COMPLEXES OF IRON(II) COBALT(II) NICKEL(II) AND COPPER(II) WITH 2-(α-PYRIDYLMETHYLENEAMINOMETHYL)-PYRIDINE

By

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INTRODUCTION

In the past 60 years there has been a great increase in interest in coordination compounds, particularly those of the transition metals. This increasing interest can be credited to the work of Alfred Werner, who did much in the way of developing and correlating valency and stereochemistry (40,41). In more recent years a number of investigations have been concerned with the magnetic properties of inorganic complexes, since the effective magnetic moment of an atom can be correlated with the bond type, coordination number, and stereochemistry of the atom (3,5, 6,7,8,15,35).

The purpose of the present investigation is to prepare complexes of iron(II), cobalt(II), nickel(II) and copper(II) chloride with the tridentate ligand 2-(α-pyridylmethyleneaminomethyl)pyridine (Structure I), which contains the -N=C-C=N-C-C=N- group, and to investigate their stereochemistry by means of magnetic, spectral and conductivity measurements. (The iron(II) perchlorate complex has been prepared (27) but the only study made of it was a determination of the room temperature magnetic moment.) This ligand contains three donor nitrogen atoms

and is constitutionally similar to that ligand which is familiarly known as terpyridine (2,6-bis-(α-pyridyl)-pyridine) (Structure II).

Terpyridine is a most important tridentate chelate compound that has been extensively studied. In 1953 a brief report was made on the preparation and use of 8-(α-pyridylmethyleneamino)quinoline (Structure III) as a tridentate chelate compound (11). This compound is constitutionally similar to terpyridine and so coordinates to iron(II) salts to give analogous diamagnetic complexes.

All of these tridentates are slightly acidic in that bases can remove one proton per coordinated tridentate residue from the complexes. Removal of the proton enhances conjugation and thus a greater resemblance to terpyridine complexes. An excellent example of this is the condensation product of 2-pyridinaldehyde with 2-pyridylhydrazine to form 1,3-bis-(2′-pyridyl)-2,3-diaza-1-propene (16) (Structure IV).

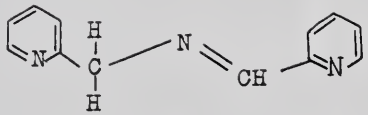
In any consideration of design of new tridentate chelate compounds related to terpyridine, cognizance must be taken of the availability of pyridine-2,6-dialdehyde (Structure V), which will condense with primary amines to give Schiff bases of the general formula VI, in which there is the same sequence of donor atoms and bonds as in terpyridine. When R = methyl, ethyl, phenyl or benzyl

groups, this ligand coordinates readily to give typical diamagnetic octahedral iron(II) complex salts, analogous to those of terpyridine.

Among the condensation products obtainable from V and primary amines are the linear polymers derivable from diamines, e.g. hexamethylenediamine (Structure VII). Reaction of this polymer with an excess of iron(II) sulfate leads to a solid composed of one molecule of iron(II) sulfate for each two residue of VII. This compound is ferromagnetic with a molar susceptibility of 155,000 x 10^{-6} c.g.s. units, but no conclusions regarding the molecular structure are drawn.

To understand the magnetic and spectral properties of these coordination compounds, recourse must be had to ligand field and molecular orbital theories (2,6,7,9,11, 14,18,23,25,28,29,30,31,32,36,38,39), the details of which will not be given here. The magnetic susceptibilities will be determined over a range of temperature since it is difficult to properly evaluate magnetic data obtained at room temperature only. It is now recognized that intra- or intermolecular antiferromagnetic interactions exist in a number of complexes and the existence of this phenomenon can be proved only by magnetic measurements over a range of temperature. A gross misinterpretation of the room temperature magnetic moment can be made by assuming that

the ground state level of a transition metal ion is always separated from the next higher level by $h\nu \gg kT$. However, if the spectral measurements provide the necessary data for an evaluation of the crystal field splitting, $10\ \underline{D}_q$, then they will also reveal the energy of separation between the ground state and the first excited state, thus allowing a more accurate evaluation of the magnetic data. Spectral measurements will be made both in solution and in the solid state to determine any change in stereochemistry upon dissolution of the complexes. Conductivity measurements will be made so as to determine whether or not the chloride ions are outside of the primary coordination sphere. Thus any change in stereochemistry upon dissolution, as revealed by the spectral measurements, will be quite important here.



