).[57]

There appears to be a delicate balance of ligand and metal ion size in order to produce paramagnetic behaviour in the palladium and the platinum systems. In the palladium system the greatest magnetic moments are observed in EDP complexes. This implies that the EDP ligand produces the greatest amount of steric hindrance to the halides in the plane thereby promoting bridging between molecules. The EDPy ligand is smaller in ring size than the EDP so it does not produce the degree of steric hindrance the EDP ligand does in the plane of the molecule. Therefore, the tendency for the halides to bridge is less in the EDPy complexes. On the other hand, the greatest steric hindrance is expected for the BHAE ligand with the seven membered rings. Even though it may have the largest tendency to promote bridging of the halides by steric hindrance in the plane, its bulk is sufficiently large out of the plane so that is actually gets in the way of bridging.

The same arguments can be made for the platinum system even though the EDPy complexes exhibit the largest magnetic moments. In the platinum system, the rings of EDPy produce the greatest amount of steric hindrance in the plane while not preventing intermolecular bridging. The reason for this is thought to be the ionic size of the Pt(II) ion. It is 3% smaller than the palladium(II) ion.[96] Actually, this 3% difference is sufficient to cause the EDPy ligand to produce the smallest out-of-

plane steric hindrance along with the greatest in-plane hindrance. Both the EDP and BHAE ligands produce more steric hindrance in the plane but also more effectively inhibit intermolecular association than does EDPy. In the $PtCl_2$ BHAE complex, intermolecular association is inhibited to the extent that the complex is diamagnetic.

The size of the halides also contribute to the steric hindrance in the coordination plane. By varying the anion with the same metal and ligand, the increasing order of paramagnetism for the complexes is $M(CNS)_2L$ < MCl_2L < MI_2L < MBr_2L. This order is also the order of increasing size of the anion with the exception of the bromide and iodide.

All the thiocyanate complexes are diamagnetic. While the thiocyanate anion is a very good bridging group, bridging does not take place in these complexes. It is well known that palladium(II) and platinum(II) complexes prefer a square planar geometry and other geometries are attained only when the molecule is forced into it. In the thiocyanate complexes the square planar geometry is retained at the expense of the preferred thiocyanate bonding mode. As mentioned in Chapter V, the preferred bonding mode for CNS-M (M=Pt,Pd), is through the sulfur when the other ligands are amines. All these thiocyanate complexes have at least one N-bonded thiocyanate group. The M-NCS bond reduces the steric requirement within the coordination plane since nitrogen is considerably smaller than sulfur. Thus, the thiocyanate complexes are square planar and diamagnetic.

All three palladium chloride complexes and two of the three platinum chloride complexes are paramagnetic. Every bromide and iodide complex is paramagnetic. Since the iodide is the largest, the iodide complexes should have the largest magnetic moments. The large degree of

steric hindrance of the iodide complexes is evident from the inability to synthesize the PtI_2BHAE, the complex with the largest ligand, the largest anion, and the smallest cation. The bromide complexes appear to have the greatest tendency to bridge, at least in the palladium system. This is based on the values of the magnetic moments. Even though the steric factors are greater in the case of the iodide complexes, the iodide anion can better compete with the ligand for the available metal orbitals than can the bromide or chloride anions since the iodide is a better trans effecting anion.[98] As a result the amine bond trans to the iodide is weakened and lengthened relieving the steric strain to some extent.

The major difference in the palladium and platinum systems is the tendency to produce variable magnetic moments from different preparations. Different preparations yield different magnetic moments for a given complex of the palladium iodides and bromides. This is attributed to the rates of complexation. The platinum complexes react much slower than the palladium complexes, thereby crystallizing from solution at a considerably slower rate. The platinum reactions allow the more thermodynamically favorable form to crystallize. In the palladium system the rate of reaction is sufficiently fast to allow precipitation to occur immediately upon the addition of the ligand. Rapid precipitation results in a non-equilibrium mixture of square-planar and pseudo-octahedral species in the solid state.

The electronic transitions have not been assigned due to the lack of a suitable model.[99] Polarized and low temperature single crystal spectra of the ligand field transitions along with x-ray crystallographic results would undoubtedly be of interest.

For several decades, Pd(II) and Pt(II) complexes reported in the literature were invariably diamagnetic and this came to be accepted as dogma. In view of this work, paramagnetism in Pd(II) and Pt(II) systems appears to be quite common with certain sterically demanding ligand systems, and, therefore, each new system should be examined on its own merits.

PART II

A STUDY OF THE COORDINATION CHEMISTRY OF 2,2'-BIS(PIPERIDINO)DIETHYLAMINE WITH DIVALENT TRANSITION METAL IONS

FOREWORD

The purpose of this research is to synthesize and study complexes formed from the potentially tridentate ligand, 2,2'-bis(piperidino)diethylamine, BPEA. The heterocyclic rings in the ligand were expected to produce considerable steric demand on the complexes. The selected anions (Cl^-, Br^-, I^-, CNS^-, NO_3^-, and NO_2^-) were chosen to produce complexes with a variety of coordination numbers and sterochemistries.

The complexes were found to have the stoichiometry $M(L)X_2$ (M = Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}; X = anions listed above). For $Ni(BPEA)Cl_2$, a hydrated form of the complex containing two moles of water was also isolated.

The initial purple cobalt halide complexes were found to be five-coordinate in solution and in the solid state. Coordination isomerism occurred with the chloride and bromide complexes upon heating in a vacuum at about 140° to form a blue tetrahedral species. The tetrahedral complex formed by breaking the ligand's terminal nitrogen-metal bond rather than the central nitrogen-metal bond. This argument was supported by infrared data showing a shift to lower energy of the

nitrogen-hydrogen stretching frequency for the tetrahedral complex. The geometries of both isomers were determined by their electronic spectra. In solution the tetrahedral complex was transformed back into the original purple complex.

Electronic spectra showed that $Co(BPEA)(NO_3)_2$ and $Co(BPEA)(NO_2)_2$ were five coordinate in the solid state. The nitrato complex was six-coordinate in solution, while the nitrito complex decomposed in solution.

The nickel halide complexes were five-coordinate both in the solid state and in solution. The chloride complex was deliquescent with the hydrate having an octahedral geometry. In a vacuum, the hydrate lost two moles of water to become the five-coordinate species.

The nitrato and nitrito nickel complexes were octahedral in both the solid state and solution. The octahedral geometry was formed by both nitrate groups and the BPEA acting as bidentate ligands. In the nitrito complex, one of the two nitrite groups was bidentate and the other was monodentate. The assignments of the nitrate and nitrite bonding were made on the basis of infrared arguments.

On the basis of the electronic spectra, the copper halide complexes were assigned a five-coordinate geometry in the solid state and a square planar configuration in solution. The nitrato and thiocyanato complexes were square planar both in the solid state and solution.

The thiocyanato complexes of Co^{+2} and Ni^{+2} were octahedral dimers in the solid state with bridging thiocyanate groups. The nickel complex remained as an octahedral dimer in solution while the cobalt complex existed as a five-coordinate monomer in solution.

CHAPTER I

INTRODUCTION

A. Statement of the Problem

This research was intended to study the effect of a sterically demanding, tridentate chelating agent on the stereochemistry of some divalent, first row transition metals (Co, Ni, Cu, and Zn). The ligand chosen was 2,2'-bis(piperidino)diethylamine, BPEA (X), because of previously shown steric demands of the ring systems within the related ligands, EDM and EDP.



(X)

Since BPEA is potentially a tridentate ligand and the metals are divalent, a pentacoordinate geometry is possible for many of the complexes. However, several different anions were used to provide a variety of possible coordination numbers and stereochemistries. The anions were Cl^-, Br^-, I^-, NCS^-, NO_2^- and NO_3^-.

Insight into the geometries was determined by infrared spectra, electronic spectra, conductivity measurements and magnetic moments, and comparing the data to the data for compounds in the literature.

B. Related Chemical Literature

Five-coordinated complexes of the first row transition metals have been known for some time. The first reported examples were low-spin complexes containing phosphorus or arsenic ligands. In the last ten years, there have been many examples of high-spin, five-coordinate complexes characterized. Their structures have been firmly established by x-ray methods.[100-105]

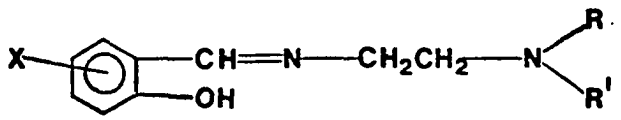
Since first row transition metals prefer a coordination number other than five, one of the most important requirements for the formation of a pentacoordinate complex is that the size and disposition of the coordinating ligands be such that only five donor atoms are allowed to approach the central metal ion closely. It has been shown that the stereochemical arrangement of these donor atoms may be based upon a trigonal bipyramid or a square pyramid; the pentagonal planar and pentagonal pyramidal geometries have been considered to be unlikely on steric grounds.[106]

To assure a high-spin complex, a second requirement of the coordinating ligand is necessary. The donor atoms must possess strong sigma bonding capabilities and little tendency to form pi bonds with the metal ions. High-spin complexes are also characterized by the large electronegativities of the donor groups. Quite often in low-spin complexes, the electronegativity of the donor atom is very near that of the metal ion. Sacconi and Luigi[104,107] have ordered different sets of donor atoms according to their values of the overall electronegativities or the sum of nucleophilic reactivity constants of the donor group. The cross over point between high-spin and low-spin complexes was located.

The first attempt at synthesizing five-coordinate complexes was reported by Prue and Schwarzenbach,[108] and later by Ciampolini, Paoletti, and Sacconi.[109] First row divalent transition metal halide salts from MnX_2 to ZnX_2 were complexed with dien to give species of the type, $M(dien)^{2+}$ in aqueous solution. With the possible exception of copper and zinc, the others were all octahedral. The $M(dien)^{2+}$ complexes attained an octahedral geometry through the coordination of three molecules of water. Moreover, Bernhard and Barclay[110] isolated the compounds $Co(dien)Cl_2$ and $Co(dien)Br_2$, which were high-spin. For these compounds, they postulated a structure either of the type [Co(dien)X]X or the type $[Co(dien)_2][CoX_4]$. Ciampolini and Speroni[111] measured the reflectance spectrum of $Co(dien)Cl_2$ and found the spectrum had characteristic absorptions of a hexamine cobalt(II) species along with a $(CoCl_4)^{2-}$ species. These data lead to the conclusion that the structure was $[Co(dien)_2][CoCl_4]$. Thus it appears that a structure which contains six and four coordinated cobalt present at the same time is more stable than one with a five-coordinated cobalt when the ligand is dien. The opposite is true when the ligand is dienMe.[111] The complexes formed between divalent transition ions from manganese to zinc with the ligand dienMe were all five-coordinate in the solid state. It is very likely that this is due to the steric requirements of the methyl group on the central nitrogen of the ligand, which causes strong steric hindrance to the coordination of two dienMe molecules to the same metal ion.

The first high-spin, five-coordinate cobalt(II) and nickel(II) complexes were reported by Sacconi, et al.[112-114] These included a series of nickel(II) complexes formed by the condensation of ring substituted salicylaldehydes with N,N-disubstituted ethylenediamines to

give the chelating agent (XI):[112]

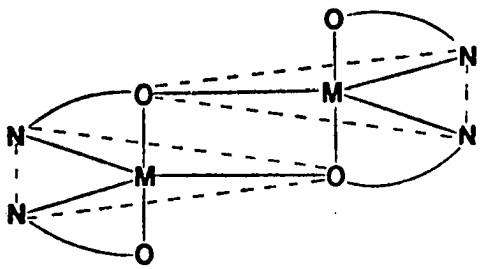


(XI)

Sacconi found that when R and R' were ethyl groups and X = 3-Cl, 5-Cl or 3,4-dibenzo, the complexes were paramagnetic and five coordinate with μ_{eff} = 3.3 B.M. An x-ray structural analysis showed the X = 3-Cl complex to most resemble a distorted square pyramid with the nickel atom lying a little above the mean basal plane. In solution the complexes existed as an equilibrium mixture of 4, 5, and 6 coordinated species.

About the same time, examples of high-spin five-coordinate cobalt(II) complexes with the same ligand (XI) were isolated by Sacconi, Ciampolini, and Speroni.[113] When both R and R' were ethyl groups and X was 5-Cl, then five-coordinated complexes were obtained. The complexes, as in the case of the pentacoordinate nickel complexes, had a distorted square pyramidal geometry.

Along with the above papers, Sacconi, Ciampolini, and Speroni published a report on cobalt(II) and nickel(II) complexes with a trigonal bipyramidal configuration.[114] The structure of bis(N-methylsalicylaldiminato)cobalt(II) was ascertained by x-ray analysis. It was found to exist as dimers, (XII). Bis(N-methylsalicylaldiminato)nickel(II) was found to be five-coordinate and isostructural with the cobalt complex only in a solid solution of the analogous zinc(II) complex.



(XII)

Even though many stable, five-coordinate, high-spin complexes have been isolated in the solid state since 1965, other geometries have been found in solution for a number of these complexes. For example, the previously mentioned pentacoordinate nickel complexes with ligand (XI) existed in solution as an equilibrium mixture of different coordinated species.[112]

Dori and Gray showed that the stability of five-coordinate cobalt(II) varies with the size of the coordinated anion.[115] $Co(Et_4$-dien)X_2 complexes were studied where X = Cl, Br, I, NCS, and N_3. They found that when X = Cl, Br, NCS, and N_3, the five-coordinate structure appeared to predominate in the solid state and in a variety of polar organic solvents. The $Co(Et_4dien)I_2$ complex apparently was an example where the steric factors were so large, that more favorable coordination geometries were formed in solution. In DMF, the iodide complex was found to be octahedral and a 2:1 electrolyte. The complex $[Co(Et_4dien)(DMF)_3]I_2$ was postulated. In chloroform and methylene chloride solutions, $Co(Et_4dien)I_2$ was found to be tetrahedral and a nonelectrolyte. It was suggested that a tetrahedral complex was formed wherein the Et_4dien ligand acted as a bidentate moiety.

Sacconi and Morassi demonstrated the stability of cobalt(II) and nickel(II) with a coordination number of five by preparing a series

of complexes with substituted bis-(2-diphenylphosphinoethyl)amine, R-N-$[CH_2-CH_2-P(\phi)_2]_2$ where R = H, CH_3, and cyclohexyl.[116] When R is H or cyclohexyl and X = Cl or Br, the complex $[Ni(ligand)X]_2[NiX_4]$ was found in the solid state. The suggested configurations were a square planar cation and tetrahedral anion. When R = CH_3 and X = Br or I, a five-coordinate complex was found for the solid $Ni(ligand)X_2$. In solution, however, the electronic spectrum was interpreted in terms of a square planar complex, [Ni(ligand)X]X. For the complex, $Ni(ligand)I_2$, where R = H, the complex remains five-coordinate in both the solid state and in solution. This is in contrast to the iodide containing complex, $Co(Et_4dien)I_2$, reported by Dori and Gray[114] whose solution spectrum showed a definite tetrahedral geometry. The work by Sacconi and Morassi showed that the stereochemistry of these complexes along with the stability of a five-coordination number greatly depend upon the ligands and the nature of the R group attached to the nitrogen atom.

