2,2'-BIPYRIMIDINE COORDINATION POLYMERS

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THESIS

2, 2'-BIPYRIMIDINE COORDINATION POLYMERS

Submitted by

Paul Arthur Westcott

In partial fulfillment of the requirements

for the Degree of Doctor of Philosophy

Colorado State University

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WE HEREBY RECOMMEND THAT THE THESIS PREPARED

UNDER OUR SUPERVISION BY PAUL A. WESTCOTT ENTITLED

2, 2'-BIPYRIMIDINE COORDINATION POLYMERS BE ACCEPTED

AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY.

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ABSTRACT OF THESIS

2, 2'-BIPYRIMIDINE COORDINATION POLYMERS

Some complexes and coordination polymers of 2, 2'-bipyrimidine were synthesized in methanol-2, 2'-dimethoxypropane media. The coordination compounds of 2, 2'-bipyrimidine were prepared from hydrated nitrate salts of Fe(III), Co(II), Ni(II), and Cu(II). Diffuse reflactance electronic absorption spectra and magnetic moment obser- vations have shown the above transition metals to be six coordinate when 2, 2'-bipyrimidine was used as a ligand. Infrared spectra of the complexes were used to determine the effects of coordination on the 2, 2'-bipyrimidine molecule and the degree of coordination that the nitrate ions had in each complex. Structures based on experimental observations were proposed. The proposed structures include simple complexes and coordination polymers. The 2, 2'-bipyrimidine com- plexes were found to be relatively stable to thermal decomposition.

Proton magnetic resonance was used to determine identity and purity of the 2, 2'-bipyrimidine. Infrared spectra and ultraviolet spectra of 2, 2'-bipyrimidine were correlated to the spectra of the

complexes. A new and efficient method of synthesizing 2, 2'-bipyri-

midine in the laboratory has been accomplished.

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INTRODUCTION

The field of coordination polymers provides new challenges in synthetic and characterizational chemistry. In order to synthesize a coordination polymer, several requirements must be met. Since a coordination polymer consists of a series of metal to ligand and ligand back to metal bonds, the ligands used to make coordination polymers must be polydentate. In order to insure polymer formation, the ligand must also have bonding sites in geometric positions which require more than one metal ion to occupy all sites. A typical coordination polymer is either insoluble in most solvents or destroyed by them. As such, instrumental methods of characterization are limited to the solid phase.

The research which provided the background for this dissertation was carried out using pyrazine (1, 2, 3, 4, 5), 4, 4'-bipyridine(6), and bis-(4-pyridyl)-alkanes(7) as the ligands. This dissertation contains a report on the research done on 2,2'-bipyrimidine (Figure I).
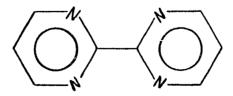
Figure I

2, 2' BIPYRIMIDINE

The compound 2,2'-bipyrimidine, like the above ligands, contains aromatic nitrogen heterocycles. It is unique, however, in that it has the potential for forming chelate bonds and bidentate coordinated polymeric complexes, as well as monodentate coordinated complexes.

THE PROBLEM

The overall problem discussed in this dissertation is the synthesis and characterization of coordination compounds of 2,2'-bipyrimidine and some transition metals. Bly and Mellon (8) first reported the synthesis of 2,2'-bipyrimidine in 1962. The compound is not commercially available and is produced in the laboratory only in low yields.

The metals Co(II), Ni(II), and Cu(II) will be used, with the intention of extending research in the area of coordination polymers using a new ligand. Co(II), Ni(II), and Cu(II) were commonly used in the previous research on coordination polymers using nitrogen heterocycles. Fe(III) will be included as an extention of the research since the Fe(III) complexes of 2,2'-bipyridine (Bipy) and o-phenanthroline are similar and well characterized (9).

Since 2,2'-bipyrimidine is potentially tetradentate and has a structure which should allow for bidentate chelation, particular attention will be paid to the synthesis of complexes which have a variety of metal to ligand stochiometric ratios. The metal ions which will be used tend to be both four and six coordinate. In considering the possible structures of complexes that could be formed with 2,2'-bipyrimidine and the chosen metal ions, the following formulae can be predicted: $(ML)A_n$, $(MLA_2)A_n$, $(M_2L_3)A_n$, and $(ML_3)A_n$. The

formulae are constructed such that M represents the metal ion, L represents 2, 2'- bipyrimidine, and A_n represents the anions. It would be expected that all these complexes would be polymers, except those having the formula $(ML_3)A_n$.

Once the complexes are made, they must be characterized. The characterization should answer the following questions: (1) Does 2, 2'-bipyrimidine form coordination polymers? (2) Do any four coordinate complexes form coordination polymers? (3) How does the ligand field strength of 2, 2'-bipyrimidine compare with those of other similar ligands in analogous complexes? (4) Is the ligand field strength of 2, 2'-bipyrimidine weaker in polymers (tetradentate complexes) as opposed to simple complexes? (5) Are there any unique properties in the complexes of this ligand?

LITERATURE REVIEW

Lever, Lewis, and Nyholm reported the first coordination polymers where a nitrogen heterocycle was used as the ligand (1, 2, 3, 4, 5). The polymers were made with pyrazine using cobalt(II), nickel(II), and copper(I) salts.

Cobalt(II) complexes were prepared having the general formulae $LCoX_2$ and L_2CoX_2. These complexes were found to be either tetrahedral or octahedral. Both magnetic moment data and electronic absorption spectra were used to determine structures. Complexes where only one nitrogen was coordinated to cobalt were also prepared (2). It was found that these complexes contained an extra infrared absorption band due to the asymmetric pyrazine.

Both octahedral and square planar complexes of nickel(II) were prepared with pyrazine. On the basis of infrared data, it was determined that some of the octahedral complexes contained only terminal pyrazines. Electronic absorption data of the four coordinate nickel (II) complexes agreed with either square planar or tetrahedral structures. An x-ray study of (2, 5-dimethylpyrazine)-dibromo-nickel(II) proved the four coordinate complex to be square planar. The complex was also found to be diamagnetic. The polymer has linear metal-ligand-metal-ligand chains with trans coordinated bromides.

The copper(I) pyrazine polymers also have a linear structure. However, since the copper(I) ion typically is two coordinate, the anions are ionically bound. Lever, Lewis, and Nyholm also attempted to prepare some copper(II) pyrazine complexes. All products were found, however, to be low in copper content.

In 1968, Musgrave and Mattson (6) reported their work on 4, 4'-bipyridine coordination polymers. Cobalt(II), nickel(II), copper(II), silver(I) and mercury(I) nitrates were used in the making of the polymers. Nickel(II) chloride was also used. Complexes having the formulae LMX_2 and L_2MX_2 were both made. Only the cobalt(II), nickel(II) and copper(II) nitrates, however, were found to have products with the L_2MX_2 formula.

The silver and mercury complexes were found to have structures analogous to the copper(I) pyrazine complex reported by Lever. The proposal of linear two coordinate polymers of silver(I), mercury(I) and copper(I) was supported by an x-ray study done by Vranka(10) on the silver pyrazine nitrate complex. The complete characterization of these complexes has enabled the synthetic chemist to obtain good infrared spectra of ionically bound nitrate ions where the metal ion is coordinated to a nitrogen heterocycle rather than water.

The cobalt and copper nitrate complexes of 4, 4'-bipyridine having the formula LMX_2 were found to have both nitrogens of the

4,4'-bipyridine coordinated. Since 4,4'-bipyridine is not flexible enough to allow for chelation, the complexes must be polymeric. The electronic absorption spectra of the cobalt complex indicated an octahedral coordination environment, and the infrared data indicated that the nitrate ions had bidentate coordination. The proposed structure for the cobalt 4,4'-bipyridine complexes is a linear polymer chain with two bidentate nitrates coordinated to each metal.

Since the electronic absorption data on the copper(II) complex could not be used to determine an octahedral or tetrahedral structure, the proposed structure for the copper(II)-4,4'-bipyridine complex had to be decided on the basis of infrared data. The nitrate absorption bands were closest to those for monodentate coordination. As such, the copper(II) complex was tentatively assigned a tetrahedral structure.

The proposed structure for the nickel(II) chloride-4,4'-bipyridine complex is generally the same as that of the cobalt(II) nitrate complex. The nickel was found to be octahedrally coordinated. In order for two chloride ions to occupy four coordination sites on each nickel, the proposed structure required each chloride ion to be bridged between two nickel ions.

The bis-4,4'-bipyridyl complexes of cobalt(II) and nickel(II) nitrates were found to have monodentate nitrates. Their proposed structures included polymer chains having four bridging bipyridyls and two coordinated nitrates per metal ion.

In an attempt to find the limits of flexibility required for poly-
mer formation as opposed to chelate formation, Westcott(7) prepared
complexes made with 1,2-bis-(4-pyridyl)-eithane and 1,3-bis-(4-
pyridyl)-propane. (These compounds will hereafter be referred to as
Dmdp and Tmdp, respectively). Cobalt(II), nickel(II), copper(II),
silver(I) and mercury(II) nitrates were used to make the complexes.
Nickel(II) chloride was also used. Only the most stable complexes
which formed with the Dmdp and Tmdp ligands were characterized.
It was found that the cobalt, nickel, and copper complexes were
polymeric and had the general formula L_2MX_2. These complexes
were all octahedrally coordinated. The proposed structures include
polymer chains in two dimensions with monodentate coordinated
anions.

The proposed structures of the silver and mercury Dmdp and
Tmdp complexes is the same as that of the 4,4'-bipyridine and
pyrazine analogs. It took more than three months for the silver
complex to show signs of photodecomposition.