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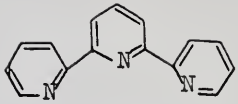

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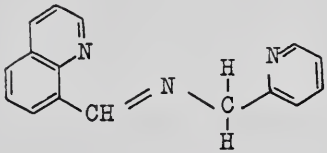

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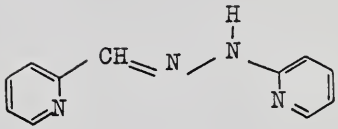

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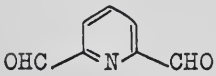

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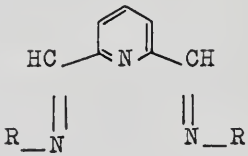

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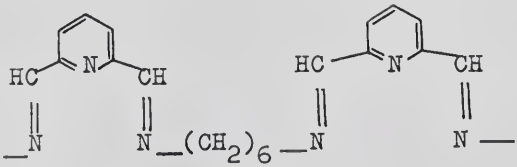

VII

EXPERIMENTAL PROCEDURES

Preparations and Analytical Data

Dichloro-2-(α-pyridylmethyleneaminomethyl)pyridine-iron(II).--To two ml. of aminomethylpyridine (0.018 mole) in 10 ml. of absolute ethanol was added 2 ml. of 2-pyridinaldehyde (0.018 mole), and the solution was gently refluxed 20 minutes and then cooled. To this was added 2.02 g. of iron(II) chloride tetrahydrate (0.009 mole) dissolved in 20 ml. of absolute ethanol. Precipitation was immediate and the slightly hygroscopic green-black microcrystalline product was separated from the mixture by filtering with suction, washed three times with 10 ml. portions of absolute ethanol, and dried over P_4O_{10} *in vacuo* for 12 hours at 25°C. and for 12 hours at 80°C. *Anal.* Calcd. for $[FeC_{12}H_{11}N_3Cl_2]\cdot H_2O$: C, 41.19; H, 3.22; N, 12.28. Found: C, 41.37; H, 3.81; N, 12.45.

Bis-[2-(α-pyridylmethyleneaminomethyl)pyridine-cobalt(II) chloride.--To two ml. of aminomethylpyridine (0.018 mole) in 10 ml. of absolute ethanol was added 2 ml. of 2-pyridinaldehyde (0.018 mole) and the solution was gently refluxed 20 minutes and then cooled. To this was added 1.68 g. of cobalt(II) chloride hexahydrate (0.007

mole) dissolved in 20 ml. of absolute ethanol. After cooling for 30 minutes precipitation was virtually complete and the pink microcrystalline product was filtered off by suction, recrystallized from absolute ethanol, washed with three 10 ml. portions of absolute ethanol, and dried over P_4O_{10} *in vacuo* for 12 hours at 25°C. and for 12 hours at 80°C. *Anal*. Calcd. for $[CoC_{24}H_{22}N_6]Cl_2 \cdot H_2O$: C, 53.14; H, 4.38; N, 14.88. Found: C, 53.35; H, 4.90; N, 14.69.

Bis-[2-(α-pyridylmethyleneaminomethyl)pyridine-nickel(II) chloride.--This complex was prepared in a manner analogous to that of the above cobalt(II) complex. *Anal*. Calcd. for $[NiC_{24}H_{22}N_6]Cl_2 \cdot H_2O$: C, 53.24; H, 4.46; N, 15.00. Found: C, 52.91; H, 4.57; N, 14.79.

Chloro-2-(α-pyridylmethyleneaminomethyl)pyridine-copper(II) chloride.--To two ml. of aminomethylpyridine (0.018 mole) in 10 ml. of absolute ethanol was added 2 ml. of 2-pyridinaldehyde (0.018 mole), and the solution was gently refluxed 20 minutes and then cooled. To this was added 1.36 g. of copper(II) chloride dihydrate (0.008 mole) without excessive stirring. After immediate precipitation the excess liquid was decanted off, absolute ethanol added, the mixture briskly stirred and cooled, and the pale green microcrystalline product was then filtered off, washed with three 10 ml. portions of absolute ethanol, and

dried over P_4O_{10} *in vacuo* for 12 hours at 25°C. and for 12 hours at 80°C. *Anal.* Calcd. for $[CuC_{12}H_{11}N_3Cl]Cl \cdot H_2O$: C, 41.22; H, 3.72; N, 12.00. Found: C, 41.06; H, 3.31; N, 11.80.