Further work along this line was published in 1973 by Sacconi et al.[117] Cobalt(II) halide complexes were prepared from the ligand N-R-N-2-(diphenylphosphino)ethyl-N',N'-diethylethylenediamine, where R = H or CH_3. All the halo complexes were found to be five-coordinate in the solid state. In solution, when R = H the spectrum indicated an equilibrium between five-coordinate and tetrahedral geometries for each halide complex. When R = CH_3, the solution spectra of the halide complexes was that of entirely tetrahedral species. Sacconi's work, along with that of Dori and Gray, suggests that for a given central metal atom and halide, the internal strain of a five-coordinate complex increases as the ligand changes in the order: NNN < NNP < PNP. NNN,

NNP, and PNP are the donor atoms for the tridentate chelating agents; each of which has H bonded to the central chelating atom.

As previously mentioned, there are two basic geometries used to define the stereochemistry of five-coordinate complexes. The idealized geometries, square pyramidal (C_{4v}) and trigonal bipyramidal (D_{3h}) are rarely found even though complexes may be reported as such. Often, the reported "trigonal bipyramidal" and "square pyramidal" complexes may be severely distorted.

Muetterties and Schunn in their review[101] have demonstrated the similarity of D_{3h} and C_{4v} symmetries and how interconversion may occur between these two geometries through an intermediate of C_{2v} symmetry (see figure XVIII).

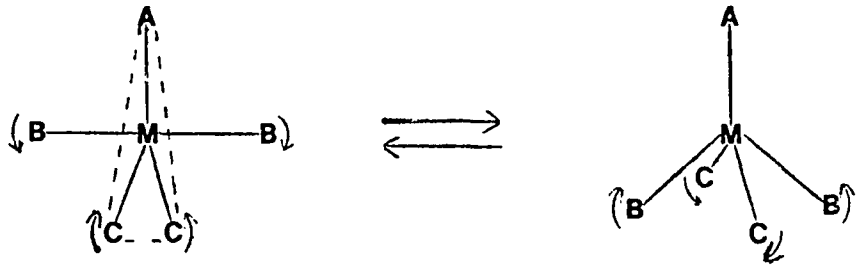


FIGURE XVIII: Interconversion of Trigonal Bipyramidal and Square Pyramidal Configurations.

By considering a trigonal bipyramid along one of its C_2 axes, interconversion of the two geometries is easily shown. By increasing the angles ∠AMB and decreasing the angles ∠AMC in the D_{3h} symmetry, the C_{4v} symmetry is attained.

On the basis of charge repulsion considerations with five similar anions, Zemann demonstrated that the trigonal bipyramid is more

stable than the square pyramid by about 5.96 Kcal/mole.[118] In addition, Zemann's treatment showed that distortion was likely to occur if the configuration was square pyramidal. A configuration more stable than a regular square pyramid could be achieved by lifting the metal ion above the plane of the four basal ligands toward the apical ligand so that apical-to-basal bond angle was about 104°. Another important find of Zemann's was that the intermediate C_{2v} symmetry is not energetically unfavorable.

On the basis of charge repulsion, D_{3h} symmetry is favored; however, Ciampolini has listed many factors that are responsible for the difference in stability between the square pyramid and the trigonal bipyramid.[119] The factors listed, other than entropy factors, are: metal-ligand attractions, ligand-ligand repulsions, crystal field stabilization energy (C.F.S.E.), solvation, and crystal-packing effects.

Metal-ligand attractions can be viewed through the nature of the bonding involved. Furlani has discussed the effect of π-bonding on the geometry of a complex.[120] The result of this treatment was that π-bonding tends to stabilize the regular square pyramidal configuration because the ligands can better effect π-bonding with bond angles of 90°. Furlani also stated that if the bonding was mainly electrostatic or sigma-covalent in nature, then the trigonal bipyramid would be more stable.

The structures of $Co(Me_5dien)Cl_2$ and $Co(Et_4dien)Cl_2$ provide an interesting example of the effect of non-bonding ligand-ligand repulsions on the stereochemistry of five-coordinate complexes. X-ray analysis shows that $Co(Et_4dien)Cl_2$ has a distorted trigonal bipyramidal geometry, while $Co(Me_5dien)Cl_2$ has neither trigonal bipyramidal or

square pyramidal geometry,[121,122] The structure of $Co(Me_5dien)Cl_2$ was rationalized to be of intermediate structure due to the short contact between one of the chlorine atoms and the central methyl group thereby forcing the geometry toward a square pyramid.

Obviously, there are several factors that affect the C.F.S.E,, such as the metal ion and its oxidation state along with the exact geometry. Generally, the C.F.S.E. will favor the regular square pyramidal geometry. For the d^7, weak field case, the square pyramidal geometry is favored by 3.69 Dq over the trigonal bipyramidal geometry; for the d^7, strong field case, the square pyramidal configuration is favored by 5.80 Dq.[123] For d^8 systems, the square pyramidal configuration is favored by 3.73 and 4.12 Dq for the strong field and weak field cases, respectively.[123]

Crystal-packing forces can be demonstrated with the previously cited example of tetrakis-(N-methylsalicylaldiminato)-dinickel(II).[114] The compound has been crystallized in three forms. The α and β forms are diamagnetic, monomeric and <u>trans</u> square planar complexes. By dissolving these forms in the crystal lattice of the analogous zinc complex, they become paramagnetic and binuclear with a trigonal bipyramidal structure. This is evidence that a host lattice can stabilize the geometry of a guest complex that would otherwise be unfavorable.

In summarizing the factors that dictate the stereochemistry of five-coordinate complexes, it is postulated that π-bonding and C.F.S.E. will promote the regular square pyramidal geometry. Ligand-ligand repulsions and chelate strain forces may be sufficient to produce a distorted square pyramidal, trigonal bipyramidal, or an intermediate geometry. Through solvation effects and the removal of crystal-packing

forces, a pentacoordinate complex may acquire a different coordination number in solution or in a host lattice.

CHAPTER II

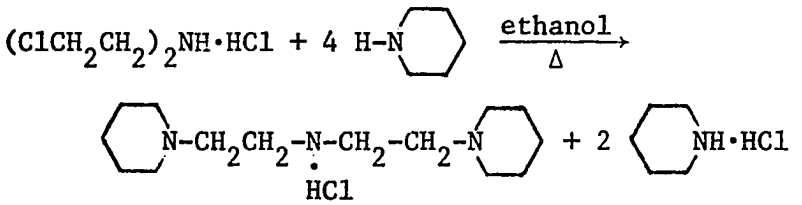
EXPERIMENTAL

A. Instruments Used

A description of techniques and instruments has been given in Chapter II of Part I for the instrumentation used in this part.

B. Reagents

2,2'-Bis(piperidino)diethylamine (BPEA) was synthesized by the condensation of piperidine and 2,2'-dichlorodiethylamine hydrochloride obtained from Eastman Chemicals and Aldrich Chemicals, respectively. The reagents, 48 g (0.269 mol) of $(ClCH_2CH_2)_2NH \cdot HCl$ and 112 ml (density = 0.8606 g/ml°, 1.13 mol) of piperidine were added to 155 ml of ethanol. The reaction was allowed to sit for 24 hours due to the highly exothermic nature of the reaction. The mixture was then gently heated to reflux and held there for 48 hours. The reaction is as follows:



After the reaction mixture cooled to room temperature, 300 ml of 5.0 M NaOH was added. The organic substances were extracted with three portions of 200 ml of ether. The volatile substances were then

removed by means of a rotary evaporator. The crude product was purified by vacuum distillation at 108°-111°C with a pressure of about 10^{-3} torr. The ligand was confirmed by N.M.R., i.r., and mass spectra.

The $ZnBr_2$ was prepared by the reaction of zinc metal and concentrated HBr. After the completion of the reaction, the solvent was removed under vacuum, and the product was dried under vacuum at 80°C.

All of the solvents were treated as reported in Chapter II of Part I.

C. Preparation of Complexes

C.1. Preparation of dichloro2,2'-bis(piperidino)diethylaminecobalt(II), $Co(BPEA)Cl_2$

C.1.a. Preparation of purple $Co(BPEA)Cl_2$

Anhydrous $CoCl_2$ (260 mg, 2.0 mmol) was dissolved in 20 ml of absolute ethanol. After the salt had dissolved, 0.60 ml (2.4 mmol) of the ligand, BPEA, dissolved in 2 ml of ethanol, was added dropwise to the stirred cobalt solution. After stirring at room temperature for 30 min, the solvent was removed on a rotary evaporator to leave a purple solid. Excess ligand was removed by washing with anhydrous ether. The purple product was purified by two methods: (1) recrystallization from acetone; and (2) sublimation at 145°C and about 10^{-3} torr.

Analysis of purple $Co(BPEA)Cl_2$:

Calculated: Carbon, 45.53%; Hydrogen, 7.91%.

Found: Carbon, 45.61%; Hydrogen, 7.85%.

C.1.b. Preparation of blue $Co(BPEA)Cl_2$

By heating purple $Co(BPEA)Cl_2$ to 135°C in vacuo, the solid turned blue. Attempts to recrystallize the blue solid from a variety

of solvents such as benzene, ethanol, and chloroform resulted in the purple product.

Analysis of blue $Co(BPEA)Cl_2$:

Calculated: Carbon, 45.53%; Hydrogen, 7.91%.

Found: Carbon, 45.50%; Hydrogen, 7.93%.

C.2. Preparation of dibromo2,2'-bis(piperidino)diethylaminecobalt(II), $Co(BPEA)Br_2$

C.2.a. Preparation of purple $Co(BPEA)Br_2$

The method of synthesis of $Co(BPEA)Br_2$ is the same as the preparation reported in section C.1.a. Purification was achieved by recrystallization from ethanol.

Analysis of purple $Co(BPEA)Br_2$:

Calculated: Carbon, 36.70%; Hydrogen, 6.38%.

Found: Carbon, 36.60%; Hydrogen, 6.45%.

C.2.b. Preparation of blue $Co(BPEA)Br_2$

By heating purple $Co(BPEA)Br_2$ at 145°C <u>in vacuo</u> ($\simeq 10^{-3}$ torr) for 45 min, blue $Co(BPEA)Br_2$ was formed. Recrystallization of the blue product in $CHCl_3$, acetone, or ethanol resulted in the purple form of the complex.

Analysis of blue $Co(BPEA)Br_2$:

Calculated: Carbon, 36.70%; Hydrogen, 6.38%.

Found: Carbon, 36.65%; Hydrogen, 6.43%.

C.3. Preparation of Diiodo2,2'-bis(piperidino)diethylaminecobalt(II), $Co(BPEA)I_2$

The preparation of the complex was accomplished by the method reported in section C.1.a. After stirring the reaction mixture for 2 hours, the purple product was filtered and purified by recrystallization

from acetone. Attempts to sublime the product at 175° and 10^{-3} torr or convert it to the blue form caused decomposition of the complex.

Analysis of $Co(BPEA)I_2$:

Calculated: Carbon, 30.45%; Hydrogen, 5.29%.

Found: Carbon, 30.49%; Hydrogen, 5.38%.

C.4. Preparation of dichloro2,2'-bis(piperidino)diethylaminenickel(II), $Ni(BPEA)Cl_2$

The complex was prepared by the method reported in section C.1.a. The product was purified by sublimation at 150°C and 10^{-3} torr to yield a yellow-brown collored solid. Exposure to air caused to product the change to a light green color.

Analysis of $Ni(BPEA)Cl_2$:

Calculated: Carbon, 45.56%; Hydrogen, 7.92%.

Found: Carbon, 45.60%; Hydrogen, 7.82%.

C.5. Preparation of dibromo2,2'-bis(piperidino)diethylaminenickel(II), $Ni(BPEA)Br_2$

The complex was synthesized similar to the complex in section C.1.a. The difference was that the product precipitated upon ligand addition. The reaction mixture was stirred for 1 hr at 40°C. The yellow-brown solid was recrystallized from acetone.

Analysis of $Ni(BPEA)Br_2$:

Calculated: Carbon, 36.72%; Hydrogen, 6.38%

Found: Carbon, 36.80%; Hydrogen, 6.42%.

C.6. Preparation of diiodo2,2'-bis(piperidino)diethylaminenickel(II), $Ni(BPEA)I_2$

The complex was prepared in an analogous manner to that reported in section C.1.a. with the exception of the amount of ethanol solvent.

The amount of ethanol used was 35 ml. Five min after the addition of the ligand, the organic product precipitated from solution. The product was recrystallized from acetone.

Analysis of $Ni(BPEA)I_2$:

Calculated: Carbon, 30.47%; Hydrogen, 5.30%.

Found: Carbon, 30.41%; Hydrogen, 5.35%.

C.7. Preparation of dichloro2,2'-bis(piperidino)diethlaminecopper(II), $Cu(BPEA)Cl_2$

The complex was prepared by the same method reported in section C.1.a. The blue product was recrystallized from ethanol.

Analysis of $Cu(BPEA)Cl_2$:

Calculated: Carbon, 44.97%; Hydrogen, 7.82%.

Found: Carbon, 45.00%; Hydrogen, 7.87%.

C.8. Preparation of dibromo2,2'-bis(piperidino)diethylaminecopper(II), $Cu(BPEA)Br_2$

The complex was synthesized in the same manner as the method reported in section C.1.a. The green product was recrystallized from acetonitrile.

Analysis of $Cu(BPEA)Br_2$:

Calculated: Carbon, 36.33%; Hydrogen, 6.32%.

Found: Carbon, 36.42%; Hydrogen, 6.27%.

C.9. Preparation of dichloro2,2'-bis(piperidino)diethylaminezinc(II), $Zn(BPEA)Cl_2$

The complex was prepared by the method reported in section C.1.a. The amount of solvent for the reaction mixture was 10 ml of ethanol. The white product precipitated from solution about 5 min after the addition of the ligand. The product was recrystallized from acetone.

Analysis of $Zn(BPEA)Cl_2$:

Calculated: Carbon, 44.78%; Hydrogen, 7.78%.

Found: Carbon, 44.70%; Hydrogen, 7.77%.

C.10. Preparation of dibromo2,2'-bis(piperidino)diethylaminezinc(II), $Zn(BPEA)Br_2$

The complex was synthesized by the method reported in section C.1.a. Upon addition of the BPEA to the reaction mixture, the product precipitated immediately. The product was recrystallized from acetone.

Analysis of $Zn(BPEA)Br_2$:

Calculated: Carbon, 36.20%; Hydrogen, 6.29%.

Found: Carbon, 36.28%; Hydrogen, 6.35%.

C.11. Preparation of diiodo2,2'-bis(piperidino)diethylaminezinc(II), $Zn(BPEA)I_2$

The complex was prepared by the method reported in section C.1.a. The product precipitated immediately upon addition of the ligand. Purification of the product was by recrystallization from acetone.

Analysis of $Zn(BPEA)I_2$:

Calculated: Carbon, 30.11%; Hydrogen, 5.24%.

Found: Carbon, 30.15%; Hydrogen, 5.30%.

C.12. Preparation of dinitrato2,2'-bis(piperidino)diethylaminecobalt(II), $Co(BPEA)(NO_3)_2$

$Co(NO_3)_2 \cdot 6H_2O$ (870 mg, 3.0 mmol) was dissolved in 25 ml of a 1:1 mixture of ethanol and 2,2-dimethoxypropane. To the stirred solution, 0.80 ml (3.2 mmol) of BPEA was added dropwise. After stirring for 1.0 hr at room temperature, the product had precipitated from the reaction mixture. The purple product was filtered from the reaction mixture and was purified by recrystallization from benzene.

Analysis of $Co(BPEA)(NO_3)_2$:

Calculated: Carbon, 39.81%; Hydrogen, 6.92%; Nitrogen, 16.59%.

Found: Carbon, 39.75%; Hydrogen, 6.85%; Nitrogen, 16.75%.