Bly and Mellon(8) reported the first synthesis of 2,2'-bipyrimi-
dine in 1962. (Hereafter 2,2'-bipyrimidine will be referred to as
Bipm). In 1963 Bly and Mellon(11) reported a pKa value for Bipm and
the stability constant for the $[Fe(Bipm)_3]^{2+}$ complex in aqueous solu-
tion. They also reported the electronic absorption spectra of aqueous
Bipm solutions containing Co(II), Ni(II), Cu(I), Zn(II) and Cr(III).

A large list of cations which would interfere with the Fe(II)-Bipm stability constant determination was also included. Bly and Mellon predicted the possibility of polymer formation in Bipm complexes but were unable to isolate any complexes including the iron(II) complex in the solid phase.

Table I lists the pKa values for various nitrogen heterocycles.

Table I

pKa's OF NITROGEN HETEROCYCLES

HETEROCYCLE	pKa
2,2'-bipyrimidine	.6(11)
pyrazine	1.1(2)
4,4'-bipyridine	4.2(6)

As can be expected from the inductive effects, Bipm is the weakest base of these polymer forming nitrogen heterocycles. Unfortunately the pKa values are only a measure of the ability of the base to hold a proton in aqueous solution and do not indicate the Lewis base strength of each nitrogen toward a metal ion.

EXPERIMENTAL

Instruments and reagents

All infrared spectra were taken on a Perkin-Elmer model 337 grating infrared spectrophotometer. Diffuse reflectance electronic absorption spectra were obtained with a Cary model 14 recording spectrophotometer. Magnesium carbonate with a quartz sample holder was used as a reference to set zero absorbance. Proton magnetic resonance spectra were recorded on a Varian model A60A NMR spectrometer. The magnetic susceptibility data were taken on a Princton Applied Research model FM-1 vibrating sample magnetometer. Metallic nickel was used as the reference. Elemental analyses were done by Huffman Laboratories, Inc. and Chemalytics, Inc.

The reagents used in the preparation of the complexes included the following:

2-aminopyrimidine- Eastman Kodak Co.

HBr- Eastman Kodak Co.

Cu-bronze- Crescent Bronze Powder Co.

HNO_3- Mallinckrodt Chemical Company

$Fe(NO_3)_3 \cdot 9H_2O$- Mallinckrodt Chemical Company

$Co(NO_3)_2 \cdot 6H_2O$- Baker Analyzed Reagent

$Ni(NO_3)_2 \cdot 6H_2O$- Mallinckrodt Chemical Company

Cu(NO$_3$)$_2$·3H$_2$O- Baker Analyzed Reagent

methanol- Mallinckrodt Chemical Company

2,2-dimethoxypropane- Eastman Kodak Company

Preparation procedures

2,2'-bipyrimidine:

The synthesis of 2,2'-bipyrimidine(Bipm) reported by Bly and Mellon(8) was an Ullman reaction which used 2-bromopyrimidine as the starting material. Bly and Mellon reported the synthesis of 2-bromopyrimidine from 2-aminopyrimidine in the same note. Although 2-bromopyrimidine is now commercially available, it was decided that a laboratory production of it was more economical.

The laboratory production of 2-bromopyromidine was carried out by a reverse addition diazotization of 2-aminopyrimidine with HBr. Since the quantity of 2-bromopyrimidine needed was much larger than the amounts reported in the Bly and Mellon note, a few minor changes were made in their procedure. The amount of water and sodium bromide were both changed. To the weighed amount of sodium nitrite, just enough water was added to dissolve about half of the sodium nitrite. Then a saturated solution of sodium bromide was added in the same volume amount as the water which was originally called for in the note. The salt solutions were then mixed, and heated, when necessary, until only a small trace of undissolved salt remained. The 2-aminopyrimidine was added at room temperature

just before the entire mixture was cooled to $-10^{\circ}C$. The remainder

of the procedure was identical to that reported by Bly and Mellon.

If the reaction mixture is not kept in the required $-10^{\circ}C$ to

$-3^{\circ}C$ range, the rate of reaction becomes more difficult to control,

and the product yield will be low. A great deal of foam is produced

during the reaction. The best method of containing the foam was to

use a large, three-necked flask and to add the acid at a sufficiently

slow rate. Temperature control was also important in controlling

the foam. A special thermometer was made for the control of this

reaction; it had a long stem to aid in visibility and a large bulb in

order to give very sensitive temperature change readings.

The Ullman coupling reaction of 2-bromopyrimidine to yield

Bipm proceeded with very low yields and many dark colored by-pro-

ducts. The greatest difficulty encountered in the production of Bipm

was in the separation and purification steps. When the reaction was

completed, the DMF solvent had to be filtered off. The filtrations

proceeded very slowly and with difficulty due to the very finely

divided copper powder that remained unreacted. Since the DMF inter-

feres with purification procedures, the reaction was successfully

attempted in the absence of DMF.

The following changes were made in the production of Bipm from

that reported in the Bly and Mellon note. The copper-bronze was

activated by the method reported in Vogel(12). An added petroleum

ether wash of the activated copper was used to aid in the removal of acetone. To insure purity the 2-bromopyrimidine was recrystallized four times. It was freshly recrystallized prior to each coupling reaction. Both the activated copper and the 2-bromopyrimidine were stored in an evacuated desiccator over CaH_2 to remove solvents and any residual water before placing them in the reaction flask. Equal masses of the copper and 2-bromopyrimidine were then placed in a flask. The flask was evacuated and sealed. The contents were shaken until thoroughly mixed. The sealed flask was submerged in a mineral oil bath and kept at $90-115^{\circ}C$ for 12 hours. Once the flask had cooled to room temperature, the seal was cracked open and the brown powder and copper products were shaken out into a beaker. The products were extracted with aqueous ammonia-cyanide solution and filtered. Following the same method of chloroform extraction and ethyl acetate recrystallization that Bly and Mellon used, Bipm was sublimed multiple times until a white product could be collected. Recrystallizations from petroleum ether, benzene, and 2,2'-dimethoxypropane and mixtures of these solvents were found to be useful when used prior to sublimation.

The purity and identity of the product was observed in NMR spectra. Table II lists the NMR spectra of 2-bromopyrimidine and Bipm in deuterochloroform and DMF.

Table II

NMR OF 2-BROMOPYRIMIDINE AND 2,2'-BIPYRIMIDINE

COMPOUND	SOLVENT	CHEMICAL SHIFT
2-bromopyrimidine	$CDCl_3$	doublet 8.70 ppm
		triplet 7.49 ppm
	DMF	doublet 8.68 ppm
		triplet 7.67 ppm
2,2'-bipyrimidine	$CDCl_3$	doublet 9.11 ppm
		triplet 7.54 ppm
	DMF	doublet 9.21 ppm
		triplet 7.78 ppm

$Fe(Bipm)_3(NO_3)_3$, $Co(Bipm)_3(NO_3)_2$, $Ni(Bipm)_3(NO_3)_2$ and $Cu(Bipm)_3$ $(NO_3)_2$

One millimole of the hydrated transition metal nitrate salt was placed in a 15 cm. test tube. Four millimoles of Bipm were added to each test tube. Five milliliters of methanol-dimethoxypropane (DMP) azeotrope freshly distilled from CaH_2 were also added to each test tube. The test tubes were placed in a large reaction vessel, and enough of the methanol-DMP solvent was added to reach a level of about 1 cm. below the level of solvents in the test tube. The reaction vessel was fitted with a large condenser whose vent was protected by a CaH_2 drying tube. The reaction system was then refluxed for two

days. During the two day reaction time the test tubes were periodically removed and their contents were crushed and mixed against the sides of the test tube. Any tubes which tended to lose solvent had more solvent added to keep the total volume in each tube at 5 ml.

During the reaction the nickel and cobalt reactants and products remained insoluble. The iron system has a dark red-brown solution as an intermediate phase of the reaction. The copper system forms an orange-brown solution as an intermediate phase.

When the reactions were completed, solid products were collected by filtration and washed with fresh methanol-DMP solvent and pure DMP as the final wash. The products were stored in a vacuum desiccator over CaH_2. The desiccator was usually kept in an evacuated condition. Stoichiometric analysis of the products is reported in Table III.

Although the tris-Bipm complexes were analysed and characterized from the products obtained by the above procedure, it is the belief of this researcher that a faster, more efficient method of preparation could be obtained if solutions of metal salts and Bipm were mixed as in the procedure given below, but using a 4:1 ligand-metal ratio. The procedure used to make the $M_2(Bipm)_3(NO_3)_n$ and $M(Bipm)(NO_3)_n$ complexes should work very well. A sample of $Co(Bipm)_3(NO_3)_2$ was prepared by this method and was characterized with equally successful results.

$\underline{Fe_2(Bipm)_3(NO_3)_6, \quad Co_2(Bipm)_3(NO_3)_4, \quad Co(Bipm)(NO_3)_2, \quad Ni_2(Bipm)_3}$

$\underline{(NO_3)_4, \quad Ni(Bipm)(NO_3)_2, \quad Cu_2(Bipm)_3(NO_3)_4, \quad \text{and } Cu(Bipm)(NO_3)_2:}$

A .2M solution of each hydrated transition metal nitrate salt was prepared in methanol. All salts were easily dissolved in the methanol. Separate solutions of Bipm in methanol-DMP azeotrope were prepared having concentrations of .1M and .15M. Five milliliters (.001 moles) of each metal salt solution were placed in separate 15 cm. test tubes. When the complexes having the 2:3 metal-ligand ratio were made, 10 ml. (.0015 moles) of the .15M Bipm solution were added to each test tube. In the same manner, using the .1M Bipm solution, 1:1 ratio mixtures were also prepared. The contents of each test tube were then thoroughly mixed by stirring, and the test tubes were then placed in a large reaction vessel. The reaction vessel was fitted with a large condenser, and the vent was protected with a CaH_2 drying tube. The vessel was filled with freshly distilled methanol-DMP azeotrope to a level about 2 cm. below the level of solution in each test tube. The reaction vessel was then heated to maintain a slow rate of reflux. Periodically each test tube was removed to have its contents mixed and any evaporated solvent replaced with methanol-DMP azeotrope. After each reaction produced a solid, homogeneous product which remained unchanged in appearance for more than twelve hours, the product was collected by filtration. Reaction times varied from two to five days for individual complexes.