All analytical measurements were made by Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

Apparatus

Magnet.--The magnetic susceptibilities of the complexes were determined by the Gouy method. The magnetic field was produced by means of a Varian Associates Model V-4004, 4" electromagnet equipped with 4" cylindrical pole pieces. The magnet was used in conjunction with a Varian Associates Model V-2300-A power supply and a Varian Associates Model V-2301-A current regulator, which was used to maintain constant current ($\pm$ 1 x 10^{-3} amp).

The 4" pole pieces, separated by a 2-1/4" air gap, gave a maximum field strength of 6,800 gauss. The magnetic field was calibrated by using standard solutions of nickel(II) chloride, water, and solid nickel ammonium sulfate-6-hydrate.*

Temperature control.--The temperature control apparatus followed the basic design of Figgis and Nyholm (15) and Clevenger (3).

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*See Appendix I.

To determine the period of time required for the sample to reach thermal equilibrium after the cryostat had attained the desired temperature, the force acting on the sample was measured at five minute intervals until the measured force became constant. It was determined that between thirty and forty-five minutes were required for the sample to reach thermal equilibrium within the cryostat.

Cryostat.--The cryostat used was a pyrex model following the basic design of Figgis and Nyholm (15) and Clevenger (3).

Sample tube.--A quartz sample tube, approximately 3.5 mm. inside diameter, was fitted with a tapered teflon stopper. The tube was suspended in the cryostat, from the balance, by a gold chain. The sample tube was calibrated for a volume of 2 ml. by using water delivered from a calibrated T.D. pipette. The position of the meniscus was marked by etching with hydrogen fluoride. The sample tube was approximately 18.6 cm. in length, so that the sample might extend from the region of maximum field strength to a region of negligible field strength. A quartz sample tube was used so as to eliminate the large paramagnetism which was obtained with the pyrex sample tubes. The small diamagnetic correction for the quartz tube was determined as a function of temperature.*

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*See Appendix II.

Balance.--A Mettler Model B-6 semi-micro balance of 0.01 mg. sensitivity was used to measure the force exerted by the magnetic field upon the sample.

Conductivity measurements.--All conductances were measured using an Industrial Instruments Inc. Model RCM 15 B1 Serfass Conductivity Bridge and a cell with a cell constant of 1.4659 cm^{-1}. All measurements were made at 25°C. in absolute ethanol, and in tetrahydrofuran, using 10^{-3} M solutions. A silicone oil bath, regulated by a Sargent Thermonitor, Model SW, was used to maintain constant temperature.

Molecular weight determinations.--A Mechrolab Model 302 Vapor Pressure Osmometer, with tetrahydrofuran as the solvent, was used to determine the molecular weights of the complexes.

Spectrophotometer.--A Cary Model 14 Recording Spectrophotometer was used to determine the ultra-violet, visible and near infrared solution spectra of the complexes. A Cary Model 1411 Diffuse Reflectance Accessory was employed to determine the solid state spectra of the complexes. A Perkin-Elmer Corporation Model 21 Recording Infrared Spectrophotometer was used to determine the infrared spectra of the complexes.

RESULTS

Magnetic Data

The complexes that were prepared, isolated and identified are bis-[2-(αpyridylmethyleneaminomethyl)-pyridine]cobalt(II) chloride, bis-[2-(α-pyridylmethylene-aminomethyl)pyridine]nickel(II) chloride, dichloro-2-(α-pyridylmethyleneaminomethyl)pyridineiron(II), and chloro-2-(α-pyridylmethyleneaminomethyl)pyridinecopper(II) chloride. The magnetic moments of these complexes determined at room temperature and two different field strengths are reported in Table 1.

TABLE 1

MAGNETIC MOMENTS AT 299°K

Complex	μ_{eff}[a] (B.M.)	μ_{eff}[b] (B.M.)
$[Fe(PMP)Cl_2]$[c]	3.49	3.11
$[Co(PMP)_2]Cl_2$	4.63	4.63
$[Ni(PMP)_2]Cl_2$	3.08	3.08
$[Cu(PMP)Cl]Cl$	2.15	1.98

[a]Field Strength = 6,770 Gauss.

[b]Field Strength = 5,860 Gauss.

[c]The ligand 2-(α-pyridylmethyleneaminomethyl)-pyridine is abbreviated as PMP.

The magnetic susceptibility of each complex was determined as a function of temperature (from approximately 90°K to the sample decomposition temperature), and were found to exhibit normal temperature dependence (Figures 1,2,3,4). A Curie constant, C, and a Weiss constant, θ, which were evaluated for each complex, are reported in Table 2.