C.13. Preparation of dinitrato2,2'-bis(piperidino)diethylaminenickel(II), $Ni(BPEA)(NO_3)_2$

$Ni(NO_3)_2 \cdot 6H_2O$ (870 mg, 3.0 mmol) was dissolved in 30 ml of a 2:1 mixture of ethanol and 2,2-dimethoxypropane. To the stirred solution, 0.80 ml (3.2 mmol) of BPEA was added dropwise. After 1 hr, no solid product had precipitated. The product was isolated by removal of the solvent by a rotary evaporator. The green solid was purified by recrystallization from acetone.

Analysis of $Ni(BPEA)(NO_3)_2$:

Calculated: Carbon, 39.83%; Hydrogen, 6.92%; Nitrogen, 16.59%.

Found: Carbon, 39.86%; Hydrogen, 6.98%; Nitrogen, 16.48%.

C.14. Preparation of dinitrato2,2'-bis(piperidino)diethylaminecopper(II), $Cu(BPEA)(NO_3)_2$

$Cu(NO_3)_2 \cdot 3H_2O$ (730 mg, 3.0 mmol) was dissolved in 30 ml of a 2:1 mixture of ethanol and 2,2-dimethoxypropane. To the solution, 0.80 ml (3.2 mmol) of BPEA was added dropwise with immediate precipitation of the purple product. The solution was stirred for 1 hr after which it was filtered. The product was recrystallized from acetone.

Analysis of $Cu(BPEA)(NO_3)_2$:

Calculated: Carbon, 39.38%; Hydrogen, 6.85%; Nitrogen, 16.41%.

Found: Carbon, 39.42%; Hydrogen, 6.79%; Nigrogen, 16.25%.

C.15. Preparation of dinitrato2,2'-bis(piperidino)diethylaminezinc(II), $Zn(BPEA)(NO_3)_2$

$Zn(NO_3)_2 \cdot 6H_2O$ (600 mg, 2.0 mmol) was dissolved in 30 ml of a

3:2 mixture of ethanol and 2,2-dimethoxypropane. To the clear solution, 0.60 ml (2.4 mmol) of BPEA was added dropwise. Within 5 minutes the product began to precipitate from solution. After 1 hr, the product was filtered from the solution and recrystallized from acetone.

Analysis of $Zn(BPEA)(NO_3)_2$:

Calculated: Carbon, 39.23%; Hydrogen, 6.82%; Nitrogen, 16.34%.

Found: Carbon, 39.17%; Hydrogen, 6.88%; Nitrogen, 16.50%.

C.16. Preparation of dinitrito2,2'-bis(piperidino)diethylaminecobalt(II), $Co(BPEA)(NO_2)_2$

$Co(NO_3)_2 \cdot 6H_2O$ (580 mg, 2.0 mmol) and $NaNO_2$ (1.04 g, 15 mmol) was dissolved in 25 ml of a 1:1 mixture of ethanol and 2,2-dimethoxypropane. The solution was stirred for 1 hr after which the solids were filtered from the solution. Air was removed from the filtrate by bubbling N_2 through the solution. The cobalt solution was added dropwise to a second solution of 10 ml of ethanol and 0.60 ml of BPEA while N_2 continually flowed through the reaction vessel. After 4 hrs of stirring, the N_2 flow had evaporated the solvent to a volume of 10 ml, with a purple solid also present. The product was filtered and washed with 10 ml of anhydrous ether under N_2.

C.17. Preparation of dinitrito2,2'-bis(piperidino)diethylaminenickel(II), $Ni(BPEA)(NO_2)_2$

$Ni(NO_3)_2 \cdot 6H_2O$ (870 mg, 3.0 mmol) and $NaNO_2$ (1.04 g, 15 mmol) was dissolved in 30 ml of a 1:1 solvent mixture of ethanol and 2,2-methoxypropane. The solution was then filtered to remove any solids and the volume of the solution was reduced to approximately 20 ml. The volume reduction was accompanied by precipitation of white salt. The salt was filtered from solution. To the green filtrate, 0.80 ml (3.2

mmol) of BPEA was added dropwise. After 0.5 hr the product began to precipitate from the reaction solution and after 1.5 hr, the green product was removed by filtration and purified by recrystallization from benzene.

Analysis of $Ni(BPEA)(NO_2)_2$:

Calculated: Carbon, 43.01%; Hydrogen, 7.49%; Nitrogen, 17.96%.

Found: Carbon, 43.07%; Hydrogen, 7.54%; Nitrogen, 18.03%.

C.18. Attempted preparation of dinitrito2,2'-bis(piperidino)diethylaminecopper(II), $Cu(BPEA)(NO_2)_2$

Various methods of preparation were attempted such as the methods reported in sections C.16 and C.17. In all cases after the addition of the ligand, a slow precipitation of a white solid formed with no isolation of the desired product.

C.19. Preparation of dinitrito2,2'-bis(piperidino)diethylaminezinc(II), $Zn(BPEA)(NO_2)_2$

The complex was prepared by the method reported in section C.17. The purification was accomplished by recrystallization from acetone.

Analysis of $Zn(BPEA)(NO_2)_2$:

Calculated: Carbon, 42.39%; Hydrogen, 7.37%; Nitrogen, 17.66%.

Found: Carbon, 42.40%; Hydrogen, 7.31%; Nitrogen, 17.58%.

C.20. Prepearation of dithiocyanato2,2'-bis(piperidino)diethylaminecobalt(II), $Co(BPEA)(NCS)_2$

$Co(NO_3)_2 \cdot 6H_2O$ (870 mg, 3.0 mmol) and KCNS (1.04 g, .011 mol) were dissolved in 30 ml of a 2:1 solvent mixture of ethanol and 2,2'-dimethoxypropane and stirred for 1 hr. The solution was then filtered to remove the insoluble salts. To the solution, 0.80 ml of BPEA dissolved in 2 ml of ethanol was added dropwise. Within 0.5 hr, a purple

solid had precipitated. The product was filtered from the solution and was purified by recrystallization from acetonitrile.

Analysis of $Co(BPEA)(NCS)_2$:

Calculated: Carbon, 46.36%; Hydrogen, 7.05%; Nitrogen, 16.90%.

Found: Carbon, 46.59%; Hydrogen, 7.10%; Nitrogen, 16.80%.

C.21. Preparation of dithiocyanato2,2'-bis(piperidino)diethylamine-nickel(II), $Ni(BPEA)(NCS)_2$

The complex was prepared by the method reported in section C.20. The green product was purified by recrystallization from acetonitrile.

Analysis of $Ni(BPEA)(NCS)_2$:

Calculated: Carbon, 46.38%; Hydrogen, 7.06%; Nitrogen, 16.90%.

Found: Carbon, 46.63%; Hydrogen, 7.01%; Nitrogen, 16.99%.

C.22. Preparation of dithiocyanato2,2'-bis(piperidino)diethylamine-copper(II), $Cu(BPEA)(NCS)_2$

KCNS (600 mg, 7.0 mmol) and BPEA (0.60 ml, 2.4 mmol) were dissolved in 25 ml of ethanol. A second solution was prepared of $Cu(NO_3)_2 \cdot 3H_2O$ (470 mg, 2.0 mmol) dissolved in 10 ml of ethanol. The copper solution was then slowly added dropwise to the solution of ligand and KCNS. Before the copper solution had been completely added, a blue solid began precipitating. The product was purified by recrystallizing from acetone.

Analysis of $Cu(BPEA)(NCS)_2$:

Calculated: Carbon, 45.85%; Hydrogen, 6.97%; Nitrogen, 16.71%.

Found: Carbon, 45.15%; Hydrogen, 7.00%; Nitrogen, 16.65%.

C.23. Preparation of dithiocyanato2,2'-bis(piperidino)diethylamine-zinc(II), $Zn(BPEA)(NCS)_2$

The complex was prepared by the method reported in section C.20. However, in this preparation there was no precipitation of the product.

The solvent was removed from the reaction mixture by a rotary evaporator to give a white solid, which was washed with ether to remove excess ligand. The white product was purified by recrystallizing from acetonitrile.

Analysis of $Zn(CNS)_2BPEA$:

Calculated: Carbon, 45.67%; Hydrogen, 6.95%; Nitrogen, 16.65%.

Found: Carbon, 45.88%; Hydrogen, 6.90%; Nitrogen, 16.73%.

CHAPTER III

RESULTS AND DISCUSSION

A. General

Each of the complexes prepared has the stoichiometry $M(BPEA)X_2$ (M = Co, Ni, Cu, or Zn; X = Cl^-, Br^-, I^-, NO_3^-, or NO_2^-) with the exception of nickel chloride. In this case, two different complexes were isolated. One (green) had the stoichiometry $Ni(BPEA)Cl_2 \cdot 2H_2O$ while the other (yellow) corresponded to $Ni(BPEA)Cl_2$. All of the complexes except the thiocyanato complexes of cobalt(II) and nickel(II) are soluble in methylene chloride, chloroform, acetone, acetonitrile and slightly soluble in benzene. The thiocyanato complexes are appreciably soluble only in acetonitrile.

Although the conductivities in methylene chloride (Table XIII) indicate the complexes are basically non-electrolytes, some dissociation was noticed for the copper halide species along with $Co(BPEA)I_2$ and $Ni(BPEA)I_2$.

All of the infrared spectra of the complexes are qualitatively similar with two exceptions: (1) the anions, NO_3^-, NO_2^- and CNS^- absorb in the region studied; (2) there is a difference in the N-H stretching frequency of the ligand for different complexes. These differences will be discussed under the appropriate headings in the text.

The solvent was removed from the reaction mixture by a rotary evaporator to give a white solid, which was washed with ether to remove excess ligand. The white product was purified by recrystallizing from acetonitrile.

Analysis of $Zn(CNS)_2BPEA$:

Calculated: Carbon, 45.67%; Hydrogen, 6.95%; Nitrogen, 16.65%.

Found: Carbon, 45.88%; Hydrogen, 6.90%; Nitrogen, 16.73%.

TABLE XIII

Effective Magnetic Moment and Conductivity Data for the BPEA

Compound	μ_{eff}[a]	Λ[b]
$Co(BPEA)Cl_2$ (Purple)	4.61	0.321
(Blue)	4.78	
$Co(BPEA)Br_2$ (Purple)	4.64	0.873
(Blue)	4.71	
$Co(BPEA)I_2$	4.61	1.44
$Co(BPEA)(NCS)_2$	5.07; 4.65[c]	0.107; 13[d]
$Co(BPEA)(NO_3)_2$	4.48; 4.85[e]	0.920
$Co(BPEA)(NO_2)_2$	4.45	
$Ni(BPEA)Cl_2$	3.27	0.273
$Ni(BPEA)Cl_2 \cdot 2H_2O$	3.21	
$Ni(BPEA)Br_2$	3.53	0.165
$Ni(BPEA)I_2$	3.46	1.34
$Ni(BPEA)(NCS)_2$	3.26	21.0[d]
$Ni(BPEA)(NO_3)_2$	3.21	0.106
$Ni(BPEA)(NO_2)_2$	3.19	0.150
$Cu(BPEA)Cl_2$	1.96	5.11
$Cu(BPEA)Br_2$	1.79	2.94
$Cu(BPEA)(NCS)_2$	1.89	0.516
$Cu(BPEA)(NO_3)_2$	1.88	0.464
$Zn(BPEA)Cl_2$	diamagnetic	0.705
$Zn(BPEA)Br_2$	diamagnetic	0.678
$Zn(BPEA)I_2$	diamagnetic	1.53
$Zn(BPEA)(NCS)_2$	diamagnetic	0.159
$Zn(BPEA)(NO_3)_2$	diamagnetic	0.247
$Zn(BPEA)(NO_2)_2$	diamagnetic	0.292

[a] All values are in Bohr magnetons and are within ±0.05 B.M. accuracy. Solid state moments were determined at ambient temperature (about 298°K).

[b] Conductivity values have the units: $ohms^{-1}cm^2moles^{-1}$. Methylene chloride was used as solvent at ambient temperature (about 298°K). A typical value for a 1:1 electrolyte is 20.

[c] Solution moment was determined at the temperature of the N.M.R. probe (310°K) in acetonitrile as the solvent.

[d] Acetonitrile as solvent has a typical value for a 1:1 electrolyte of 140.

[e] Solution moment determined in methylene chloride.

The electronic absorption spectral data for all the complexes are given in Tables XIV and XV and representative spectra of complexes are discussed in the text.

Magnetic moments of the complexes are listed in Table XIII. The significance of the magnetic moment values will be discussed in the text for the individual complexes.

Mass spectra of the complexes either show isotopic cluster patterns at m/e ratio which corresponds to that expected for the parent ion or to that expected for the parent ion minus one or two of the halides. All of the spectra have the characteristic peaks for the ligand, BPEA. Only mass spectra of the halide complexes were obtained due to the tendency of the NO_3^-, NO_2^- and CNS^- complexes to decompose at elevated temperatures. Only the parent peaks of the bromide and chloride complexes of Co(II) and Ni(II) were observed.

B. Cobalt Complexes

B.1. Cobalt Halide Complexes

There are many examples of five-coordinate cobalt(II) complexes formed by linear tridentate ligands. They have the general formulation $CoLX_2$ (X = halide or pseudohalide).[111,115-117,124,125] While five-coordinate in the solid state, many of these species exist as tetrahedral species, octahedral species, or as an equilibrium mixture of the different geometries in solution.[115-117] The greater the steric requirements of the ligand, the greater is the percentage of coordination numbers other than five in solution. When the solvent is removed, these compounds always revert to the five-coordinate form. There are no reports where both the four and five coordinate forms have been isolated in the solid state for any of the linear tridentate ligands.

TABLE XIV

Solid Reflectance Spectroscopic Data for the BPEA Complexes

Compound	Absorption Maxima kK
$Co(BPEA)Cl_2$ (Purple)	20.16, 16.18, 12.05, 5.76
(Blue)	18.18sh, 17.39, 15.43, 9.96, 7.25, 5.88
$Co(BPEA)Br_2$ (Purple)	20.41, 16.53, 11.83, 8.81, 6.43
(Blue)	18.18sh, 15.50, 9.65, 6.92, 5.80
$Co(BPEA)I_2$	18.87, 15.38, 12.01, 10.00sh, 5.40
$Co(BPEA)(NCS)_2$	20.00sh, 18.83, 8.33, 7.09, 16.67sh
$Co(BPEA)(NO_3)_2$	20.83, 17.24, 13.99, 10.00, 7.69, 7.14
$Co(BPEA)(NO_2)_2$	19.80, 16.78, 13.50, 7.70, 7.14, 5.88
$Ni(BPEA)Cl_2$	23.26, 19.61sh, 13.74, 12.02, 10.20, 5.00
$Ni(BPEA)Cl_2 \cdot 2H_2O$	24.51, 19.23sh, 15.04, 12.74sh, 9.34
$Ni(BPEA)Br_2$	23.92, 19.23sh, 13.33, 11.76, 10.53, 4.80
$Ni(BPEA)I_2$	24.09, 17.86sh, 14.71, 12.89, 10.87, 9.92, 4.70
$Ni(BPEA)(NCS)_2$	25.25, 16.30, 11.79, 8.99, 7.14sh
$Ni(BPEA)(NO_3)_2$	25.91, 15.92, 9.92
$Ni(BPEA)(NO_2)_2$	27.03, 15.67, 9.71
$Cu(BPEA)Cl_2$	14.08
$Cu(BPEA)Br_2$	14.54
$Cu(BPEA)(NCS)_2$	15.15
$Cu(BPEA)(NO_3)_2$	17.54

sh: shoulder

TABLE XV

Electronic Spectral Data for the BPEA Complexes

in Methylene Chloride

Compound	Absorption Maxima kK (ε)
$Co(BPEA)Cl_2$	21.55 (96), 18.38 (98), 16.84 (133), 12.94 (24), 5.80 (13)
$Co(BPEA)Br_2$	20.88 (96), 17.39 (127), 16.29 (162), 12.80 (40), 6.2 (61)
$Co(BPEA)I_2$	20.28 (129), 18.18 (102), 16.50 (227), 15.87 (246), 15.15 (165), 12.58 (35)
$Co(BPEA)(NCS)_2$	22.47 (127), 21.50 (123), 17.45 (159), 14.82 (36), [a]22.22 (281), 17.39 (327), 14.60 (81), 6.06 (40)
$Co(BPEA)(NO_3)_2$	20.50 (30), 20.00 (40), 8.70 (5)
$Ni(BPEA)Cl_2$	25.06 (124), 20.20 (28), 14.71 (31), 12.63 (28), 11.44 (34), 5.10 (11)
$Ni(BPEA)Br_2$	23.42 (168), 20.00 (41), 14.45 (39), 12.27 (37), 11.30 (38), 5.00 (25)
$Ni(BPEA)I_2$	23.26 (907), 19.05 (99), 14.39 (55), 11.57 (53), 10.58 (48), 4.90 (29)
$Ni(BPEA)(NCS)_2$	[a]25.97 (25), 16.95 (13), 10.53 (25), 9.43 (21)
$Ni(BPEA)(NO_3)_2$	26.46 (33), 16.23 (19), 10.78 (28)
$Ni(BPEA)(NO_2)_2$	16.81 (14), 10.64 (17)
$Cu(BPEA)Cl_2$	15.62 (268)
$Cu(BPEA)Br_2$	15.55 (311)
$Cu(BPEA)(NCS)_2$	15.53 (432)
$Cu(BPEA)(NO_3)_2$	16.67 (285)

[a]Acetonitrile was used as the solvent.