Each product was washed with methanol-DMP azeotrope and pure DMP as a final rinse. Air was pulled through the filter until the last sign of dampness disappeared. The product was then immediately placed in a vacuum desiccator. The desiccator was charged with CaH_2 and usually kept evacuated. According to the infrared data, the solvent traces were usually removed after eight hours of evacuation.

The colors of the methanol solutions of Fe(III), Co(II), Ni(II) and Cu(II) nitrate solutions are, respectively, red-orange, pink, green and blue-green. When the metal-salt solutions were mixed with a 2:3 ratio of Bipm, there is an immediate color change to deep red, yellow, lavender-white, and green for the respective mixtures. When the mixing ratio was 1:1, the colors turned to red, yellow, light-blue and blue-green, respectively.

The type of sample holder used to take the diffuse reflectance electronic absorption data allowed each complex to be exposed to air for periods of up to one half-hour. It was found that some complexes had picked up water bands in their infrared spectra after this exposure to air. Since the diffuse reflectance data were obtained prior to the stoichiometric analysis, instructions were given to the analysing lab on a drying procedure. The samples were successfully dried in a vacuum desiccator at $50^{\circ}C$. for two days.

Stoichiometric analyses are reported in Table III. It should be noted that only 1:3 and 2:3 complexes of iron are reported. The

analysis of the iron sample made from 1:1 stoichiometric ratio reaction mixture proved the actual product to be $Fe_2(Bipm)_3(NO_3)_6$. No further attempt was made to prepare a 1:1 complex.

Table III

STOICHIOMETRIC ANALYSES OF BIPM COMPLEXES

COMPLEX	$\frac{\%C^*}{C^{**}}$	$\frac{H^*}{H^{**}}$	$\frac{N^*}{N^{**}}$
$Fe(Bipm)_3(NO_3)_3$	40.27 42.32	2.51 3.16	29.34 28.25
$Fe_2(Bipm)_3(NO_3)_6$	30.10 30.15	1.88 2.13	26.40 24.21
$Co(Bipm)_3(NO_3)_2$	43.88 42.59	2.74 3.29	31.97 28.46
$Co_2(Bipm)_3(NO_3)_4$	34.32 32.58	2.14 1.92	28.34 25.77
$Co(Bipm)(NO_3)_2$	28.18 28.21	1.76 1.79	24.64 ---
$Ni(Bipm)_3(NO_3)_2$	43.89 41.53	2.74 3.35	31.98 27.10
$Ni_2(Bipm)_3(NO_3)_4$	34.34 34.13	2.14 2.31	28.35 24.30
$Ni(Bipm)(NO_3)_2$	28.20 28.04	1.76 1.83	24.65 22.95
$Cu(Bipm)_3(NO_3)_2$	43.57 42.01	2.72 2.95	31.74 28.28
$Cu_2(Bipm)_3(NO_3)_4$	33.95 33.20	2.12 1.93	28.03 26.01
$Cu(Bipm)(NO_3)_2$	27.80 27.67	1.74 1.54	24.31 ---

*Calculated
**Observed

RESULTS AND DISCUSSION

2, 2'-Bipyrimidine

Table IV is a list of the infrared bands observed in free Bipm.

Spectra were taken from both nujol and halocarbon mulls. All bands,

whether weak, medium or strong, are fairly sharp. When Bipm is

Table IV

INFRARED BANDS OF 2, 2'-BIPYRIMIDINE

3120 w	1565 s	1262 w	1105 w	770 m
3070 s	1552 s	1243 w	1075 w	686 w
3025 m	1445 w	1155 m	990 m	678 w
2970 m	1398 s	1150 m	822 m	642 m
		cm^{-1}		

Relative intensities are denoted by w=weak, m-medium, s=strong.

used as a ligand, there are three regions in the infrared spectra of

Bipm complexes which demonstrate significant shifts. The first

region is the strong bands at 1565 cm^{-1}, 1552 cm^{-1} and 1398 cm^{-1}.

The second region is the medium band at 990 cm^{-1}. The third area

of interest is in the 770 cm^{-1} to 640 cm^{-1} region. This last region is

usually ascribed to the out of plane C-H rocking modes.

An ultraviolet spectrum of Bipm was taken in methyl cyclo-

hexane. The n $\longrightarrow$ π^* and π $\longrightarrow$ π^* transitions were observed at

34, 200 cm^{-1} and 43, 150 cm^{-1}, respectively. The bands are rela-

tively sharp, and no fine structure was observed. The extinction

coefficient was not determined since the solution concentration was unknown. However, the relative peak heights are 1:18.3.

$Ni(Bipm)_3(NO_3)_2$, $Ni_2(Bipm)_3(NO_3)_4$, and $Ni(Bipm)(NO_3)_2$

One of the most striking results of the synthesis of these complexes is the variation of color between each product. The 1:3 complex is pink, the 2:3 complex is an off-white and the 1:1 complex is light-blue. Although all of these products are different in color from the nickel nitrate starting solution, the first spectroscopic evidence that Bipm has coordinated to the nickel came from the infrared spectra.

Table V lists the infrared absorption bands of the nickel complexes. First, consider the two strong bands of uncomplexed Bipm at 1565 cm^{-1} and 1552 cm^{-1}. These bands are assigned to the carbon-carbon and carbon-nitrogen stretching modes of the aromatic heterocyclic Bipm. In the three nickel complexes, the greatest shifts are observed in the higher energy band. Since the nitrogen atoms of Bipm are the coordination sites, it would follow that the greatest infrared band shifts should be observed in the carbon-nitrogen mode. Therefore, the three bands of the three nickel-Bipm complexes at 1574 cm^{-1}, 1582 cm^{-1} and 1580 cm^{-1} are tentatively assigned to the carbon-nitrogen stretching mode. This leaves the bands at 1555 cm^{-1}, 1568 cm^{-1}, and 1564 cm^{-1} as carbon-carbon stretching modes. Another significant band shift is observed in the carbon-hydrogen

Table V

INFRARED BANDS OF NICKEL BIPM COMPLEXES

$Ni(Bipm)_3(NO_3)_2$	$Ni_2(Bipm)_3(NO_3)_2$	$Ni(Bipm)(NO_3)_2$
3080 w	3080 w	3070 w
3040 w	3025 w	2995 w
2950 w	2920 w	--
2910 w	--	2890 w
1574 s	1582 s	1580 s
1555 s	1568 w	1564 w
--	1475 w	1476 m
--	--	1448 m
1408 s	1419 m	1416 s
1345 s, br	1356 s, br	--
1330 s, br	1302 w	1300 m
1018 m	1030 m	1025 m
827 w, br	830 w	830 m, br
--	825 w	--
--	807 w	805
760 s	749 m	750 s
692 m	687 m	688 m
663 m	680 w	682 m

bending band of Bipm. Free Bipm absorbs at 1398 cm^{-1}. The three nickel complexes show absorptions for the C-H bend at 1404 cm^{-1}, 1419 cm^{-1}, and 1416 cm^{-1}. Further shifts are observed in the C-H rocking bands. Four bands, at 770 cm^{-1}, 686 cm^{-1}, 678 cm^{-1} and 642 cm^{-1} are observed for Bipm in this region. The most significant band shift is from the 770 cm^{-1} band of free Bipm to lower energies on the three nickel complexes. This particular band will have further significance in the Bipm complexes discussed later in this dissertation.

The infrared spectra of the nickel complexes also contribute information concerning the character of the nickel nitrate bands in each complex. In the $Ni(Bipm)_3(NO_3)_2$ complex, the nitrate ion absorbs strongly in a broad band centered around 1345 cm^{-1}. The band contains some shoulders at 1345 cm^{-1} and 1330 cm^{-1}. The entire broad band and its shoulders are typical of free nitrate ions in cationic complexes.

In contrast to the 1:3 complex, the $Ni(Bipm)(NO_3)_2$ 1:1 complex has infrared nitrate absorption bands at 1476 cm^{-1} and 1300 cm^{-1}. These bands are relatively sharp and there is no absorption in the 1345 cm^{-1} region. In effect, the nitrate band has been split. The splitting is caused by the asymmetry which is imposed on the ion when it is coordinated to a metal. The degree of splitting can be compared to the spectra of the other coordinated nitrates which have either monodentate or bidentate coordination (13). Such a comparison is indicative of monodentate coordination.

$Ni_2(Bipm)_3(NO_3)_2$ has a broad infrared absorption at 1356 cm^{-1}. This band is attributed to free nitrate ions. There are also some weak bands at 1474 cm^{-1} and 1302 cm^{-1}. These bands indicate a small impurity of the 1:1 complex present in the sample. The stoichiometric analysis would have been low in carbon content if the impurity was 1:1 complex alone. If 1:3 portions of 1:3 and 1:1 com-plexes were present, however, the stoichiometric analysis would be
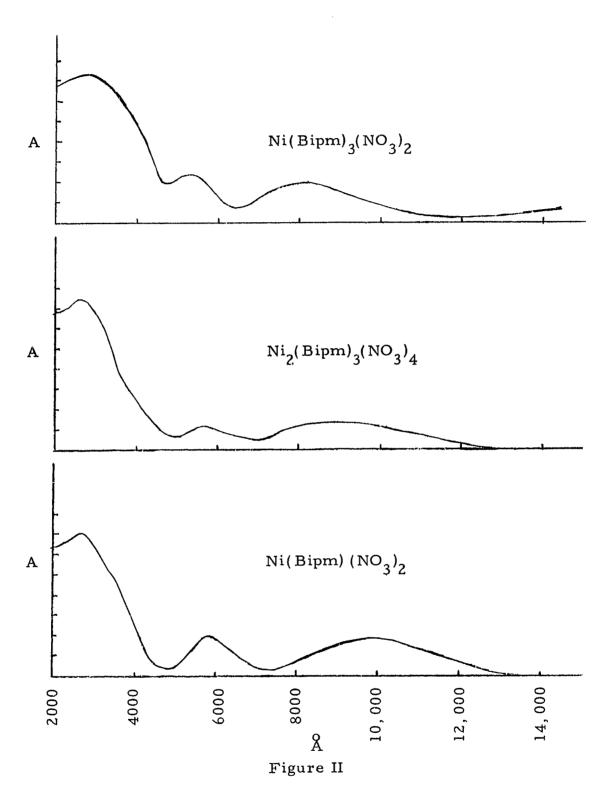
unchanged. The presence of 1:3 complex in the 2:3 complex would be difficult to detect in the infrared spectra since the nitrate modes for both complexes are nearly identical.