TABLE 2

CURIE AND WEISS CONSTANTS FOR NORMAL TEMPERATURE DEPENDENT COMPLEXES

Complex	C	θ°	μ_a* (B.M.)	μ_o* at 299°K (B.M.)
$[Fe(PMP)Cl_2]$	1.58	11.53	3.57	3.49
$[Co(PMP)_2]Cl_2$	2.64	20.60	4.70	4.63
$[Ni(PMP)_2]Cl_2$	1.30	16.20	3.23	3.08
$[Cu(PMP)Cl]Cl$	.672	35.62	2.33	2.15

$$\mu_a = 2.84 \sqrt{C}$$

The susceptibilities were corrected for the diamagnetism of the ligands and metal ions (40)+ and are reported, together with the corresponding magnetic moments and temperatures, in Tables 3, 4, 5 and 6.

*Field Strength = 6,770 Gauss.
+See Appendix III.

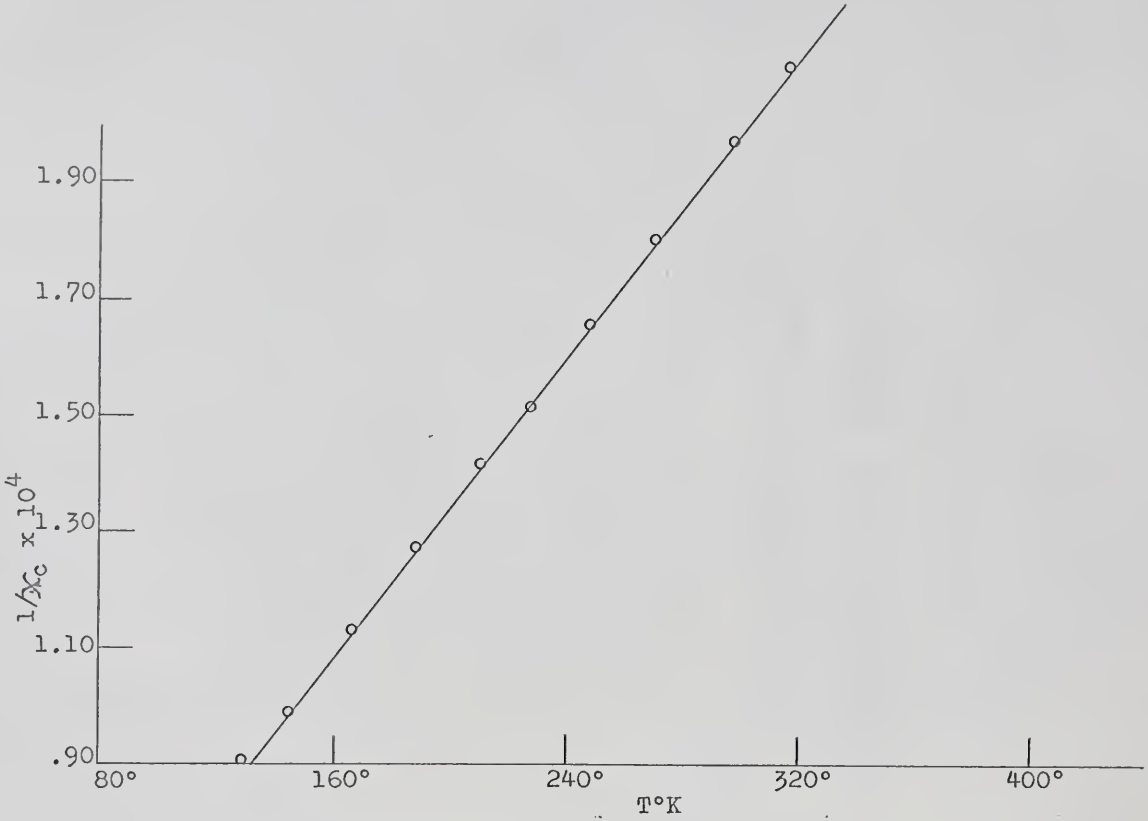

Fig. 1.--Temperature dependent susceptibility of $[Fe(PMP)Cl_2]$

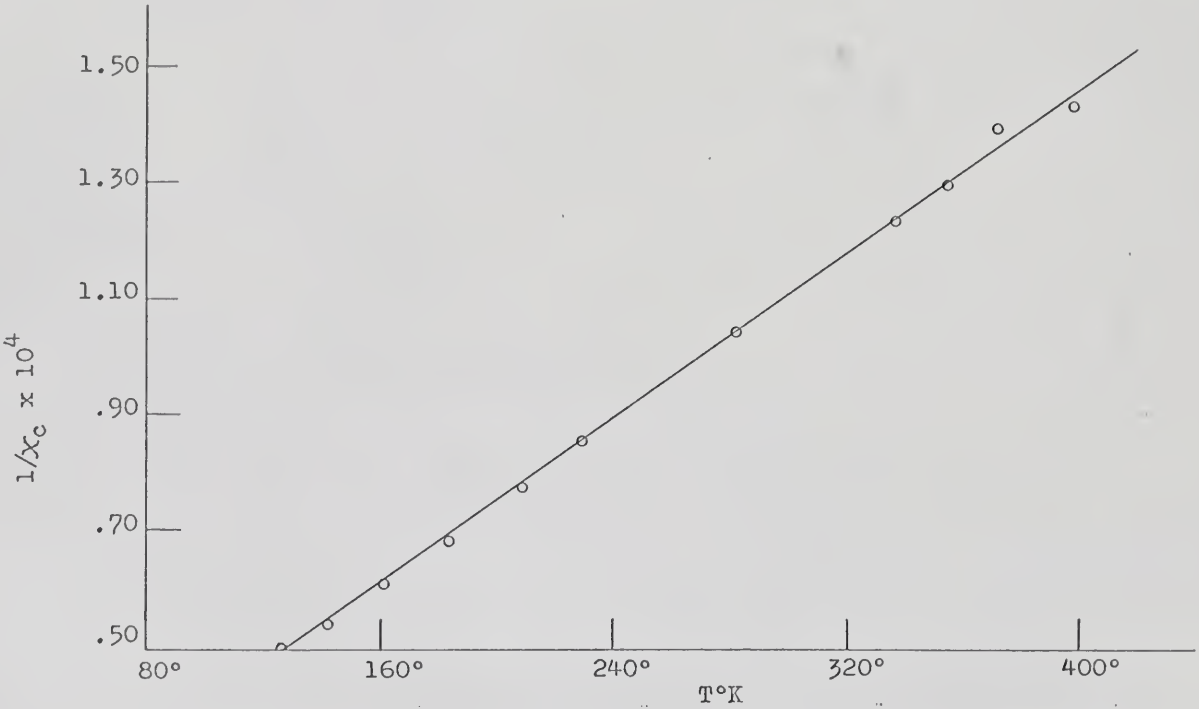

Fig. 2.--Temperature dependent susceptibility of $[Co(PMP)_2]Cl_2$

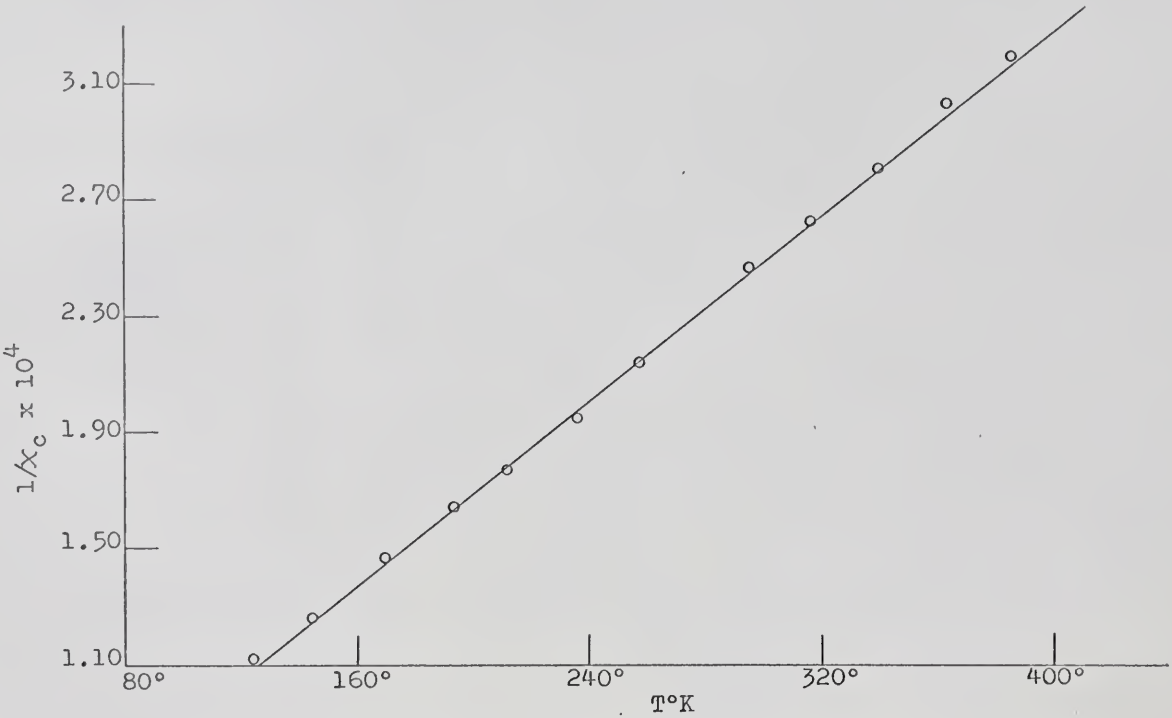

Fig. 3.--Temperature dependent susceptibility of $[Ni(PMP)_2]Cl_2$

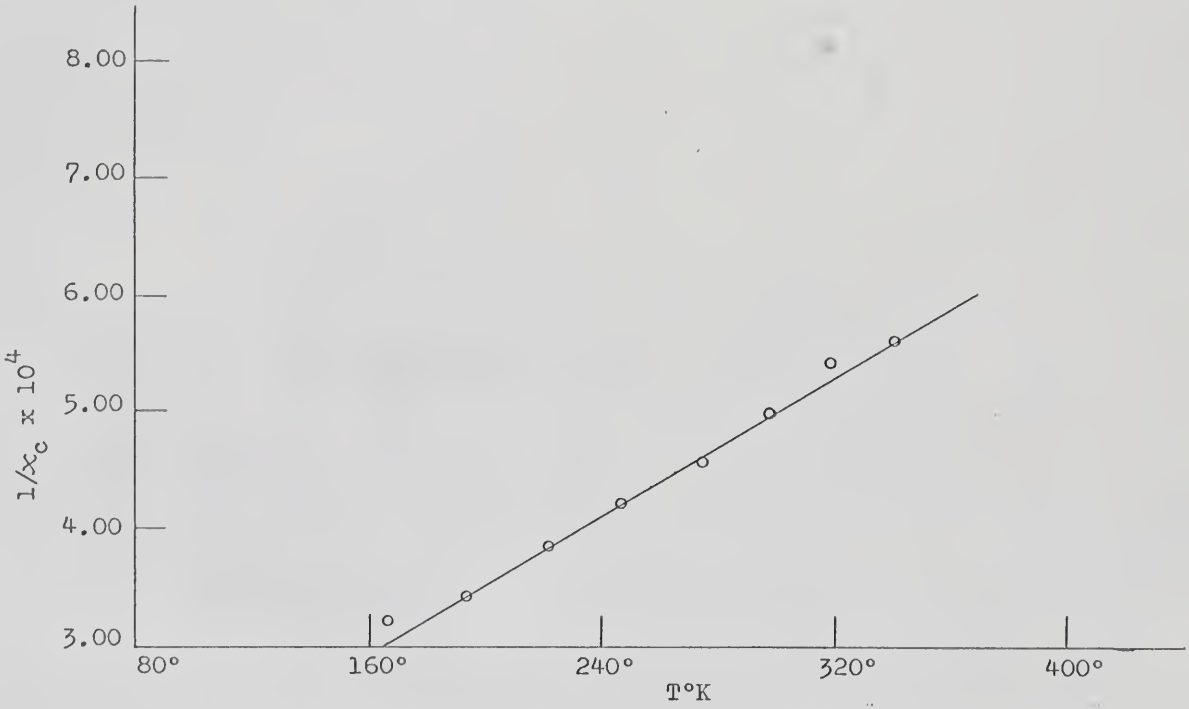

Fig. 4.--Temperature dependent susceptibility of [Cu(PMP)Cl]Cl

TABLE 3

VARIATION OF MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF $[Fe(PMP)Cl_2]$ WITH TEMPERATURE

T°K	$\chi_c \times 10^6$ (c.g.s.units)	μ_{eff}[a] (B.M.)	μ_{eff}[b] (B.M.)
129.8	11245	3.40	3.11
146.2	10105	3.45	3.17
167.7	8900	3.47	3.17
189.1	7920	3.46	3.22
212.2	7100	3.48	3.21
228.6	6655	3.51	3.26
250.1	6070	3.50	3.28
271.5	5575	3.49	3.27
300.2	5105	3.51	3.30
319.4	4790	3.52	3.30