In this respect, the reversible five to four coordination isomerizations of $Co(BPEA)Cl_2$ and $Co(BPEA)Br_2$ are quite unusual. Upon crystallization, the cobalt halide complexes (Cl^-, Br^- and I^-) formed a purple solid. The reflectance spectra of the complexes were quite similar and indicated a coordination number of five.[115,126] The magnetic moments of the complexes were also consistent with cobalt(II) being in a five coordinate, high-spin configuration (Table XIII).[115]

The purple chloride complex isomerized to a blue complex when heated in a vacuum (10^{-3} torr) for 30 minutes at 135°. The bromide complex isomerized at 145° to give a blue form while the iodide complex decomposed at a temperature of 175° without isomerization. Reflectance spectra and magnetic moments for both of the blue complexes were interpreted on the basis of a tetrahedral coordination geometry[127] (Tables XIV and XIII). The four coordinate forms of the chloride and bromide complexes were readily converted back to five coordinate species by recrystallization from polar organic solvents. The cycle was repeated with only small mechanical losses. Dissolution of either the blue or purple form gave a purple solution whose electronic spectrum is indicative of a pentacoordinate species.

There are three possible five to four coordinate isomerizations to take place. The two most probable isomerizations are the terminal nitrogen-metal bond or the central nitrogen-metal bond breaking. A less likely possibility is the breaking of a metal-halide bond.

In other linear tridentate systems, it has been postulated in solution, the central Co-N bond breaks because of the close approach of one of the halides to the central nitrogen.[117,121,128] In this case space filling molecular models indicated the greatest amount of steric

strain is relieved if one of the terminal Co-N bonds is broken. An insight into which bond is actually broken was obtained from the infrared spectra. In the five coordinate species, the N-H stretching frequency ν(N-H), is at 3267 ± 2 cm^{-1}. After isomerization ν(N-H) is shifted to lower energies: 3205 ± 5 cm^{-1}. These shifts are compatible with either a terminal Co-N or a Co-X bond being broken. Breaking the central Co-N bond would increase the electron density on the central nitrogen strengthening the N-H bond. This would shift ν(N-H) to higher energies. Breaking a terminal Co-N bond or a Co-X bond would decrease the electron density on the cobalt making it a better Lewis acid. This would have the effect of increasing all the remaining cobalt ligand bond strengths thereby decreasing the N-H bond strength leading to the observed shift in ν(N-H) upon isomerization.

Reflectance spectra indicated the terminal Co-N bond breaks rather than the Co-X bond. A terminal nitrogen bond breaking would give an approximate C_{2v} symmetry, whereas a Co-X bond breaking would cause the molecule to approach C_{3v} symmetry.

The observed spectra of the complexes are very similar to the spectra reported for $Co(EDP)X_2$[9] and $Co(EDM)X_2$,[76] ($X = Cl^-$ and Br^-). The only difference is a small shift in absorptions according to the spectrochemical series for the ligands. A structure determination of $Co(EDM)Cl_2$ has shown the complex to have C_{2v} symmetry. Actually, it has only C_2 symmetry in the crystal structure.[4]

It is interesting to note that the halide complex that should be the least stable with respect to five coordination, due to steric factors, is actually the most stable in the solid state. The iodide complex does not undergo isomerization and the bromide complex undergoes

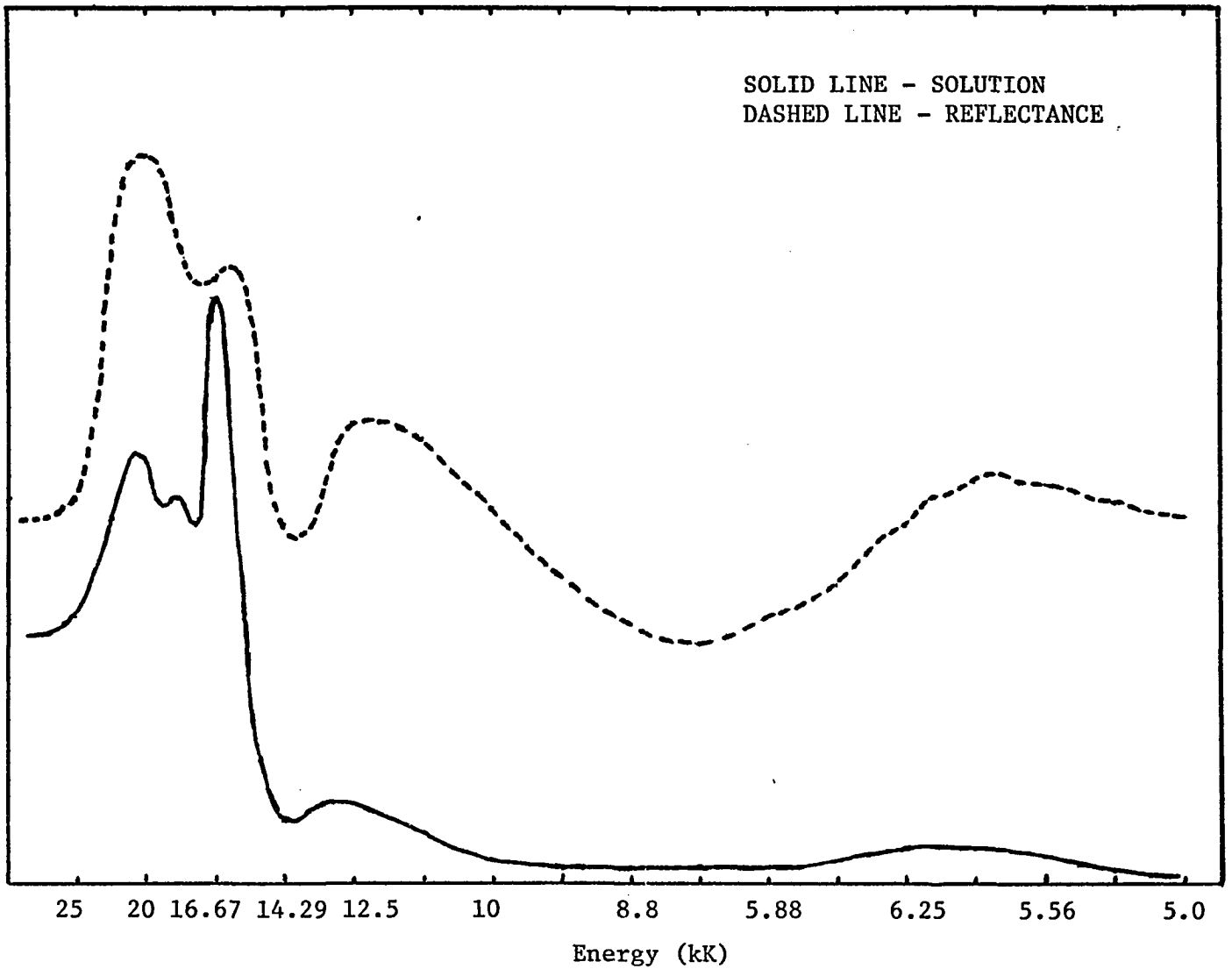


FIGURE XIX. Electronic Spectra of Purple $Co(BPEA)Cl_2$

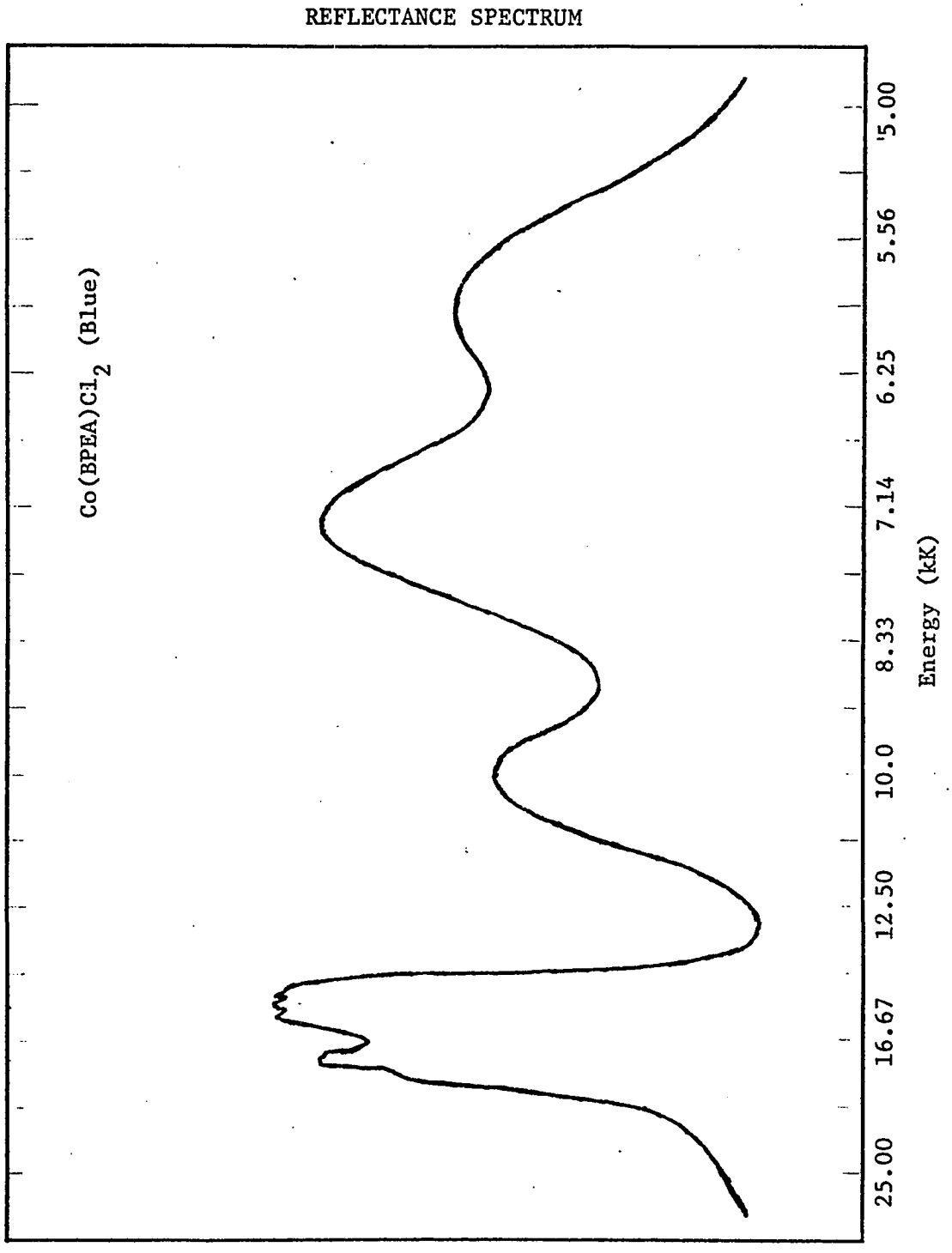
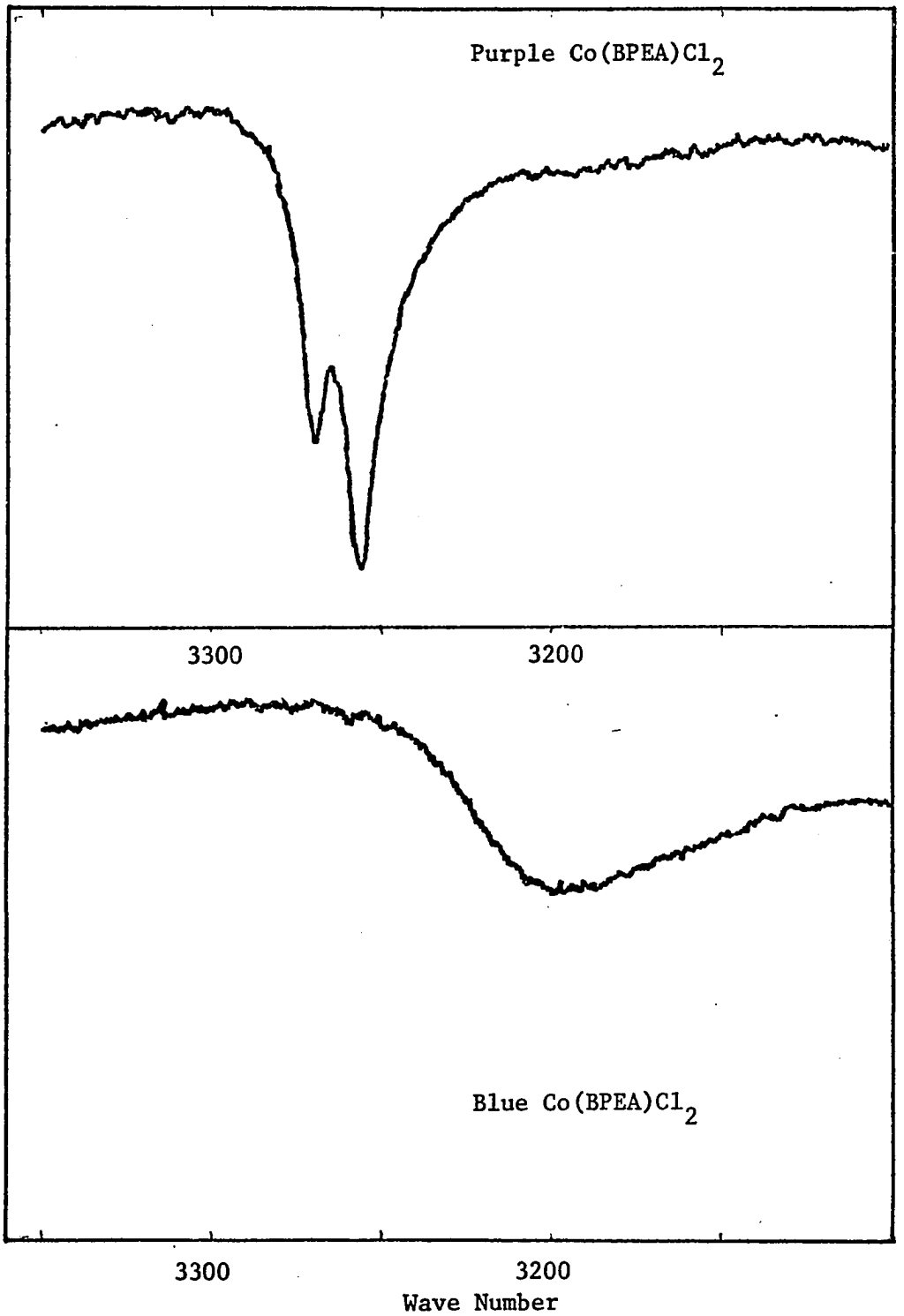


FIGURE XX. Electronic Spectrum of Solid Blue $Co(BPEA)Cl_2$

FIGURE XXI. A Portion of the Infrared Spectrum Showing ν(N-H) for Both Isomers of $Co(BPEA)Cl_2$



isomerization at a temperature 10° higher than the chloride. The reason for this unusual behavior can be explained on the basis of the electroneutrality principle and back bonding.[129,130] In the pentacoordinate complexes the five ligands share ten electrons with the cobalt and all of the electrons come from the ligands. This results in a formal charge of -5 on the metal that is only partially cancelled by the ionic charge of +2. In comparing the halides, the chloride has a greater electronegativity, but the tendency for the d-electrons of the metal to back bond to the iodide has a larger stabilizing effect; thus, the high formal charge is sufficiently reduced so as to make the iodide complex sufficiently stable in a 5-coordinate geometry.