The electronic absorption of the nickel-Bipm complexes were all taken in the solid state using a diffuse reflectance technique. Figure II contains the spectra which were obtained from the nickel complexes. The $MgCO_3$ and quartz sample holder baseline reference has been subtracted from the original spectra. All three spectra are typical of octahedral nickel II.

Even though no shoulders are observed in the UV region, the large absorption band should contain several electronic transition modes. The greatest absorptions in the UV would occur from the metal-ligand charge transfer and the $\pi \longrightarrow \pi^*$ aromatic transitions. Other absorptions in the UV would arise from the $n \longrightarrow \pi^*$ ligand transition and the $\nu_3 - {}^3T_{1g}(P)$, ${}^3A_{2g}$ nickel d-d transition.

The unique colors of the pink 1:3 complex and the white 2:3 complex can be explained from the spectra. In the 1:3 complex, the UV band is broad enough to tail off into the visible region. This, combined with the ν_2 absorption in the center of the visible region, permits red light transmittance while violet and green light are absorbed. The 2:3 complex has weak absorption bands in the visible region. The visible absorption consists of tails from both the UV and near IR bands, as well as weak ν_2 absorption in the center of the

Figure II

ELECTRONIC ABSORPTION SPECTRA OF

NICKEL-BIPM COMPLEXES

visible region. The net effect is weak absorption and coincidental mixing of complementary colors, giving the complex an off white appearance.

A calculation of the $\nu_3 - {}^3T_{1g}(P)$, ${}^3A_{2g}$ transition and the Racah parameter B was done on each nickel complex. Table VI lists the calculated values of ν_3 and B, as well as the ν_1 and ν_2 assignments which were used to make the calculation. The calculation was done

Table VI

ν_3 AND RACAH PARAMETERS OF NICKEL COMPLEXES

Complex	ν_1	ν_2	ν_3 calc	B
$Ni(Bipm)_3(NO_3)_2$	12,250	18,850	29,450	808
$Ni_2(Bipm)_3(NO_3)_2$	11,450	17,850	28,220	781
$Ni(Bipm)(NO_3)_2$	10,230	17,120	31,350	1,185
$Ni(Bipy)_3^{2+}$	12,650	19,200	29,900	744

using a method reported by Lever (14). The experimental ν_1 and ν_2 values and the calculated ν_3 and B values of the $Ni(Bipy)_3^{2+}$ complex is included in the table for comparison.

The values of ν_3 and B should not be considered as highly accurate. Since the ν_3 bands of all three nickel complexes cannot be distinguished, the B values and the tolerance of the ν_1 and ν_2 assignments cannot be tested by alternative calculations. Further lack of reliability arrives from making an absorption maximum assignment

on the ν_1 band. This band is quite broad and the λ max changes when the reference spectrum is subtracted.

In all three complexes the Racah parameter has a high value. It is particularly high in the 1:1 complex. The high B values indicate strong metal-ligand covalent bonding.

The assumption that the nickel complexes are octahedrally coordinated is further supported by magnetic moment data. The magnetic moments are 2.81, 2.64, and 2.76, for the respective 1:3, 2:3, and 1:1 nickel-Bipm complexes. (Further explanation of the calculation of these magnetic moments is in the appendix.) Although these values are low, they are still in better agreement with an octahedral ligand field than any other geometry.

The proposal of a structure for the $Ni(Bipm)_3(NO_3)_2$ complex appears to be straight forward. The complex should be six coordinate, contain uncoordinated nitrate ions and have three Bipm molecules coordinated to each nickel atom. The structure which is proposed is the same as the $Ni(Bipy)_3^{2+}$ complex. Each Bipm acts as a bidentate ligand and occupies two adjacent coordination sites of the nickel ion. (See Appendix I).

The $Ni_2(Bipm)_3(NO_3)_4$ complex also has free nitrate ions, and is six coordinate, but has an average of only one and a half Bipm's per nickel ion. The proposed structure still has each nickel ion surrounded by three Bipm molecules. In order to fill the six
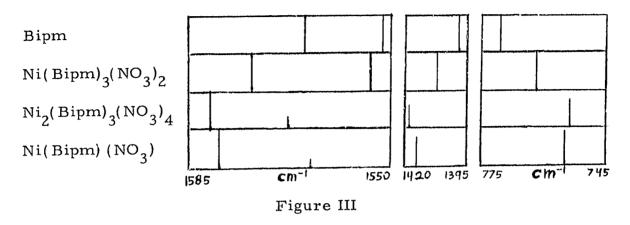
coordination sites of each nickel ion without coordinating the nitrate ions, however, each Bipm must be four coordinate. The stoichiometry is then satisfied since two nickel ions require twelve electron pair donors, and three Bipm molecules can supply the twelve electron pairs. The overall structure is a three dimensional polymer having Bipm bridges between every nickel ion. (See Appendix I).

In contrast to the other two nickel complexes, the $Ni(Bipm)$ $(NO_3)_2$ complex has shown evidence of coordinated nitrates. The nickel is still six coordinate, and Bipm is also coordinated to each nickel ion. In order to fill the six coordination sites of the nickel ion with two monodentate nitrates and a Bipm molecule, the Bipm must be quadradentate. The proposed structure is a polymer chain of alternating nickel ions and Bipm molecules. Each nickel ion also has two coordinated nitrates. (See Appendix I).

It is not possible to predict whether the nickel-Bipm chain is linked in a cis or trans fashion. The electronic absorption spectra show no splitting or even broadening of the v_2 mode. Had a splitting been observed, it would have been a good indication that the chain was trans oriented. A lack of splitting, however, is not proof of a cis configuration (15).

Now that the structures for the nickel complexes have been proposed, it is possible to discuss further correlations of spectroscopy and the proposed structures. Figure III contains a schematic

diagram of the more interesting infrared bands of free Bipm and the

three nickel complexes. As previously stated, significant shifts are

Bipm

$Ni(Bipm)_3(NO_3)_2$

$Ni_2(Bipm)_3(NO_3)_4$

$Ni(Bipm)(NO_3)$

|585 cm^{-1} 1550   1420 1395   775 cm^{-1} 745

Figure III

INFRARED CORRELATION DIAGRAM OF NICKEL COMPLEXES

observed where Bipm has been complexed. A further correlation can

be seen in the degree of shift and in the intensities of absorption of

the 1:3 complex as opposed to the 2:3 and 1:1 complexes. The pro-

posed structure of the 1:3 complex has only half of the nitrogens in

each Bipm molecule coordinated. The 2:3 and 1:1 complexes have

proposed structures where all four nitrogens are coordinated. In all

three regions of the infrared spectra, the degree of band shift is both

similar and greater for the 2:3 and 1:1 complexes than for the 1:3

complex. There is also a large decrease in the intensity of the lower

energy absorption band of the two polymeric complexes in the 1585

cm^{-1} to 1550 cm^{-1} region. The 775 cm^{-1} to 745 cm^{-1} region demon-

strates a similar change in intensities, but to a lesser degree.

The greater band shifts in the 2:3 and 1:1 complexes demonstrate the higher degree of coordination that each Bipm molecule has in these complexes versus the 1:3 complex. A decrease in the intensity in a given infrared mode represents the loss of a dipole moment. Since dipole moments are caused by asymmetry, the loss of a band intensity represents a gain in overall symmetry. In the environment of the Bipm molecules, the polymeric 2:3 and 1:1 complexes have greater symmetry than the 1:3 complex. As such, the intensity changes correlate with the proposed structures.

The electronic absorption spectra show decreasing 10 Dq values as the ligand to metal ratio decreases. The values are 12,250 cm^{-1}, 11,450 cm^{-1} and 10,230 cm^{-1} for the respective 1:3, 2:3, and 1:1 complexes.

$Fe(Bipm)_3(NO_3)_3$ and $Fe_2(Bipm)_3(NO_3)_6$

When the Bipm complexes of Fe(III) nitrate are prepared, the methanolic solutions immediately turn deep-red as the ligand solution is added. The development of dark-red precipitated products is gradual, and several days are allowed for the completion of the reaction. It is interesting to note that when the ligand solutions are added, the solutions turn red rather than blue. Both $Fe(Bipy)_3^{3+}$ and $Fe(phen)_3^{3+}$ are blue in solution and solid states (9). The $Fe(Bipy)_3^{2+}$ and $Fe(phen)_3^{2+}$ complexes are red. A question immediately arose as to whether the products are Fe(II) or Fe(III) complexes.
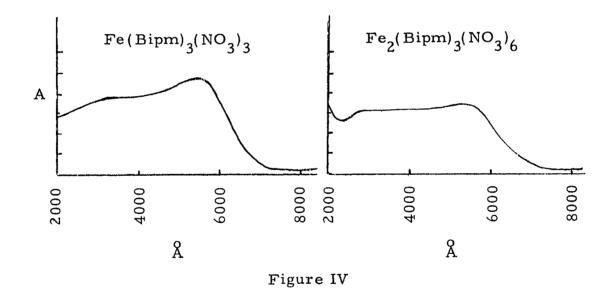
The stoichiometric analyses are in better agreement with Fe(III) products than with Fe(II) products. The calculated weight per cent values for Fe(II) nitrate-Bipm complexes are: $Fe(Bipm)_3(NO_3)_2$: C = 44.27, H = 2.75, and N = 27.83; $Fe_2(Bipm)_3(NO_3)_4$: C = 34.57, H = 2.16, and N = 21.83. Refer to Table III for the calculated and observed values of the Fe(III) complexes.