[a]Field Strength = 6770 Gauss

[b]Field Strength = 5860 Gauss

TABLE 4

VARIATION OF MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF $[Co(PMP)_2]Cl_2$ WITH TEMPERATURE

T°K	$\chi_c \times 10^6$ (c.g.s.units)	μ_{eff} (B.M.)
124.6	19816	4.49
139.7	18370	4.54
160.2	16251	4.58
181.8	14572	4.62
206.8	12889	4.64
227.6	11677	4.62
299.1	9160	4.70
336.3	8147	4.70
354.1	7744	4.70
371.3	7193	4.64
397.0	7004	4.73

TABLE 5

VARIATION OF MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF $[Ni(PMP)_2]Cl_2$ WITH TEMPERATURE

T°K	$\chi_c \times 10^6$ (c.g.s.units)	μ_{eff} (B.M.)
125.1	8981	3.01
145.2	7896	3.04
170.4	6841	3.07
193.5	6103	3.08
211.8	5664	3.11
236.8	5156	3.14
257.6	4706	3.13
296.2	4060	3.11
318.0	3822	3.13
341.3	3568	3.14
364.7	3317	3.12
387.0	3139	3.13

TABLE 6

VARIATION OF MOLAR SUSCEPTIBILITIES AND MAGNETIC MOMENTS OF [Cu(PMP)Cl]Cl WITH TEMPERATURE

T°K	$\chi_c \times 10^6$ (c.g.s.units)	μ_{eff}[a] (B.M.)	μ_{eff}[b] (B.M.)
166.3	3240	2.08	1.91
192.7	2900	2.12	1.96
221.4	2600	2.15	2.01
246.5	2365	2.17	2.02
273.9	2200	2.21	2.04
296.9	2005	2.19	2.04
318.5	1860	2.19	2.06
340.0	1775	2.20	2.06

[a]Field Strength = 6770 Gauss

[b]Field Strength = 5860 Gauss

Conductivity Data

The specific conductance of each complex, which was determined at 25°C, is reported in Table 7.* The conductance values for the cobalt(II) and nickel(II) complexes are within the range of those expected for complexes of the type $[ML_2]Cl_2$. The data for the copper(II) complex indicate that it is of the type [MLCl]Cl. The iron(II) complex is indicated to be of the type $[MLCl_2]$. The low conductivity of this complex probably results from a solvation reaction in which the chloride ions undergo a slight dissociation.

TABLE 7

SPECIFIC CONDUCTANCES AT 25°C

Complex	Concentration (moles per liter)	K (ohm^{-1} $cm.^{-1}$)	
$[Fe(PMP)Cl_2]$	1×10^{-3}	20.9[a]	4.3[b]
$[Co(PMP)_2]Cl_2$	1×10^{-3}	44.7	36.8
$[Ni(PMP)_2]Cl_2$	1×10^{-3}	42.1	39.2
[Cu(PMP)Cl]Cl	1×10^{-3}	31.7	19.4

[a]Ethanol Solution.
[b]Tetrahydrofuran Solution.
*See Appendix IV.

Molecular Weight Determinations

The values determined for the cobalt(II) and nickel(II) complexes are within the range of those expected for complexes of the type $[ML_2]Cl_2$. Despite the low solubility of the iron(II) and copper(II) complexes in tetrahydrofuran, the values found indicate that these species are uni-molecular, in solution, with only one tridentate ligand, PMP, around each metal ion. The values are reported in Table 8.*

TABLE 8

MOLECULAR WEIGHTS

Complex	Values (a.m.u.) Calculated	Observed
$[Fe(PMP)Cl_2]$[a]	324	300
$[Co(PMP)_2]Cl_2$[b]	524	550
$[Ni(PMP)_2]Cl_2$[b]	524	560
$[Cu(PMP)Cl]Cl$[a]	332	350

Spectroscopic Data

The results from the spectral measurements are reported in Tables 9, 10, 11, 12, and 13.

[a]Concentration = .03m.
[b]Concentration = .08m.
*See Appendix V.