B.2. Cobalt Nitrate and Nitrite Complexes

Both nitrate and nitrite, as ligands, can coordinate to a central transition-metal ion in several different ways. Nitrate can coordinate as either a monodentate or bidentate ligand bonding through one or two of the oxygens. Being a relatively weak ligand, it can also act as a noncoordinating anion. Nitrite being a much stronger ligand has never been found to act as a noncoordinating ligand or ionic anion in coordination compounds. It can bond through the nitrogen to give the well known nitro complexes or through one of the oxygens to give the less common nitrito species. It can also act as a bridging ligand, bonding through the nitrogen and one of the oxygens.[131,132] A fourth mode of coordination is also known with the nitrite acting as a bidentate ligand, coordinating through the two oxygens.[133]

The $Co(BPEA)(NO_3)_2$ complex is air stable both in solution and the solid state. $Co(BPEA)(NO_2)_2$ must be handled under a nitrogen atmosphere. Even then, solutions or the solid species decompose over a period of 24 hours or less to give a brown residue.

The reflectance spectra of both the nitrate and nitrite complexes exhibit the same general features and indicate a pentacoordinate geometry (see Table XIV). The magnetic moments for both solids are consistent with a coordination number of five. While the solution spectrum of the nitrite complex was not obtained because of decomposition, the solution spectrum of the nitrate complex is that of an octahedral species. The three absorption bands, 8.7, 20.0 and 20.4 kK are interpretable on the basis of an octahedral model with the bands being assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, (ν_1); $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, (ν_2); and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, (ν_3) transitions, respectively.[134] The magnetic moment in a solution of CH_2Cl_2 is 4.85 B.M., well in the range of 4.8 to 5.1 B.M. for octahedral cobalt(II).

Since the BPEA ligand can be a tridentate chelating agent and the nitrates and nitrates are possible bidentate ligands, a maximum coordination number of seven is imaginable. However, with an observed coordination number of five in the solid state and six in solution, the infrared spectrum was useful in determining the bonding modes of the ligands. Infrared absorptions due to the nitrate and nitrite moieties were determined by comparison of the spectra obtained from the corresponding halo complexes.

In the solid state, the nitrite complex exhibits absorptions at 1350, 1290 and 810 cm^{-1}.[135] The only mode of coordination that is compatible with these shifts from the nitrite free ion absorptions is monodentate nitrogen coordination.[133] In nitro complexes, the bands are increased in energy from the free ion values of 1335 and 1250 cm^{-1}, while in nitrito complexes the 1335 cm^{-1} band is increased in energy and the 1250 cm^{-1} band is decreased in energy. Also, only in the case

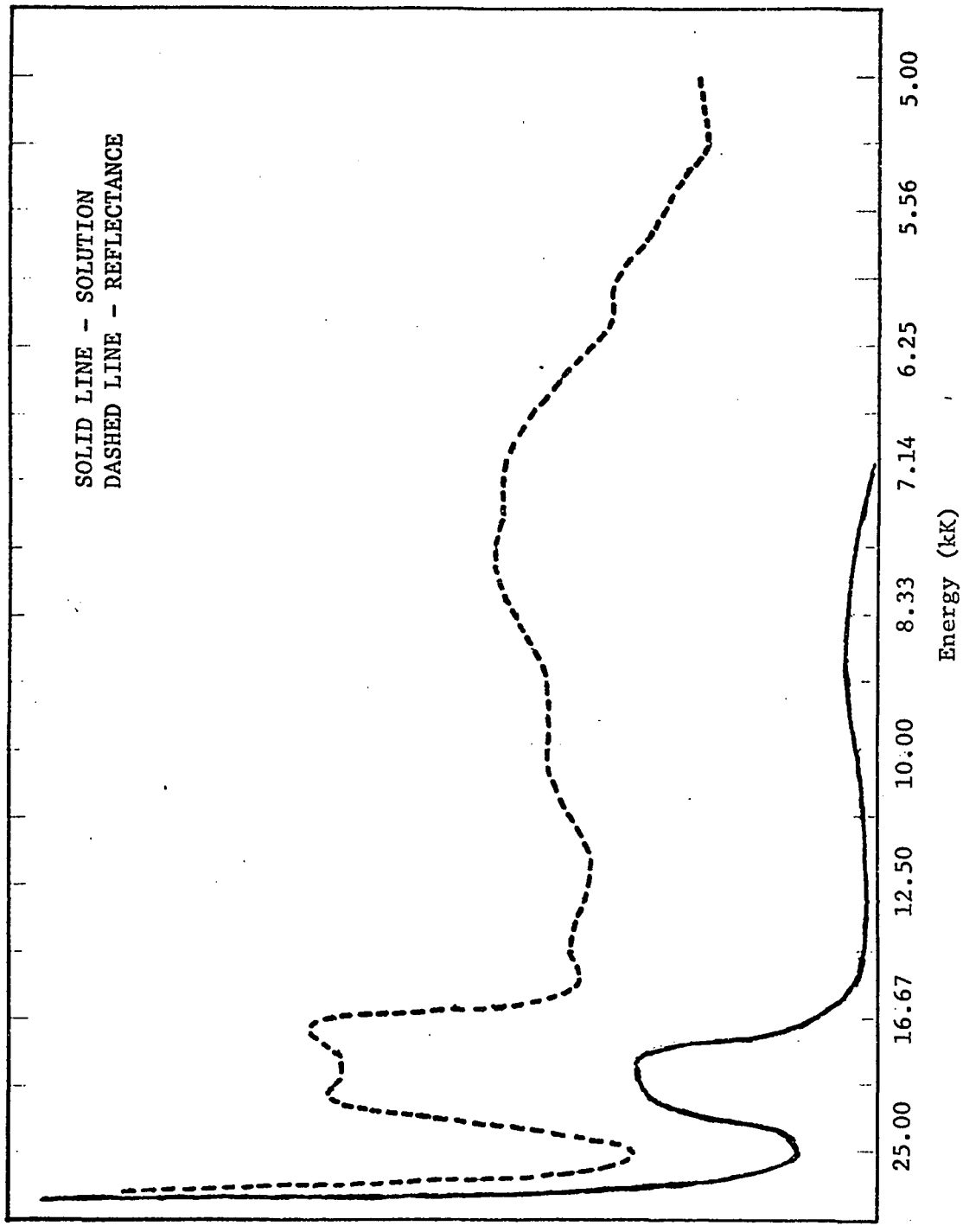


FIGURE XXII. Electronic Spectra of $Co(BPEA)(NO_3)_2$

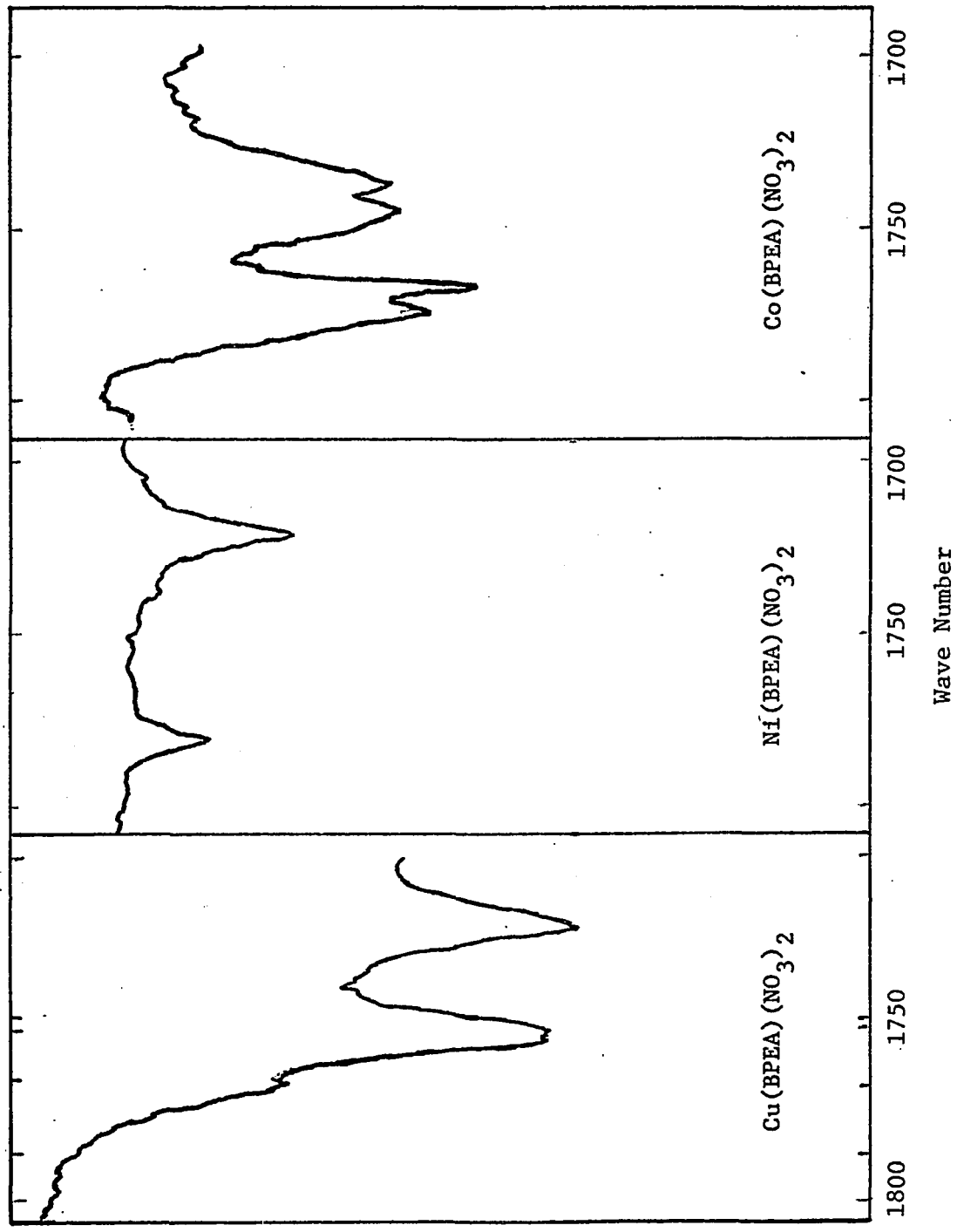


FIGURE XXIII. Infrared Spectra Showing ($\nu_1 + \nu_4$) Combination Band for the Nitrate Complexes

of bidentate coordination is the 830 cm^{-1} band of the free ion increased in energy, which was not seen here.

In the case of the nitrate complex it is more difficult to differentiate between bidentate and monodentate coordination. The shifts and splittings of the various absorptions upon going from ionic to either monodentate or bidentate coordination are the same. However, Lever, Mantovani and Ramaswamy[136] have found the splitting of the $(\nu_1 + \nu_4)$ combination band useful for structural information on nitrato complexes. In the region of 1700 to 1800 cm^{-1}, bidentate nitrate groups give rise to a split combination band which is separated by 38-56 cm^{-1}. For monodentate nitrate groups, the splitting of the combination band is smaller, 15-26 cm^{-1}. Complexes with both monodentate and bidentate show four absorption bands because a pair of frequencies is generated from each coordination mode. Ionic nitrates give rise to a single sharp narrow band in the region 1750-1800 cm^{-1}.

For the solid state, the nitrato complex, $Co(BPEA)(NO_3)_2$, exhibits four absorption bands from 1730 to 1790 cm^{-1} (see Figure XXV). It appears one nitrate is monodentate and the other is bidentate. In order to achieve a coordination number of five, BPEA must be bonded to the metal through only two of three nitrogens in the ligand. This is supported by ν(N-H) for BPEA in the infrared. As in the case of the four-coordinate halide complexes, ν(N-H) for the nitrate complex is at a slightly lower energy, 3235 cm^{-1}, than is the ν(N-H) for the five-coordinate halides. Also, the half-width of ν(N-H) is broader in both the four-coordinate halo complexes and $Co(BPEA)(NO_3)_2$ compared to ν(N-H) for the five-coordinate halo complexes and $Co(BPEA)(NO_2)_2$. The half-widths are 60-80 cm^{-1} for the lower energy bands compared to 30-40 cm^{-1} for the higher energy bands.

Specifically, both $Co(BPEA)(NO_3)_2$ and $Co(BPEA)(NO_2)_2$ are five-coordinate in the solid state; however, in the nitrato complex, BPEA acts as a bidentate ligand with one monodentate and one bidentate nitrate groups. In the nitrito complex, BPEA is tridentate with two monodentate nitrite groups.

C. Nickel Complexes

C.1. Nickel Halo Complexes

The electronic spectra of the chloro, bromo, and iodo complexes all exhibit the same general features. All three complexes show basically six absorption maxima both as a solid and in solution (see Tables XIV and XV). The spectra of these complexes are similar to those reported for high-spin, five-coordinate Ni(II) complexes.[111,119] Ciampolini[119] calculated the splittings for the crystal field spectra of the free nickel(II) ion arranged in trigonal-bipyramidal and square-pyramidal configurations. For a trigonal-bipyramidal structure, the calculated frequencies are 7.00, 13.90, 14.90, 22.50, and 26.2 kK and for the square-pyramidal configuration, the predicted absorptions are 7.20, 10.80, 12.30, 17.300, 26.40 and 28.40 kK. The observed absorptions for $Ni(BPEA)X_2$ do not fit either of Ciampolini's models. Instead, the absorptions are quite similar to those reported by Ciampolini and Speroni[111] for a series of five-coordinate nickel(II) complexes using the ligand, bis(2-dimethylaminoethyl)methylamine,(dienMe). The proposed structure for the complexes was neither strictly a trigonal bipyramid nor a square pyramid, but an intermediate structure between these two stereochemical extremes.

Of the three, the chloro complex is unique in that upon being exposed to air for 1 to 24 hr, the color changes from yellow to green.