The oxidation state of most transition metal ions in complexes is usually easy to determine from the electronic absorption data. Difficulty in determining oxidation states can occur when the spectra have charge transfer or other strong absorptions obscuring the d-d transitions of the transition metal. The iron complexes of Bipm, Bipy and o-phen have electronic absorption spectra containing large, broad charge transfer bands. Table VII lists the absorption maxima of the $Fe(Bipm)_3(NO_3)_3$ and $Fe_2(Bipm)_3(NO_3)_6$ complexes; the absorption maxima of some Fe(II) and Fe(III) Bipy complexes are also included. Figure IV demonstrates the broad nature of these bands. The spectra represented in Figure IV were diluted with $MgCO_3$. Pure complexes of the solid iron complexes yield such intense absorption that the spectrophotometer is "maxed out" through most of the visible and ultraviolet region.

Table VII

ELECTRONIC ABSORPTION OF IRON-BIPM COMPLEXES

Complex	Absorption Bands cm^{-1}			
$Fe(Bipm)_3(NO_3)_3$			18,500	30,300
$Fe_2(Bipm)_3(NO_3)_6$			18,750	30,800
$Fe(Bipy)_3^{3+}$			16,670	31,000 (9)
$Fe(Bipy)_3^{2+}$		12,260	18,500	29,000 (16)
$Fe(Bipy)_2Cl_2$	8,400	10,600	16,900	18,800 (17)

Figure IV

ELECTRONIC ABSORPTION OF IRON-BIPM COMPLEXES

The absorption bands above 15,000 cm^{-1} for all Fe(II) and

Fe(III) complexes listed in Table VII are assigned to charge transfer

transitions. There was some low intensity absorption tailing off into

the near infrared region on the first three iron complexes listed in

the table. No distinguishable maxima have been observed in this

region. Even though the spectrum of $Fe(Bipy)_3^{3+}$ is a better match

for the spectra of the Bipm complexes than the spectra of the Fe(II)

complexes. The electronic absorption evidence is far from being

conclusive. The spectra of the Fe(II) complexes are quite similar to

Fe(III) complexes. They also have charge transfer bands in the same

region and low intensity absorption in the near infrared. The most

distinguishing characteristic of the Fe(II) complexes is that definite

absorption maxima are observable in the near infrared region (16,

17).

The magnetic moments of some iron complexes, as well as

some reference compounds, are listed in Table VIII. All of the

Table VIII

MAGNETIC MOMENTS OF SOME IRON COMPLEXES

Complex	μ
$Fe(Bipm)_3(NO_3)_3$	2.05
$Fe_2(Bipm)_3(NO_3)_3$	3.09
$Fe(Bipy)_3(ClO_4)_3 \cdot 3H_2O$	2.36 (18)
Fe(III) high spin complexes	5.90 (20)
$Fe(Bipy)_3(ClO_4)_2$	0.00 (19)
$Fe(Bipy)_2Cl_2$	5.20 (21)

moments reported are room temperature values. The values for the

Bipm complexes are believed to be slightly low. Further explanation

of the iron-Bipm magnetic moment data is covered in the appendix.

Given that the values for the Bipm complexes are slightly low, the

$Fe(Bipm)_3(NO_3)_3$ complex is in good agreement with a low spin

Fe(III) assignment. The 3.09 value for the $Fe_2(Bipm)_3(NO_3)_6$ com-

plex does not match any assignment of Fe(II) or Fe(III) complexes.

This value could be considered intermediate between high and low

spin complexes of either Fe(II) or Fe(III). It has been well verified

that the magnetic moments of both Fe(II) and Fe(III) complexes are

highly temperature dependent (20, 21). In the Fe(II) case, however,

the temperature dependence of $Fe(Bipy)_2Cl_2$-type complexes is

believed to be caused by changes in metal-metal interactions between

doubly-bridged dimers (21). A similar dimerization interaction in

the $Fe_2(Bipm)_3(NO_3)_6$ does not seem likely. (This point will be

further clarified by the infrared discussion, and the proposed struc-

tures).

The analogous Bipy complexes of Fe(II) and Fe(III) require

three Bipy molecules per metal atom for a low-spin complex to be

formed. It is possible that the $Fe_2(Bipm)_3(NO_3)_6$ complex has

reached a point just intermediate between the high and low spin ligand

field strengths. If this is the case, a temperature-magnetic sus-

ceptability study should be useful in proving this hypothesis.

It would be expected that at lower temperatures, the vibrational

motions of the ligand would relax and allow each Bipm to exert a

greater ligand field strength. At the low temperature limit, the magnetic moment should be zero if the complex is an Fe(II) compound, or around 2.3 if the complex is an Fe(III) compound. In the high temperature limit an Fe(II) complex should have a magnetic moment around 5.3 and the Fe(III) complex around 5.9. These predicted trends in temperatures are the reverse of the trend observed in the Fe(II) metal-metal interaction reported by Baker and Bobonich (21). After considering the stoichiometric analyses, electronic absorption data, magnetic moment data, and visual observation of the synthesis reaction, the Bipm complexes of iron are believed to be compounds of Fe(III).

The infrared spectrum of $Fe(Bipm)_3(NO_3)_3$ very closely resembles the spectrum of $Ni(Bipm)_3(NO_3)_2$. The shifts in the Bipm modes are slightly greater than those observed in the nickel complex. In contrast, the $Fe_2(Bipm)_3(NO_3)_6$ has a spectrum which is more complex than the spectrum of $Ni_2(Bipm)_3(NO_3)_4$. Table IX lists the infrared absorption bands of the iron-Bipm complexes.

The mode assignments for the Fe 1:3 complex are the same as they were for the Ni 1:3 complex. The bands at 1576 cm^{-1} and 1555 cm^{-1} are assigned to the C-C and C-N aromatic stretching modes. The C-H band is at 1405 cm^{-1}. The broad ionic nitrate band is centered at 1343 cm^{-1} and has sharp shoulders at 1343 cm^{-1} and 1325 cm^{-1}. The strong band at 728 cm^{-1} is assigned to the C-H out-of-plane rocking mode.

Table IX

INFRARED SPECTRA OF THE IRON-BIPM COMPLEXES

$Fe(Bipm)_3(NO_3)_3$ cm^{-1}	$Fe_2(Bipm)_3(NO_3)_6$ cm^{-1}
3070 w	3080 w
3030 w	3020 w
2950 w	
2920 w	2900 w
1576 s	1572 s
1555 m	1545 m
1449 w	1510 s
1405 s	1410 s
1343 s	1345 s
1325 s	1330 s
	1278 s
1030 m	1020 m
	980 w
835 w	823 m
820 m	808 w
790 w	788 w
758 s	758 s
688 w	685 w
670 w	667 w
645 w	642 w

As long as the minor shifts are recognized, the $Fe_2(Bipm)_3$ $(NO_3)_6$ complex is given all of the same vibrational assignments for the Bipm modes. The most interesting part of the spectrum comes from the bands which are assigned to nitrate modes. There are four bands which are assigned to nitrate vibrations: 1510 cm^{-1}, 1345 cm^{-1}, 1330 cm^{-1}, and 1278 cm^{-1}. All four bands are of nearly equal intensity. The central bands are shoulders to the free-ionic nitrate band centered at 1345 cm^{-1}. The bands at 1510 cm^{-1} and 1278 cm^{-1} correspond to monodentate coordinated nitrate modes. Although this

splitting is greater than that observed in the nickel 1:1 complex, it is still within the range of monodentate rather than bidentate coordination.

The proposed structure for $Fe(Bipm)_3(NO_3)_3$ assumes that the iron is octahedrally coordinated and that only Bipm molecules are coordinated to the metal ion. Each Bipm is bidentate and coordinated in the same fashion as that proposed for the $Ni(Bipm)_3(NO_3)_2$ complex and the Bipy analogs. (See Appendix I).
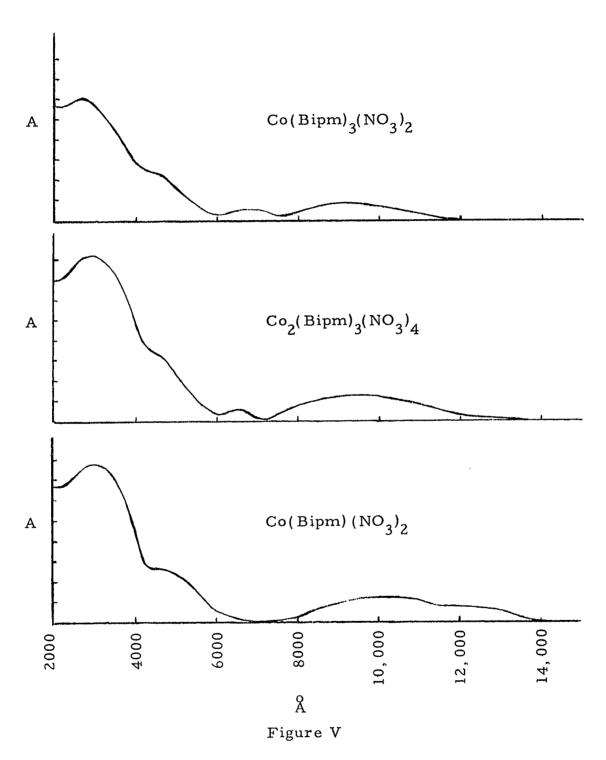
Since the infrared data indicated that the $Fe_2(Bipm)_3(NO_3)_6 \cdot$ complex has two types of nitrate ions, monodentate coordinated and free ions, the overall structure must take this into account. Borrowing what was learned from the nickel-Bipm complexes, the nitrate infrared data indicated that there was a mixture of Fe 1:3 and Fe 1:1 complexes in the $Fe_2(Bipm)_3(NO_3)_6$ compound. It appears from the synthetic data that a Fe 1:1, by itself, is not easily made. If the $Fe_2(Bipm)_3(NO_3)_6$ complex forms a polymer with alternating sites of iron coordinated to three Bipms, adjacent to the next iron coordinated to two nitrates and two Bipm molecules, the stoichiometry can be true without an actual 1:1 complex having been formed. Such a structure would have a continuous chain of metal to tetradentate bridged Bipm molecules, one terminal Bipm molecule on one metal atom with the adjacent metal atom having only two coordinated nitrate ions, and one free nitrate ion. (See Appendix I).