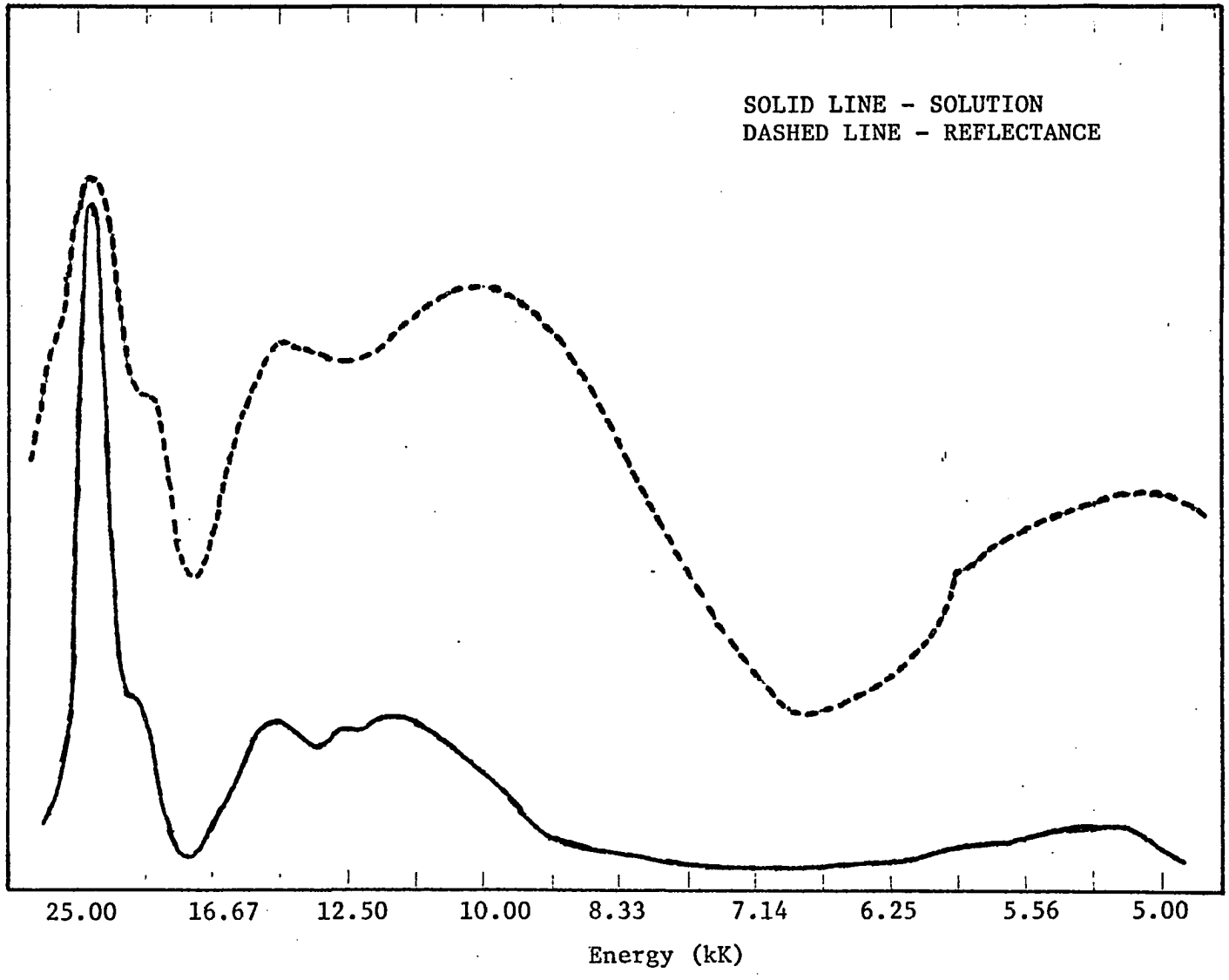


FIGURE XXIV. Electronic Spectra of $Ni(BPEA)Cl_2$

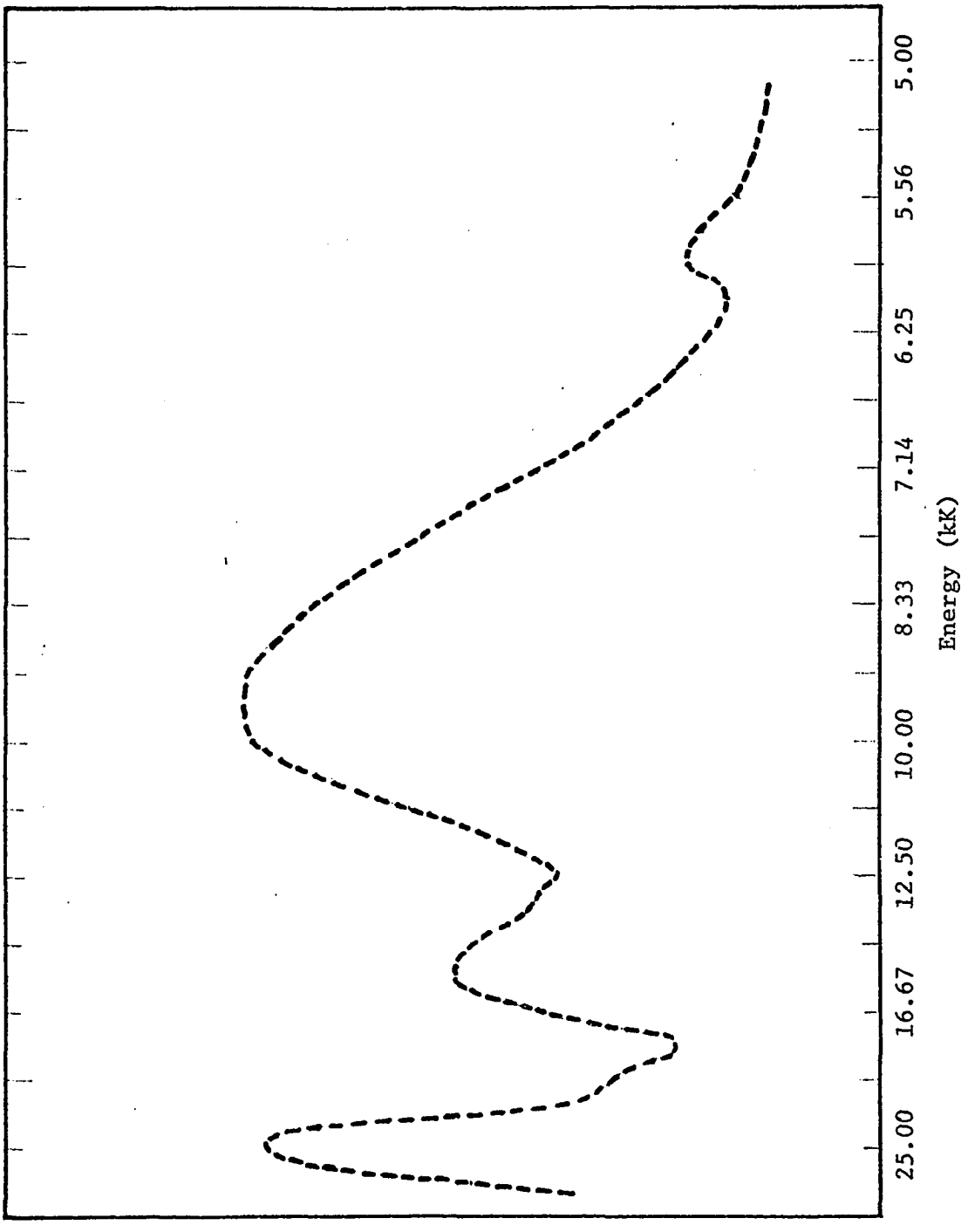


FIGURE XXV. Reflectance Spectra of $Ni(BPEA)Cl_2 \cdot 2H_2O$

The reflectance spectrum of the green form of the complex is indicative of an octahedral geometry. The infrared spectrum of the green form shows water present which is absent in the yellow form. The addition of the green solid to a solvent such as acetone or chloroform gives a yellow solution. The electronic spectrum of the solution shows a penta-coordinate species. Also, the water can be removed from the green solid in vacuo to give the original yellow, five coordinate complex. The stoichiometry of the hydrate was found to be 1 mole of complex to 2 moles of water. While the bromo and iodo complex do not change co-ordination number, the bromo complex does absorb water as evidenced by the infrared spectrum.

As in the case of the halo complexes of Co(II), it was found that the chloro complex is the least stable of the nickel halides with respect to a coordination number of five. Again, this is probably due to the better ability of the iodide and the bromide to accept back bonding d-electrons from the metal ion, thus, reducing the electron density on the metal ion.

C.2. Nickel(II) Nitrate and Nitrito Complexes

The electronic spectra of both the nitrato and nitrito complexes show octahedral geometries in the solid state and in solution. $Ni(BPEA)(NO_3)_2$ absorption bands are found at 9.9, 15.9, and 25.9 kK in the reflectance spectrum and 10.8, 16.2, 26.5 kK in the solution spectrum. The frequencies for $Ni(BPEA)(NO_2)_2$ are 9.7, 15.7, and 27.0 kK for the solid and 10.6 and 16.8 kK for the solution. The high energy band in solution is not observed due to a charge transfer band. The spectra was interpreted on the basis of an octahedral model with the bands assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2), and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3) transitions for the low to high energy absorptions.[137]

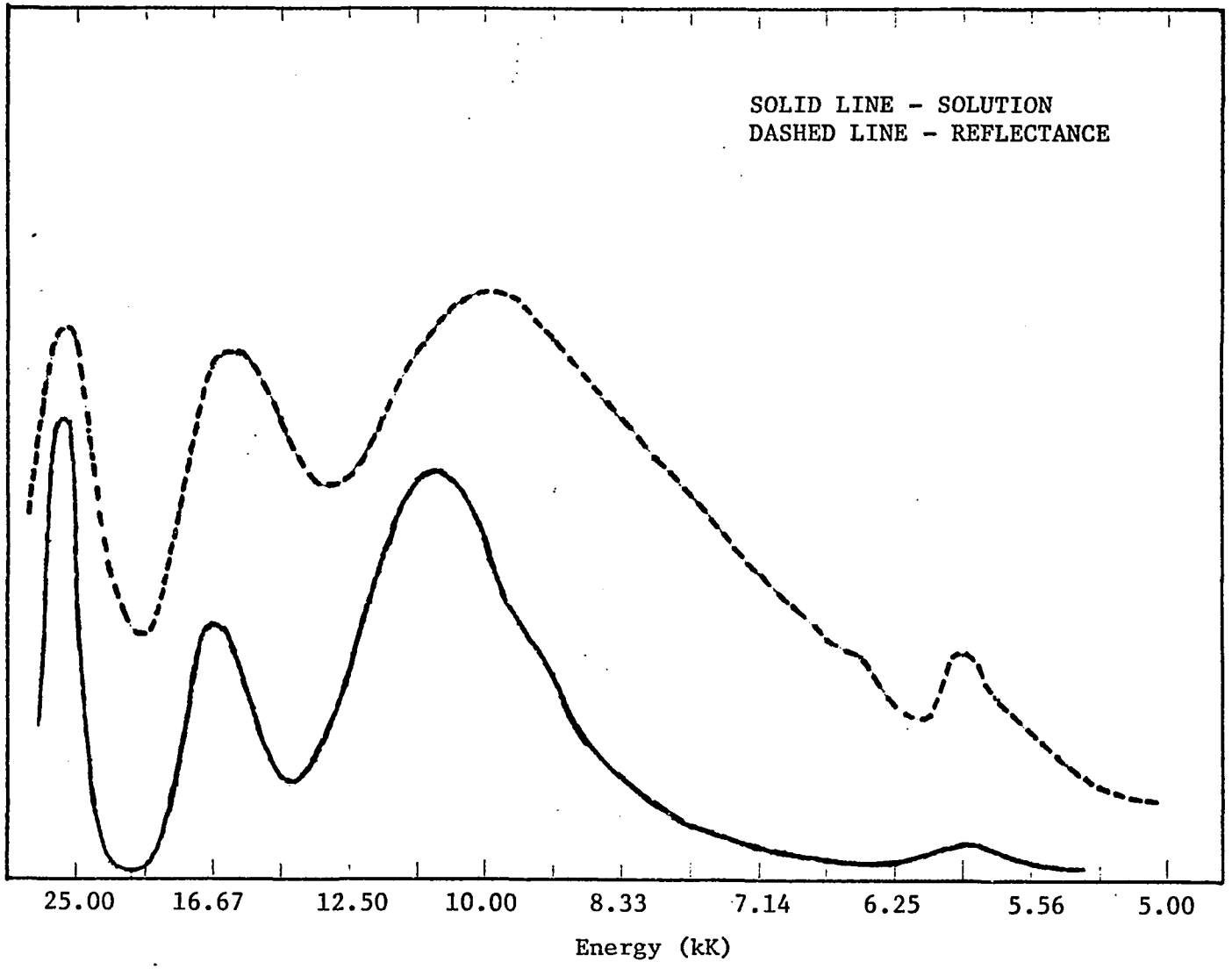


FIGURE XXVI. Electronic Spectra of $Ni(BPEA)(NO_3)_2$

In determining the bonding modes of the nitrate groups, the infrared spectrum of $Ni(BPEA)(NO_3)_2$ shows a split combination band between 1700-1800 cm^{-1}. The splitting is 60 cm^{-1} (see Figure XXIII). As was pointed out in section B.2. of this chapter, a splitting of that magnitude is indicative of both nitrate groups acting as bidentate ligands.[136] With the complex in an octahedral configuration, then BPEA must act as a bidentate ligand; however, ν(N-H) is not consistent with the aforementioned i.r. spectra of complexes in which BPEA is bidentate. The observed ν(N-H) for $Ni(BPEA)(NO_3)_2$ is a sharp band at 3270 ± 5 cm^{-1}. This can be explained by assuming the central nitrogen-metal bond is broken thereby giving a coordination number of six.

The infrared spectrum of the nitrite complex is more complicated than the spectrum of $Co(BPEA)(NO_2)_2$. There are bands for the nickel nitrite complex at 1350, 1290, 1200, 840, and 810 cm^{-1} that are not observed in the halo complexes. Since nitro complexes show an increase in energy over the free ion absorptions of 1335 and 1250 cm^{-1} of the nitrite, it appears that one nitrite in the complex is bonding through its nitrogen atom. The second nitrite group is bidentate coordinating through the two oxygens. This is shown by the 1200 and 840 cm^{-1} bands. The free nitrite ion absorption is increased above 830 cm^{-1} only in the case of bidentate coordination.[133] In order to achieve octahedral geometry with the observed stoichiometry the BPEA must be tridentate since the nitrites are utilizing three coordination sites on the nickel ion. This is observed in ν(N-H) for the complex with a sharp band at 3230 cm^{-1} with a half-width of 30 cm^{-1}.

D. Copper(II) Complexes

D.1. Copper(II) Halide Complexes

Both $Cu(BPEA)Cl_2$ and $Cu(BPEA)Br_2$ have similar electronic spectra. In each reflectance spectrum, there is a broad assymetric band with its maximum at about 14.00 kK and with a tail toward lower energy. Meek and Ehrhardt have studied copper(II) complexes with N,N'-substituted ethylenediamine ligands.[138] They have shown that the complexes with a square planar structure have a complex broad band, at higher frequencies, 15-20 kK, while octahedral complexes have a diffuse band at 13-18 kK and a band at 21-23 kK. Since the BPEA complexes do not conform to either the square planar or octahedral configurations, this leads to the assignment of a pentacoordinate structure for the complexes in the solid state studied here.

The solution spectra for both the chloro and bromo complexes show a high energy shift in absorption bands to about 15.6 kK in chloroform which is well in the range of square planar complexes. Also, the conductivity measurements show considerable dissociation in CH_2Cl_2, 25% and 15% for the chloro and bromo complexes, respectively. In view of the amount of dissociation present, it is probable that a mixture of five-coordinate and square planar species exist in solution. Due to the fairly broad absorption bands of the complexes, two distinct maxima were not observed for the two components of the mixture. The limitation of the recording spectrophotometer may also contribute to the inability to resolve two maxima since it records linearly in nanometers. While the difference in the maxima for the solution and reflectance spectra is about 1.5 kK, the difference in nanometers is only 70 in this region of the spectra.

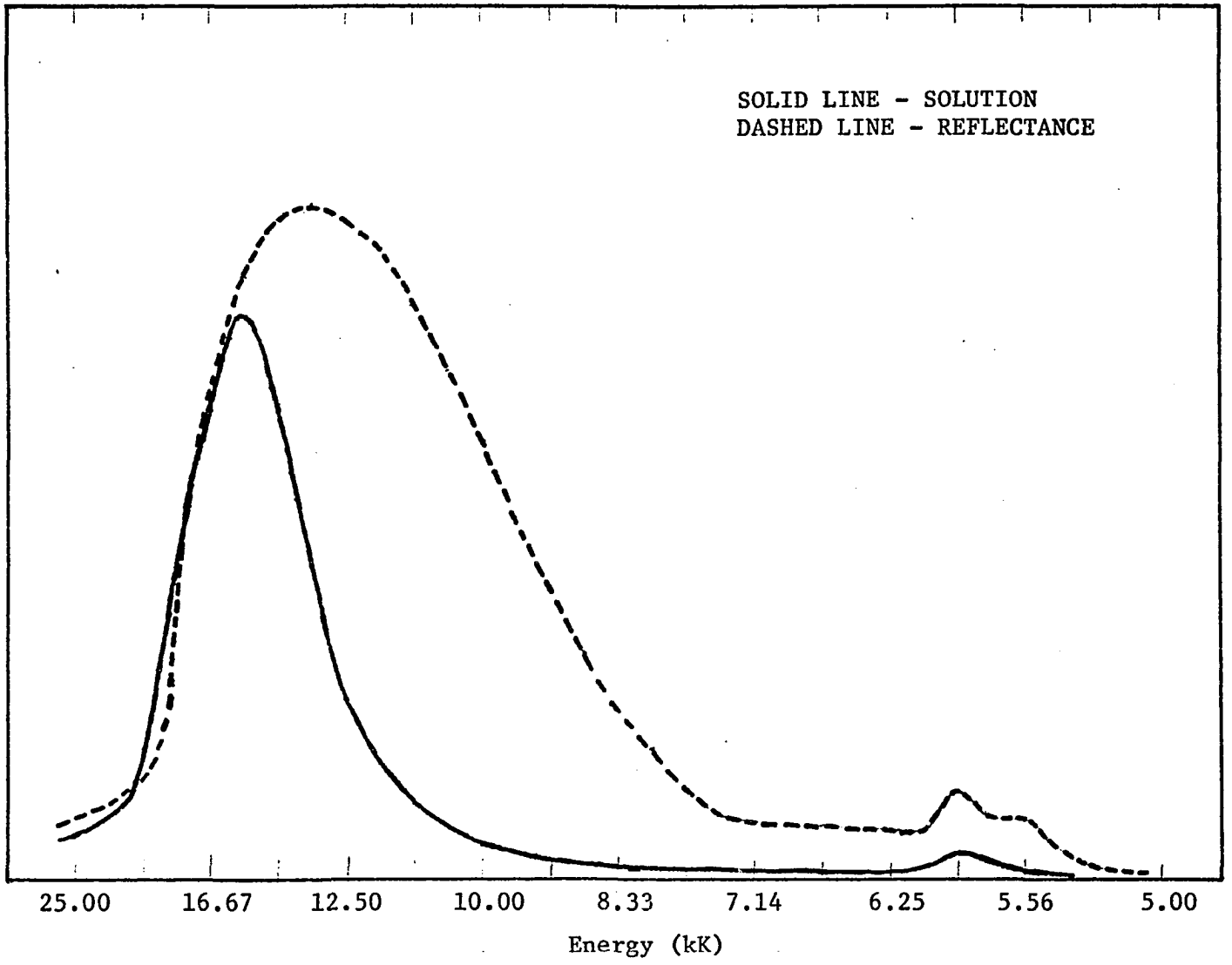


FIGURE XXVII. Electronic Spectra of $Cu(BPEA)Cl_2$

The trend in stability for the five-coordinate halo complexes of Co^{2+} and Ni^{2+} was also observed for the copper(II) species in their degrees of dissociation. Full correlation of the trend was not possible since attempts to synthesize $Cu(BPEA)I_2$ failed. Methods analogous to the preparation of $Cu(BPEA)(NCS)_2$ were tried, but no complex in the solid state was isolated. The addition of a large excess of BPEA and I^- to a solution of Cu^{2+} gave a green solution, but upon the removal of the solvent decomposition took place.

D.2. Copper(II) Nitrate Complex

The electronic spectra of $Cu(BPEA)(NO_3)_2$ show single symmetric absorption bands at 17.5 and 16.7 kK for the solid state and solution, respectively. On this basis together with the infrared spectrum, the assignment of a square planar configuration was made. The i.r. data show the splitting for the $(\nu_1 + \nu_4)$ combination band to be 27 cm^{-1} (see Figure XXIII). This small splitting is consistent with monodentate nitrate groups. Furthermore, the ν(N-H) for BPEA is a sharp peak found 30 cm^{-1} higher in energy than the same peak for the corresponding halo complexes. It is reasonable then that the BPEA is bonding to the metal through the two terminal nitrogens only, as in the case of $Ni(BPEA)(NO_3)_2$, thus giving a coordination number of four.

All attempts to synthesize $Cu(BPEA)(NO_2)_2$ failed to yield characterizable product. The addition of BPEA to a solution of $Cu(NO_2)_2$ gave a green solution but the removal of the solvent gave a brown residue with a tar-like consistency.

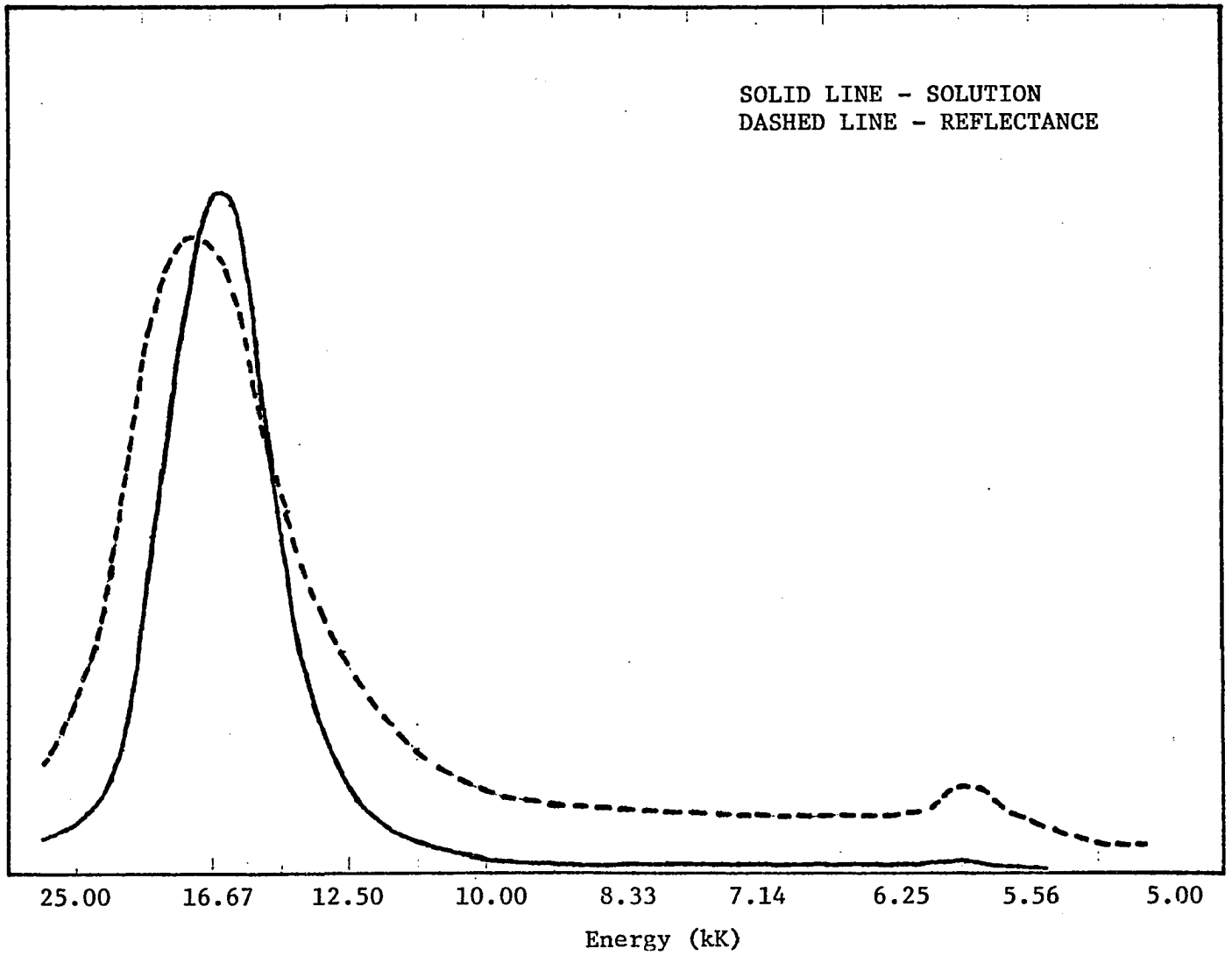


FIGURE XXVIII. Electronic Spectra of $Cu(BPEA)(NO_3)_2$

E. Zinc(II) Complexes

E.1. Zinc(II) Halide Complexes

All the zinc(II) halide complexes were assigned a coordination number of five based upon their stoichiometry, conductivities and the infrared spectra. Since none of the complexes exhibit dissociation, the halides are coordinated. A coordination other than five would have to be achieved through bridging of the halides or by the BPEA coordinating through less than three nitrogen atoms. The high degree of solubility suggests that no bridging is present. The infrared spectra show the ν(N-H) to be sharp and at 3220 cm^{-1}, which is the same region found for the ν(N-H) of the five-coordinate nickel halide complexes; therefore, BPEA is tridentate and the complexes are pentacoordinate. For the zinc(II) complexes, where the electronic spectral arguments fail, there is no proof that the species predominantly present in solution are not also five-coordinate, as they are in the solid state.

E.2. Zinc(II) Nitrate and Nitrite Complexes

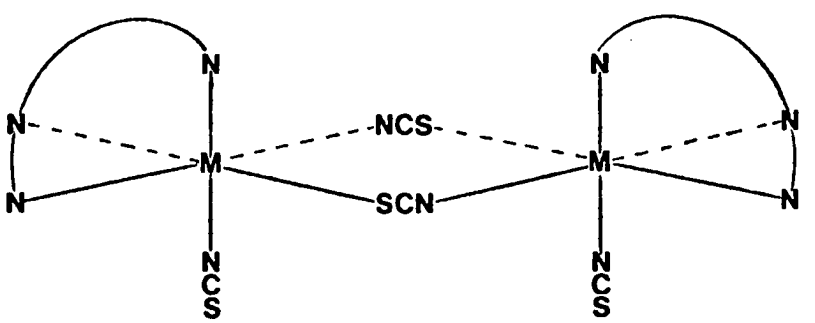
The infrared spectrum of $Zn(BPEA)(NO_3)_2$ shows the splitting of the combination band, $(\nu_1 + \nu_4)$, to be 27 cm^{-1}. This is consistent with the two nitrate groups acting as monodentate ligands. Furthermore, with the sharp ν(N-H) at 3225 cm^{-1}, the BPEA is tridentate giving the complex a pentacoordinate configuration.

The zinc nitrite complex has an infrared spectrum identical to $Co(BPEA)(NO_2)_2$ where the two nitrite groups were shown to be nonbridging and monodentate while coordinating through the nitrogen atoms. Since the similarity of the two spectra is so great, $Zn(BPEA)(NO_2)_2$ is also assigned a five-coordinate geometry. Again, there is no proof that the configuration of the nitrato and nitro complexes in solution is any different than the solid state configuration.

F. Metal Thiocyanate Complexes

The reflectance spectra of both the thiocyanato complexes of Ni(II) and Co(II) show the metals to be in an octahedral environment. However, solution spectra show the nickel complex to be octahedral while the cobalt complex is five-coordinate. Octahedral configurations are also suggested by the solid state magnetic moments. Magnetic moments of 3.26 B.M. for the nickel complex and 5.07 B.M. for the cobalt complex were observed. These are within the respective ranges for octahedral values.

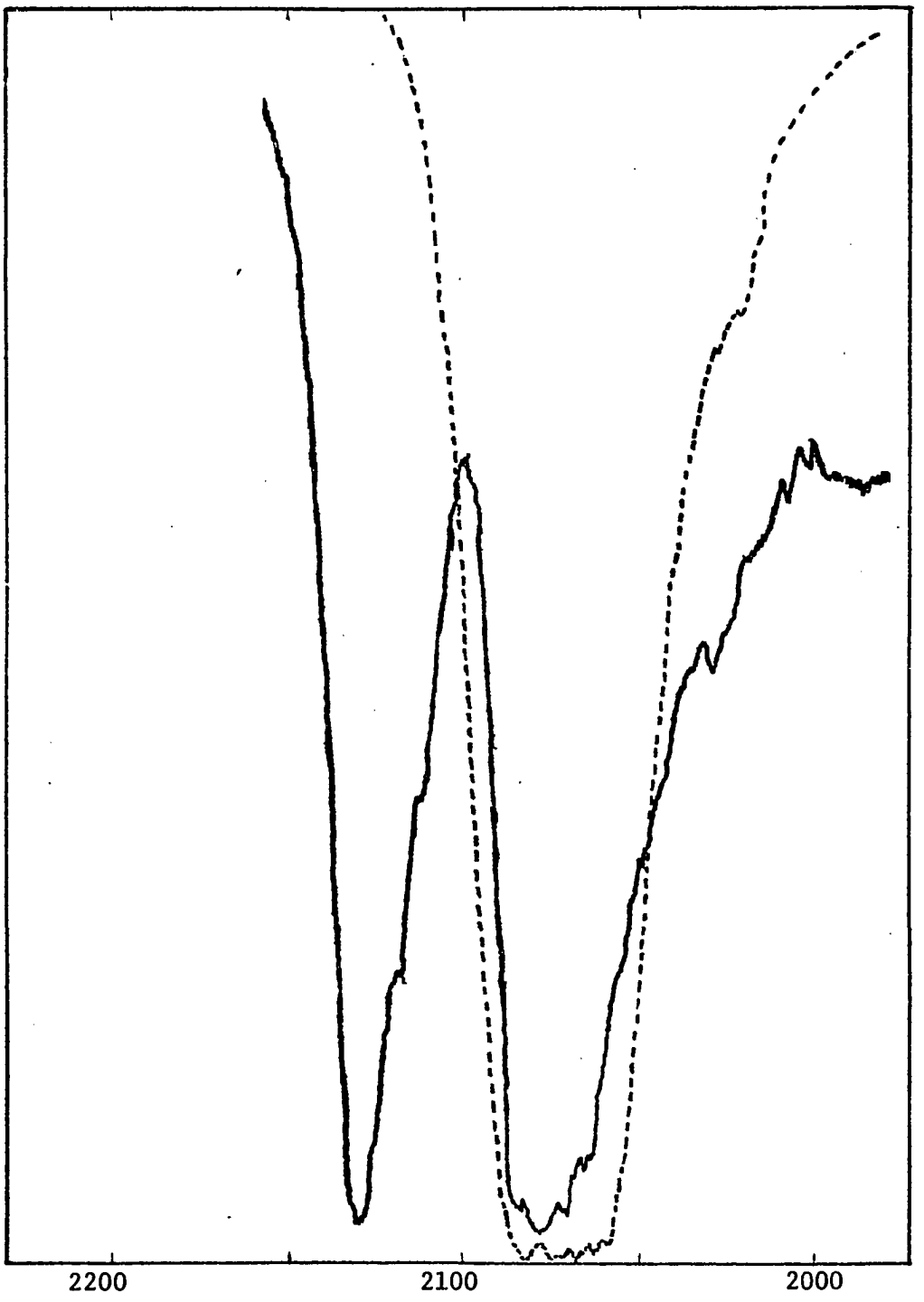
In order for these complexes to achieve a coordination number of six, the thiocyanate groups must act as bridging ligands. The $\nu(C\equiv N)$ in the infrared confirms both M-SCN and M-NCS bonding for both complexes. A broad band at 2080 and 2090 cm^{-1} is observed in cobalt and the nickel spectra respectively. This broad band below 2100 for $\nu(C\equiv N)$ is indicative of the M-NCS band.[138,139] Sharp absorptions in the solid state at 2130 cm^{-1} for the cobalt complex and 2140 cm^{-1} for the nickel complex show the sulfur atom bonded to the metals.[138,139] The stoichiometry of the complexes together with the spectra serve to support the following structure which is postulated to exist in the solid state.