$Co(Bipm)_3(NO_3)_2$, $Co_2(Bipm)_3(NO_3)_4$, and $Co(Bipm)(NO_3)_2$

All three cobalt complexes of Bipm are light-colored. Both the $Co(Bipm)_3(NO_3)_2$ and the $Co_2(Bipm)_3(NO_3)_4$ complexes are light yellow-orange in color; their colors can be distinguished. The $Co(Bipm)(NO_3)_2$ complex precipitated and was collected as an orange-salmon pink product. After several days of evacuated desication, the 1:1 complex becomes predominently pink. Simultaneous with this change in appearance, trace solvent modes in the IR spectrum disappeared.

The yellow appearance of the cobalt complexes came as an initial surprise. Yellow cobalt complexes are usually observed only for Co(III) complexes. Unlike the iron-Bipm complexes, there is little reason for suspicion. The analogous tris-Bipy complexes of Co(II) were also found to be yellow (18), and the stoichiometric and magnetic moment data left little room for question.

Figure V demonstrates the diffuse reflectance electronic absorption spectra of the three cobalt-Bipm complexes. From the spectra, it can be seen that the v_3-$^4T_{1g}(P)$, $^4T_{1g}$ band appears as a shoulder on the charge transfer band. The v_2-$^4A_{2g}$, $^4T_{1g}$ bands are typically weak and are not observed in the 1:1 complex. The v_1-$^4T_{2g}$, $^4T_{1g}$ bands are broad, making exact absorption maxima assignments difficult.

A

Co(Bipm)$_3$(NO$_3$)$_2$

A

Co$_2$(Bipm)$_3$(NO$_3$)$_4$

A

Co(Bipm)(NO$_3$)$_2$

2000   4000   6000   8000   10,000   12,000   14,000

$\overset{\circ}{A}$

Figure V

ELECTRONIC ABSORPTION SPECTRA OF

COBALT-BIPM COMPLEXES

Table X lists the assignments of the cobalt-Bipm complexes.

These assignments cannot be considered highly accurate since the ν_3

assignments are taken from shoulders, and the ν_1 bands are very

broad. Calculations of the 10 Dq values and Racah parameters B

Table X

ELECTRONIC ABSORPTION ASSIGNMENTS OF

COBALT-BIPM COMPLEXES

Complex	$\nu_1 - {}^4T_{2g}, {}^4T_{1g}$	$\nu_2 - {}^4A_{2g}, {}^4T_{1g}$	$\nu_3 - {}^4T_{1g}(P), {}^4T_{1g}$	C. T.
$Co(Bipm)_3(NO_3)_2$	11,500	14,700	21,700	38,900
$Co_2(Bipm)_3(NO_3)_4$	10,870	15,130	21,300	34,400
$Co(Bipm)(NO_3)_2$	9,700		20,900	33,900

would be considered meaningless if the calculations were made from

these spectral assignments. In order to make such calculations, at

least two bands must be considered accurate. The ν_3 band should be

excluded because the maxima appear only as shoulders on the charge

transfer band. The ν_1 band is very broad, and the apparent maxima

are at higher wave numbers than would be appropriate for the ligand

field strength of Bipm (22).

Even though these spectra, as well as the spectra of other

Co(II) complexes are difficult to interpret, their interpretation is in

good agreement with the assignment of these complexes to an

octahedral Co(II) configuration. Tetrahedral Co(II) complexes and all Co(III) complexes have electronic absorption spectra which would have very poor fits with the spectra of these cobalt-Bipm complexes.

The magnetic moment data further supports the octahedral Co(II) configuration chosen for these complexes. The magnetic moments are 4.44, 4.27, and 4.19 B.M. for the respective 1:3, 2:3 and 1:1 cobalt complexes. These moments are considered low with respect to the typical high spin Co(II) complexes. They should range from 4.7 to 5.2 B.M. Further explanations of the magnetic moments are included in the appendix.

The infrared spectra of the cobalt-Bipm complexes are listed in Table XI. The spectrum of the Co 1:3 complex compares very closely to the 1:3 complexes of iron and nickel. Allowing for small shift differences in the Bipm modes, all bands are given the same assignments as they were in the iron and nickel 1:3 complexes. The infrared spectrum clearly shows the nitrate ions to be noncoordinated. The spectrum also shows that all Bipm molecules are coordinated.

Both the 2:3 and 1:1 complexes have extra absorption bands compared to the nickel 2:3 and 1:1 complexes. The extra bands are most noticeable in the regions where the coordinated nitrate ions absorb. In the 2:3 complex, the extra bands have weaker intensities and weaker splitting shifts than the normal monodentate nitrate. The 1:1 complex appears to have an equal number of stronger and weaker

Table XI

THE INFRARED SPECTRA OF COBALT-BIPM COMPLEXES

$Co(Bipm)_3(NO_3)_2$	$Co_2(Bipm)_3(NO_3)_2$	$Co(Bipm)(NO_3)_2$
3065 w	3080	3110
3040 w	3025	3080
2950 w		
2920 w	2920	2930
1576 s	1580 s	1582 s
	1572 s	1572 w
1557 s	1555 w	
	1480 s	1485 s
	1463 m	1463 s
		1430 w
1410 s	1414 s	1414 s
1345 s	1345 s	1303 w
1330 s	1332 s	1292 w
	1270 s	1272 s
1010 m	1025 m (multiple)	1018 m (multiple)
825 w	822 w	830-795 m (multiple)
760 s	755 s	751 s
	725 w	
692 m	693 m	687 m
	678 m	675 m
657 m	662 w	

split nitrate ions. A possible cause for this phenomena is a distortion in the octahedral symmetry about each cobalt ion. The distortion may be caused by the Jahn-Teller effect.

The absorption bands assigned to the nitrate modes in the 2:3 complex are 1480 cm^{-1}, 1463 cm^{-1}, 1345 cm^{-1}, 1332 cm^{-1} and 1270 cm^{-1}. The two types of monodentate nitrates are assigned to the 1480 cm^{-1} and 1463 cm^{-1} bands at the high end and at 1270 cm^{-1} at the low end. The 1270 cm^{-1} is more broad than usual and has the

appearance of a shoulder on the higher wave-number side. The broad band at 1345 cm^{-1} with shoulders at 1345 cm^{-1} and 1332 cm^{-1} was assigned to the free nitrate ions.

The nitrate modes of the 1:1 complex appear at 1485 cm^{-1}, 1463 cm^{-1} and 1272 cm^{-1}. The 1272 cm^{-1} band is, again, broad enough to accomodate the two types of monodentate nitrate splittings.

The proposed structure of the 1:3 complex is the same as that proposed for the nickel 1:3 and iron 1:3 complexes. The nitrate ions are all free, and the three Bipm molecules are bidentate. (See Appendix I).

The structure proposed for the 2:3 complex is the same as that proposed for the iron 2:3 complex, but not the same as the nickel 2:3 complex. The nitrate bands in the infrared spectrum indicate that there are both free ions and monodentate coordinated ions. The electronic absorption spectrum is unique in comparison with the 1:3 and 1:1 complexes. As such, it is not likely that the stoichiometry is made up of mixtures of 1:3 and 1:1 complexes. The proposed structure contains a polymer chain of metal atoms bound to bridging tetradentate Bipm molecules. On alternating metal atoms, there is an extra Bipm molecule adjacent to the next metal atom with two monodentate nitrate ions coordinated to it. The infrared data suggests that there is also a distortion from octahedral symmetry at the site of the metal atoms which have coordinated nitrate ions. (See Appendix I).
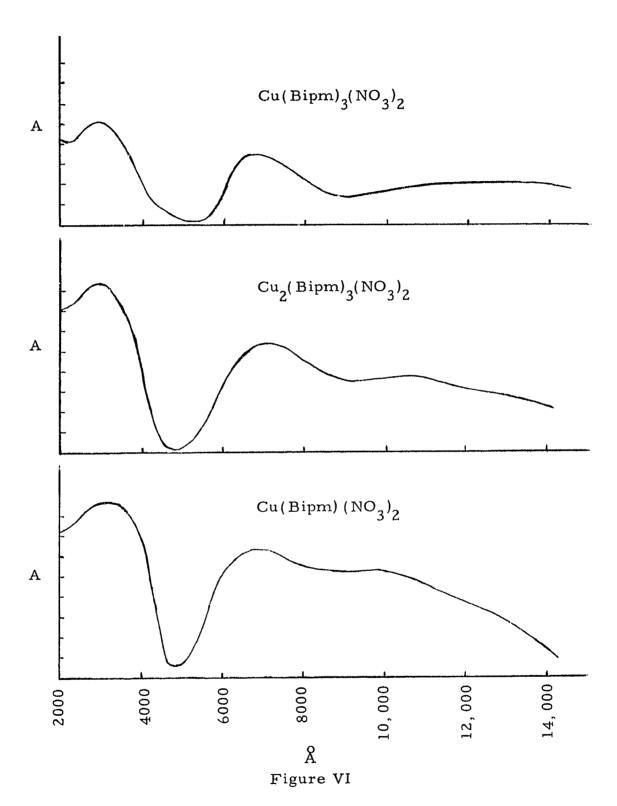
The 1:1 complex has only monodentate coordinated nitrate ions. Since the electronic absorption spectrum indicates that the cobalt is six-coordinate, each Bipm molecule must then be tetradentate. The proposed structure is a polymer chain of alternating metal and Bipm linkages with each metal atom having two nitrate ions also coordinated to it. This structure is identical to the one proposed for the nickel 1:1 complex, with the exception that each cobalt coordination sphere appears to be distorted from pure octahedral symmetry. (See Appendix I).

$Cu(Bipm)_3(NO_3)_2$, $Cu_2(Bipm)_3(NO_3)_4$, and $Cu(Bipm)(NO_3)_2$

The copper-Bipm complexes precipitate as blue to green products from their reaction mixtures. The dried products are dirty green for the 1:3 complex and blue-green for both the 2:3 and 1:1 complexes.

Figure VI contains the electronic absorption spectra of the three copper-Bipm complexes. The spectra show an interesting trend: as the ligand to metal ratio decreases, the absorption window in the visible region becomes more narrow. The intensity of absorption also increases with decreasing ligand to metal ratios. A further interesting observation is the high degree of absorption these complexes have in the near-infrared region. This phenomena is not unique to these copper complexes, however (22).

Table XII lists the absorption maxima for the copper-Bipm complexes. The maxima in the $14,500$ cm^{-1} region are low compared to the $16,000$ cm^{-1} bands of most copper complexes. The low

Figure VI

ELECTRONIC ABSORPTION SPECTRA OF

COPPER-BIPM COMPLEXES

position of these maxima is caused by the d-d transition sitting on the

tail of the large, broad near-infrared absorption.

Table XII

ELECTRONIC ABSORPTION MAXIMA OF

COPPER-BIPM COMPLEXES

Complex	ν_1	ν_2-C.T.
$Cu(Bipm)_3(NO_3)_2$	14,730	34,400
$Cu_2(Bipm)_3(NO_3)_4$	14,200	33,900
$Cu(Bipm)(NO_3)_2$	14,400	30,800

Jorgensen (23) was the first to observe the low energy absorp-

tion phenomena in tris-Bipy and tris-o-phen complexes of Cu(II).

The absorption was found to persist in solution, solid, and solid-

solid-solution phases of the copper complexes. He attributed the

absorption to a D_3 symmetry distortion of the octahedral Cu(II) ion.

In spectroscopy terminology, the $^2T_{2g}$ level is split into ^2E and $^2A_1$

levels. Palmer and Piper (24) made assignments of the $Cu(Bipy)_3^{2+}$

absorption bands using polarization spectroscopy. Their assignments

are $^2A_1$, ^2E for the 6,400 cm^{-1} absorption and ^2E, ^2E for the 14,400

cm^{-1} absorption.

Since the Bipm molecule has a geometry nearly identical to the

Bipy molecule, it is reasonable to assume that the $Cu(Bipm)_3(NO_3)_2$

complex, if not the 2:3 and 1:1 complexes, has the same D_3 symmetry

as the $Cu(Bipy)_3^{2+}$ complex. Three conclusions can be drawn from this assumption: (1) the copper-Bipm complexes are six coordinate and distorted; (2) the abnormally low position of the v_1 absorption band is caused by a distortion from octahedral symmetry; and (3) the Jahn-Teller distortion, although usually significant, is not as important as the distortion caused by the Bipm ligands alone.

The magnetic moments of the copper-Bipm complexes are 1.84, 1.82, and 1.56 for the respective 1:3, 2:3 and 1:1 compounds. These values are generally low for Cu(II) complexes. In fact, the entire set of magnetic moment data for all Bipm complexes, is low. Further explanations are covered in the appendix. These magnetic moments, however, supply additional evidence that the copper-Bipm complexes are composed of Cu(II) ions.

The distortion of the Cu(II) ion is also observed in the infrared spectra. More multiplicity is observed, and "extra" absorption bands are also seen. Table XIII contains the band assignments for the three copper-Bipm complexes.

The infrared spectrum of the copper 1:3 complex is a close match to the spectra of the other 1:3 Bipm complexes. For the 1:3 complex, a D_3 distortion from octahedral symmetry should have no net effect on the vibrational modes of the Bipm molecule. The Jahn-Teller distortion, however, should introduce some minor shifts and extra peaks. The extra bands which are observed are all of weak

intensity and in regions where little meaning other than minor distortions in symmetry can be attributed to their appearance. The nitrate mode in the 1:3 complex is clearly that of a free ion.

Table XIII

INFRARED SPECTRA BANDS OF THE COPPER-BIPM COMPLEXES

$Cu(Bipm)_3(NO_3)_2$ cm^{-1}	$Cu_2(Bipm)_3(NI_3)_4$	$Cu(Bipm)(NO_3)_2$ cm^{-1}
3080 w	3085 w	3100 w
3035 w		3060 w
2950 w		
2910 w		2920 w
	1600 w	1595 m
1576 s	1582 s	1580 s
1557 s	1562 s	1568 w
1470 w	1472 s	1508 s
1452 w	1459 w	
1410 s	1416 s	1417 s
	1391 m	1371 s
1343 s		
1330 s	1329 m	1323 s
	1301 m	1290 s
1013 w	1015 m	1045 m
1008 m	840 w	1005 s
835 w	830 w	830 m (multiple)
825 w	808 w	805 m
761 s	757 s	755 s
		742 m
693 m	693 m	695 m
658 m		683 m
639 w	672 m	672 m

The 2:3 complex, for some unknown reason, has only one weak peak in the C-H stretching region. An additional weak band in the C-H bend region, however, is observed at 1459 cm^{-1}. The most interesting shift observed in the infrared spectrum is seen in the

nitrate modes. Four bands assigned to nitrate modes are at 1472 cm^{-1}, 1391 cm^{-1}, 1329 cm^{-1} and 1301 cm^{-1}. The two bands at 1472 cm^{-1} and 1301 cm^{-1} are typical of monodentate coordinated nitrates. The unique bands are at 1391 cm^{-1} and 1329 cm^{-1}. These bands are quite sharp and definitely not just shoulders on a free nitrate ion band. There is no free nitrate ion band. The appearance of this doublet seems to indicate that some nitrate ions are very weakly coordinated. The weak splitting of the nitrate mode appears to be further evidence of a strong distortion from octahedral symmetry in the 2:3 complex.

The 1:1 complex has three regions of unique interest. The first region is where the C=N and C=C stretching modes are observed. A band at 1595 cm^{-1} has appeared with medium intensity. The only other Bipm complex with an observable band near 1595 cm^{-1} is the 2:3 copper complex. The band at 1568 cm^{-1} is quite weak. According to the correlation diagram of nickel complexes, the Bipm molecule must be highly symmetric with respect to the four nitrogens. If the Bipm molecule is being exposed to a twisting distortion, it would be possible to introduce a new, vibrationally active dipole (the 1595 cm^{-1} band) without destroying the symmetry of the four nitrogens.

The second region of interest contained the four nitrate modes at 1508 cm^{-1}, 1371 cm^{-1}, 1323 cm^{-1} and 1290 cm^{-1}. The two bands at 1508 cm^{-1} and 1290 cm^{-1} represent a strongly split monodentate

coordinated nitrate ion. The two center bands at 1371 cm^{-1} and 1323 cm^{-1} appear to be very weakly coordinated nitrate modes. All four bands are of equal intensity, indicating a 1:1 relationship of the strong and weak coordinated nitrates.

The third region of interest is where the C-H out-of-plane rocking modes absorb. McWhinnie (25) reported that trans complexes of bis-Bipy complexes have only two absorption bands in the 700-800 cm^{-1} region. On the other hand, some bis-octahedral and all trigonal bipyramidal bis-Bipy complexes show a splitting of the high wave-number band, giving three absorption bands in the 700-800 cm^{-1} region. Two conclusions were drawn in this article to explain the observations: (1) a cis-out-of-plane configuration alone introduces an asymmetry, accounting for the splitting; (2) the out of plane configuration tends to place each end of a given Bipy molecule in a different environment, thereby imposing each Bipy to a dipolar field.

The copper 1:1 complex has the same type of splitting in the 700-800 cm^{-1} region. The bands at 755 cm^{-1} and 742 cm^{-1} show a splitting which is not observed in any other Bipm complex. The comparable third band is the band observed around 693 cm^{-1} in all Bipm complexes. The fact that this splitting is observed only in the copper 1:1 complex may be helpful in deciding which explanation of McWhinnies has more credance. It is very likely that most of the Bipm complexes have the cis-out of plane configurations with respect

to the Bipm molecules in each complex. In some of the 2:3 complexes there appear to be local $M(Bipm)_2(NO_3)_2$ geometries. These complexes do not show any splitting in the C-H out of plane rocking region. The first explanation of McWhinnie's appears to be invalid.

The best evidence of splitting that McWhinnie observed was in the trigonal bipyramidal copper complexes. Although the copper 1:1 complex is apparently six coordinate, the fact that one nitrate ion is very weakly coordinated indicates a strong distortion in the complex. The limit of that distortion is a five coordinate trigonal bipyramid. From this evidence, it appears that the cause of the peak splitting is an environmental dipole field, rather than out of plane symmetry.

The proposed structure of the 1:3 copper Bipm complex is generally the same as that proposed for the other 1:3 complexes. The structure is probably more distorted than the others. (See Appendix I).

Proposing a structure for the 2:3 copper complex is difficult. The fact that no completely free nitrate ions are observed implies that no metal ion can have only Bipm molecules coordinated to it. The stoichiometry can be satisfied if the compound is in fact a mixture of 1:1 polymer with 1:2 monomers mixed in equal amounts. This possibility is rejected on the basis that certain distinctive infrared bands of the 1:1 complex are not present in the 2:3 spectrum. (See Appendix I).