(XIII)

FIGURE XXIX. A Portion of the Infrared Spectra of $Co(BPEA)(NCS)_2$

SOLID LINE - SOLID STATE SPECTRUM
DASHED LINE - SOLUTION SPECTRUM



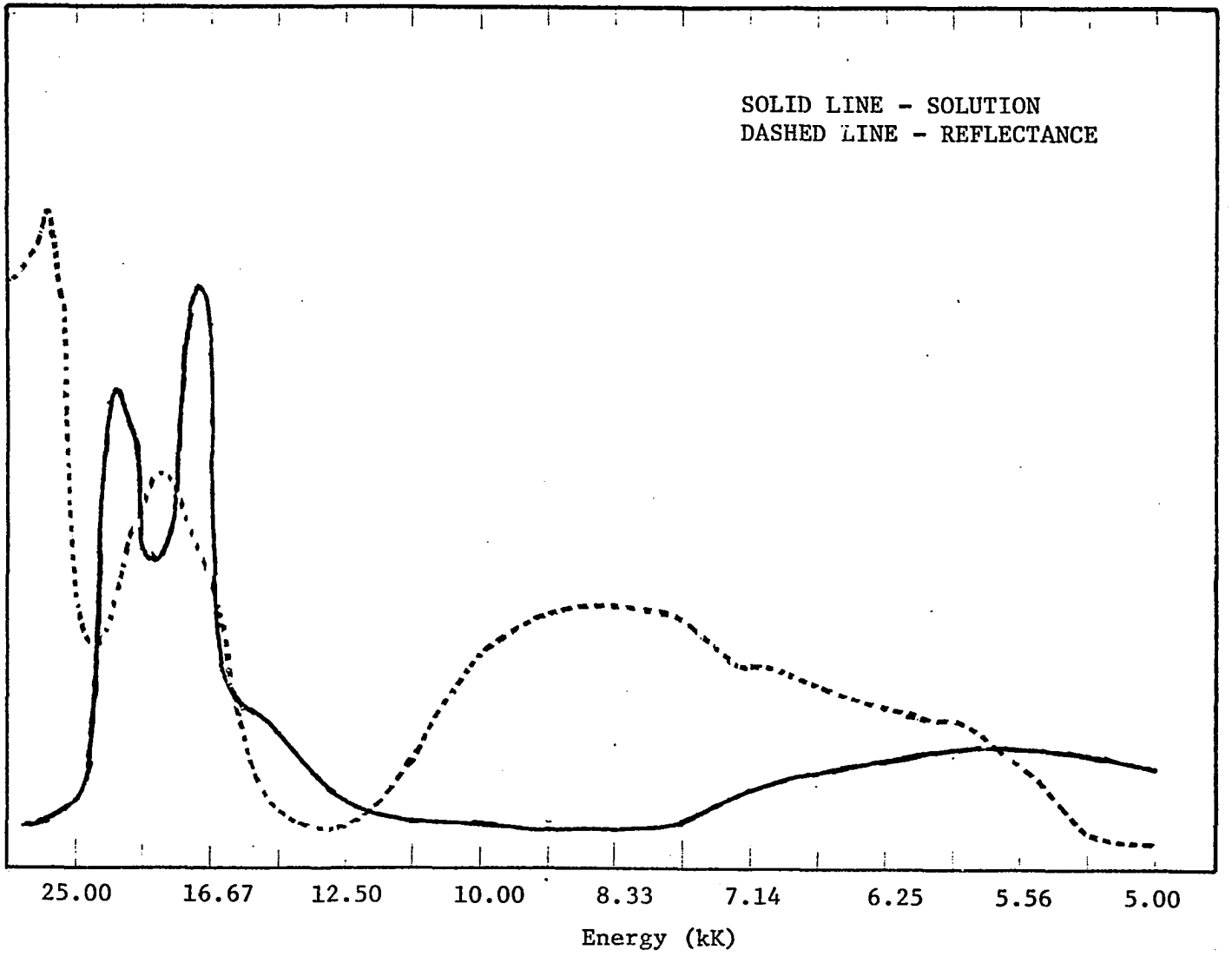


FIGURE XXX. Electronic Spectra of $Co(BPEA)(NCS)_2$

The structure is the same as the one proposed for the related compound, $Ni(Et_4dien)(NCS)_2$ reported by Burmeister and coworkers.[138] The ligand Et_4dien is similar to BPEA in structure and both are sterically demanding due to organic substituents on the terminal nitrogens. Burmeister found that in solution, however, the complex existed as an equilibrium mixture of square planar and five-coordinate species. The dimeric structure was unique for nickel; the cobalt complex, $Co(Et_4dien)(NCS)_2$ was found to be five-coordinate in the solid state and solution.[115]

The low solubilities of $Co(BPEA)(NCS)_2$ and $Ni(BPEA)(NCS)_2$ compared to the other BPEA complexes is in accord with the dimeric structures. The cobalt complex shows its greatest solubility in acetonitrile and is slightly soluble in dichloromethane while the nickel complex shows a slight solubility in acetonitrile and is virtually insoluble in other common solvents.

The greater solubility of $Co(BPEA)(NCS)_2$ and the solution spectrum of a five-coordinate species is evidence of the dissociation of the dimer upon dissolution. The infrared spectrum of an acetonitrile solution of the cobalt complex has the $\nu(C\equiv N)$ absorption above 2100 cm^{-1} absent. Only the $\nu(C\equiv N)$ for the nitrogen coordinating thiocyanate group is seen. Furthermore, the solution magnetic moment of 4.65 B.M. in acetonitrile is more in line with that expected for a five-coordinate complex.

Apparently, $Ni(BPEA)(NCS)_2$ remains as the dimer in solution, as suggested by its low solubility and the acetonitrile solution spectrum characteristic of octahedral nickel. Even though acetonitrile is a fairly good coordinating solvent, it is not likely that the octahedral configuration is achieved by dissociation of the dimer and then solvent coordination. The differences in the reflectance spectrum and the

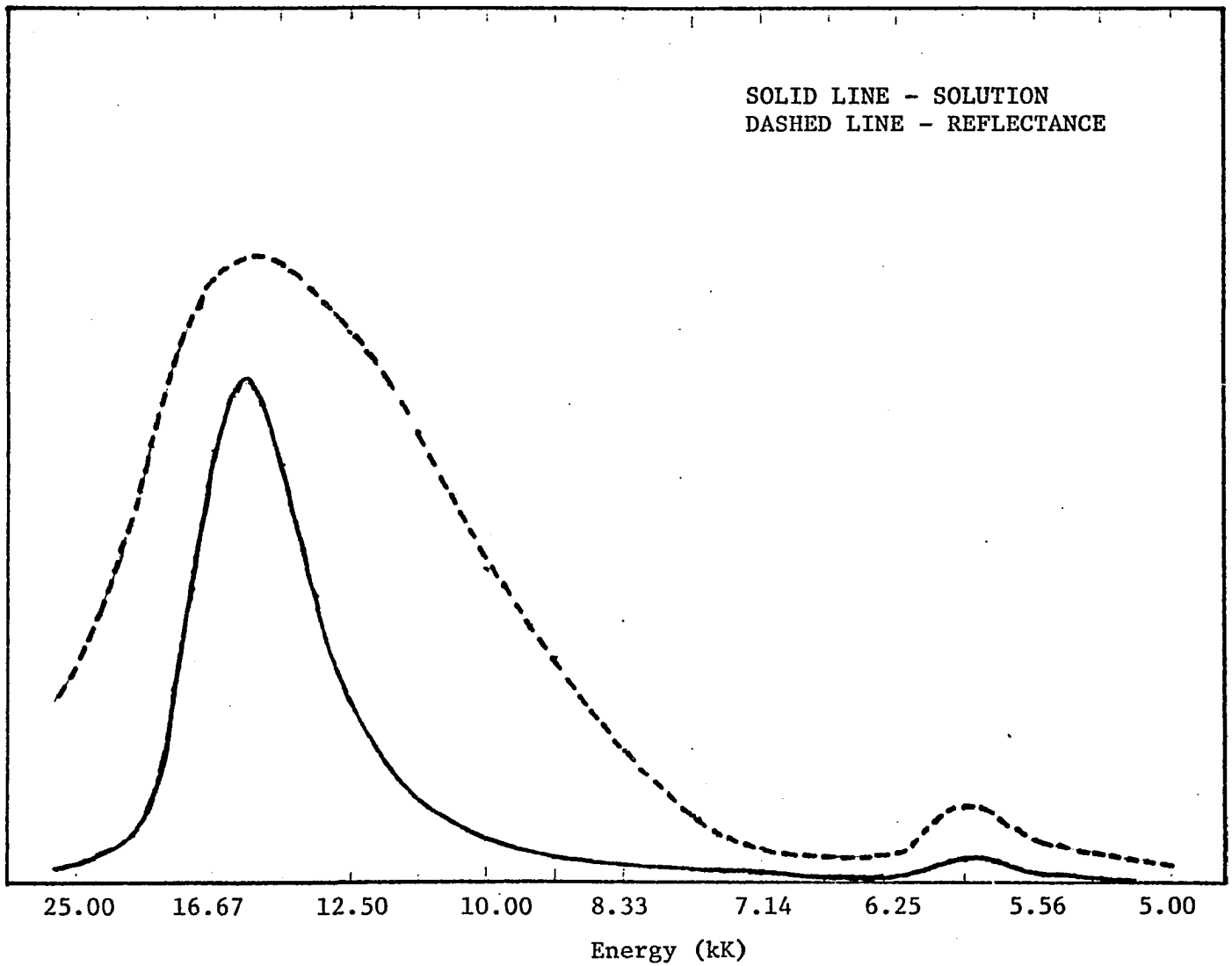


FIGURE XXXI. Electronic Spectra of $Ni(BPEA)(NCS)_2$

solution spectrum are quite small. If a coordination number of six was attained by the coordination of a solvent molecule rather than the existence of a dimer, a larger shift in energies of the maxima would be expected. Also, the infrared spectrum of $Ni(BPEA)(NCS)_2$ in acetonitrile indicates the presence of both S-bonded and N-bonded thiocyanates, which further support the existence of the dimer in solution.

$Cu(BPEA)(NCS)_2$ and $Zn(BPEA)(NCS)_2$ both show only one bonding mode for the thiocyanate in the infrared spectrum. The broad band below 2100 cm^{-1} is assigned the $\nu(C\equiv N)$ for N-bonded thiocyanates. The two complexes are nonelectrolytes and are quite soluble in polar organic solvents.

The copper thiocyanate complex is assigned a square planar configuration, both in solution and in the solid state, on the bases of infrared and electronic spectral data. The solid state infrared spectrum shows the terminal nitrogen of BPEA not to be bonded. The $\nu(N-H)$ is found to be 3175 ± 5 cm^{-1} with a half-width of 90 cm^{-1}. In the electronic spectrum, there are single symmetrical bands at 15.1 kK in the reflectance spectrum and 15.5 kK in solution, which is in accord with spectra of square planar copper(II).[138]

In the absence of other criteria, $Zn(BPEA)(NCS)_2$ is assigned a five-coordinate geometry on the bases of its stoichiometry and the two absorption bands in the infrared, $\nu(C\equiv N)$ and $\nu(N-H)$. The $\nu(N-H)$ is sharp and at 3220 cm^{-1}, which is consistent with tridentate BPEA as shown in previously discussed complexes.

G. Summary

Based upon the observed data, the stability of BPEA complexes in a pentacoordinate geometry vary with the metal ion and the anions

present. Table XVI shows how the coordination number changes with respect to metal ion, anion or the phase. The stability trend of the metal ion toward a five-coordinate BPEA complex appears to follow: $Zn^{2+} > Co^{2+} > Ni^{2+} > Cu^{2+}$. All of the cobalt complexes exhibit a coordination number of five in the solid state or in solution. Of the copper complexes, only the halides in the solid state have a five-coordinate geometry. The nickel complexes are intermediate between the cobalt complexes and the copper complexes in their stability with the three halide complexes having a five-coordinate configuration in both the solid state and in solution.

The observed trend for five-coordinate stability based on the ligands other than the BPEA is: $I^- > Br^- > Cl^- > NO_3^- \simeq NO_2^- > NCS^-$. (See Table XVI).

It was found that the anions capable of bidentate coordination, i.e. the nitrate and nitrite, are bidentate in three specific cases. In $Co(BPEA)(NO_3)_2$, one nitrate group is bidentate while the other is monodentate; however, the complex retains a pentacoordinate geometry because BPEA is bidentate. The nitrate and nitrite nickel(II) complexes attain octahedral geometries by the anions being bidentate with bidentate BPEA.

The absolute geometry of the five-coordinate complexes reported herein cannot be determined by any means other than x-ray methods. The electronic spectra of the BPEA complexes do not resemble those of trigonal bipyramidal[115] or square pyramidal geometries.[111] They are more characteristic of the first row transition metal complexes formed by dienMe,[121,122] which have been reported to be five-coordinate with a geometry intermediate of the two extremes.

TABLE XVI

Summary of Coordination Numbers for BPEA Complexes

	Co^{2+}		Ni^{2+}		Cu^{2+}		Zn^{2+}	
	a	b	a	b	a	b	a	b
Cl^-	5 & 4	5	5 & 6[c]	5	5	4	5	5
Br^-	5 & 4	5	5	5	5	4	5	5
I^-	5	5	5	5			5	5
NO_3^-	5	6	6	6	4	4	5	5
NO_2^-	5		6	6			5	5
NCS^-	6	5	6	6	4	4	5	5

[a]Coordination number in the solid state

[b]Coordination number in solution

[c]$Ni(BPEA)Cl_2 \cdot 2H_2O$

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