The 1:1 complex appears to be a polymeric chain of metal ions bridged by tetradentate Bipm molecules. Each metal ion has one

strongly coordinated nitrate ion and one weakly coordinated nitrate

ion. All of the copper complexes appear to be six coordinate, but

they contain a high degree of distortion. (See Appendix I).

Thermal Stabilities of the Bipm Complexes:

Observations on the stability of the Bipm complexes were made

using standard melting point tubes and an oil bath. Table XIV con-

tains the observations which were made. The temperatures listed

Table XIV

THERMAL STABILITY OF BIPM COMPLEXES

Ligand to metal ratio	Fe	Co	Ni	Cu
1:3	270	305	310	230
2:3	250	315	330	230-248 l.d.
1:1		323	315	250 257 d.

are the points at which a color change is observed or the first appear-

ance of sublimed ligand is noticed in the melting point tube. As the

temperature increased, the samples remained solid and very slowly

decomposed. The copper 1:3 complex turned liquid and rapidly

decomposed at 248°C. The copper 1:1 complex underwent instant

decomposition at 257°C. Whether polymeric or not, the cobalt and

nickel complexes were the most stable thermally.

Spectrochemical Series:

Only the nickel complexes of Bipm have spectra where good values of $10D_q$ can be obtained. The value of $10D_q$ in the $Ni(Bipm)_3 (NO_3)_2$ complex is $12,300 \text{ cm}^{-1}$. This value is just below that of Bipy, but above ethylene diamine in the spectrochemical series (24). Considering the inductive effects of two extra nitrogens, the experimental placement in the series is exactly where it would be predicted.

SUMMARY

An improved procedure for the laboratory synthesis of 2, 2'-bipyrimidine was described. The procedure eliminated the DMF solvent which was used in the original synthesis reported by Bly and Mellon (8). The infrared absorption bands and the ultraviolet absorption bands of Bipm were reported. Proton magnetic resonance data of 2-bromopyrimidine and Bipm dissolved in DMF and deutero-chloroform were also reported.

Complexes of Bipm were prepared using the transition metal ions iron(III), cobalt(II), nickel(II) and copper(II). The complexes were prepared in a methanol-2, 2'-dimethoxypropane solvent medium. Reaction times varied from two to five days for the Bipm-hydrated metal nitrate mixtures to produce homogeneous products. Stoich-iometric analyses showed the products to have the formulae of $M^{n+}L_3A_n$, $M_2^{n+}L_3A_n$, and $M^{n+}LA_n$, where M represents the metal ion, L represents 2, 2'-bipyrimidine, and A represents the anions.

The infrared and electronic absorption bands of all products were reported. The spectroscopic data, combined with the magnetic moment data and the stoichiometric analyses, were used to propose structures for the Bipm complexes.

The proposed structure for the $M^{n+}L_3A_n$ complexes was typical of six coordinate complexes containing tris-bidentate ligands. A

close similarity in spectroscopic data was found for the tris-Bipm
and tris-Bipy complexes.

The proposed structure for the nickel 2:3 complex had a three
dimensional array of tetradentate Bipm bridges between every metal
ion and its nearest neighbor. All nitrates were found to be free ions.
Structures for the other $M_2^{n+}L_3A_n$ complexes were difficult to pro-
pose. The proposed structure of the iron and cobalt 2:3 complexes
introduced the concept of alternating sites of metal ions having two
different coordination environments in the same compound. At one
site a metal ion is surrounded by three Bipm molecules. At the
other site the metal ion has two Bipm molecules and two monodentate
nitrates also coordinated. Electronic absorption data was not able to
differentiate two types of metal ions in the iron and cobalt 2:3 com-
plexes. A structure for the copper 2:3 complex was not proposed,
although some possible structures were refuted.

All $M^{n+}LA_n$ complexes proved to be six coordinate, although
no iron 1:1 complex was found. The 1:1 complexes have a proposed
structure involving a linear polymer chain of metal ions bridged by
tetradentate Bipm molecules. Each metal ion also has two mono-
dentate coordinated nitrate ions. It was not possible to predict
whether the metal ions were in trans, cis or mixed configuration.

The following observations of Bipm complexes can be made:

(1) The Bipm ligand coordinates in both bidentate and tetradentate

fashions. (2) Bipm can form coordination polymers. (3) Bipm complexes tend to have six coordinate metal ions. (4) The ligand field strength of bidentate Bipm is just below Bipy, but above ethylenediamine. (5) The ligand field strength of tetradentate Bipm is less than bidentate Bipm.

The Bipm ligand appears to be unique in that the 1:3 complexes of iron(III) was found to be low spin, but relatively stable to reduction. The ligand field strength of Bipm appears to be just borderline for the high to low spin transition of iron(III) in the 2:3 complex.

The copper-Bipm complexes appeared to be distorted from octahedral symmetry beyond the point of typical Jahn-Teller distortion. The D_3 distortion that the Bipm ligands imparted to the copper ions allowed the electronic absorption data, as well as the infrared data and stoichiometric analyses to assign the copper ions as six coordinate. The apparent high degree of distortion in the copper 1:1 complex gave rise to two unique phenomena in its infrared spectrum. First, a nitrate ion showed a splitting pattern indicating that it was very weakly coordinated. Second, a splitting pattern was observed in a C-H out of plane rocking band of the Bipm molecule in the copper 1:1 complex. A correlation of the structure of the Bipm complexes and the observation of this splitting pattern indicated the cause of the splitting. The splitting appears to be caused by the Bipm molecule being exposed to a length-wise dipole field.

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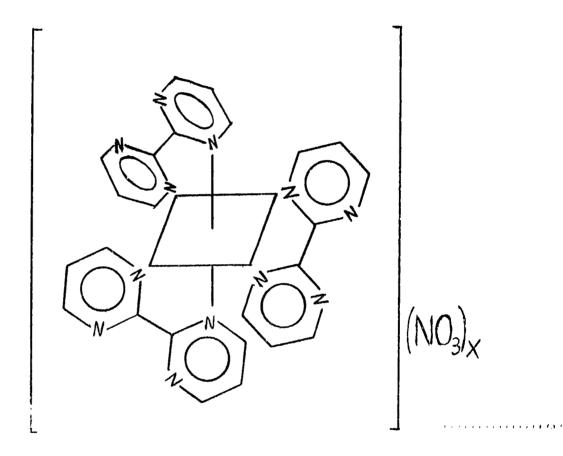
APPENDICES

APPENDIX I

FIGURE I

PROPOSED STRUCTURE OF $M(Bipm)_3(NO_3)_n$ COMPLEXES

FIGURE II
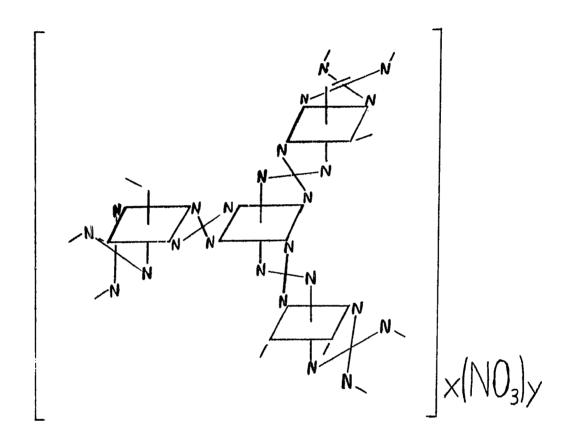
PROPOSED STRUCTURE OF $Ni_2(Bipm)_3(NO_3)_2$

FIGURE III

PROPOSED STRUCTURE OF IRON AND COBALT 2:3 COMPLEXES

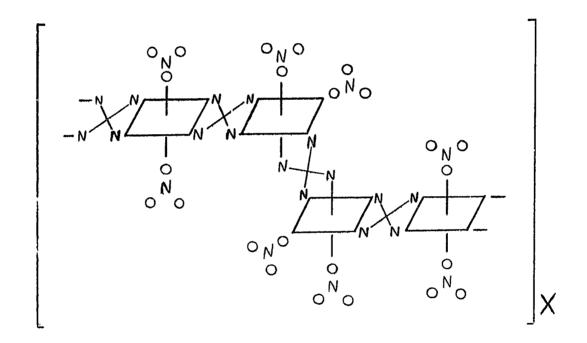FIGURE IV

PROPOSED STRUCTURE OF M(Bipm)A$_n$ COMPLEXES

APPENDIX II

MAGNETIC MOMENTS

As mentioned in the Experimental section, the magnetic sus-
ceptibility data was collected from a vibrating magnetometer. Al-
though the instrument used is capable of achieving good precision,
there were certain limitations of the instrument when used with
coordination compounds. A major drawback was the sample holder.
The holder was machined from teflon and was small in size. A
typical sample contained only .6 grams of complex. The high formula
weights of the Bipm complexes restricted the instrumental read-out
to the lower ranges and poor accuracy. There was also a difficulty
in calibrating the instrument. A sample of pure nickel was used as
a reference. In a vibrating magnetometer the geometry and ridgidity
of the sample holder is critical. The design of the sample holder is
such that it is difficult to achieve a well packed, rigid sample and
match the geometry of the nickel reference at the same time. It is
possible that the results tended to be low due to the difficulties of
achieving a good calibration. The magnetic susceptibility calculations
are based on a proportion of the instrument read-out with respect to
the nickel reference. Unfortunately the nickel reference cannot be
run at the same time as the sample.

Corrections for diamagnetism were based on two moles of
pyrazine being equal to one mole of 2, 2'-bipyrimidine. The value for
the pyrazine molecule was obtained from: The Chemical Rubber

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value of the metal ions was obtained from: Selwood, P. W., Mag-

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