TABLE 9

ABSORPTION MAXIMA AND MOLAR EXTINCTION COEFFICIENTS DETERMINED FROM THE ULTRA-VIOLET SPECTRA OF LIGAND AND COMPLEXES

Wavelengths (angstrom units)	Concentrations (moles per liter)	Molar Extinction Coefficients
PMP		
2450	2×10^{-4}*	8.5×10^{3}
$[Fe(PMP)Cl_2]$		
2665	1×10^{-4}	1.2×10^{4}
$[Co(PMP)_2]Cl_2$		
2475	1×10^{-4}	7.7×10^{3}
2560	1×10^{-4}	9.6×10^{3}
$[Ni(PMP)_2]Cl_2$		
2500	1×10^{-4}	4.4×10^{3}
2620	1×10^{-4}	9.5×10^{3}
[Cu(PMP)Cl]Cl		
2500	1×10^{-4}	2.0×10^{4}
2900	1×10^{-4}	1.5×10^{4}

*Not isolated from solvent.

TABLE 10

ABSORPTION MAXIMA AND MOLAR EXTINCTION COEFFICIENTS DETERMINED FROM THE VISIBLE SPECTRA OF LIGAND AND COMPLEXES

Wavelengths (angstrom units)	Concentrations (moles per liter)	Molar Extinction Coefficients
PMP		
3750	1×10^{-2}*	1.4×10^{2}
$[Fe(PMP)Cl_2]$		
3520	1×10^{-4}	1.4×10^{3}
4800	1×10^{-3}	1.3×10^{2}
5750	1×10^{-3}	1.1×10^{3}
$[Co(PMP)_2]Cl_2$		
5175	1×10^{-2}	1.5×10^{2}
5550	1×10^{-2}	1.3×10^{2}
$[Ni(PMP)_2]Cl_2$		
5800	1×10^{-2}	1.2×10^{2}
[Cu(PMP)Cl]Cl		
3730	1×10^{-3}	1.5×10^{2}
3900	1×10^{-3}	1.4×10^{2}
5050	1×10^{-3}	1.1×10^{2}

*Not isolated from solvent.

TABLE 11

ABSORPTION MAXIMA DETERMINED FROM THE SOLID STATE VISIBLE SPECTRA OF THE COMPLEXES

Wavelengths (angstrom units)
$[Fe(PMP)Cl_2]$
4850
5900
$[Co(PMP)_2]Cl_2$
5100
5500
$[Ni(PMP)_2]Cl_2$
4450
5750
]Cu(PMP)Cl]Cl
5050

TABLE 12

ABSORPTION MAXIMA DETERMINED FROM THE SOLID STATE NEAR INFRARED SPECTRA OF THE COMPLEXES

Wavelengths (angstrom units)
$[Co(PMP)_2]Cl_2$
10600
$[Ni(PMP)_2]Cl_2$
8100
9700

TABLE 13

INFRARED ABSORPTION BANDS ($cm.^{-1}$) FOR 2-(α-PYRIDYLMETHYLENEAMINOMETHYL)-PYRIDINE AND ITS COMPLEXES

Assignment	PMP	$[Fe(PMP)Cl_2]$	$[Co(PMP)_2]Cl_2$	$[Ni(PMP)_2]Cl_2$	$[Cu(PMP)Cl]Cl$
st CH	2820 vw 2945 vw	2875 vw 2995 vw	2875 vw 2950 vw	2940 vw 2975 w	2880 2998
st C=N (acylic)	1650 m	--	1627 m	1643 m	1648 m
Band I (py ring)	1590 s	1595 s	1595 s	1585 s	1588 s
Band II (py ring)	1560 (sh)	1562 (sh)	1562 (sh)	1562 (sh)	1562 (sh)
Band III (py ring)	1460 s	1458 s	1471 s	1462 s	1462 s
Band IV (py ring)	1420 s	1424 s	1428 s	1425 s	1424 s
d CH (py ring)	1130 s 1037 s	1147 s 1045 s	1137 s 1044 s 747 m	1142 s 1042 s	1143 s 1042 s
	754 m 772 m(b)	757 m(b) --	772 m(b)	747 m 772 m(b)	-- 772 (sh)

DISCUSSION

A number of complexes formed between iron(II), cobalt(II), nickel(II) and copper(II) and tridentate ligands containing the basic terpyridine linkage have been prepared by Lions and coworkers (11,16,17,27). Many of the ligands formed bis-tridentate complexes with the metal ions, i.e., six-coordination compounds of the type $[ML_2]Cl_2$. However, some ligands, e.g. 2-methyl-8-(6 - methyl-α-pyridylmethyleneamino)quinoline, formed only one-to-one complexes with copper(II) of the type [CuLCl]Cl, and complexed not at all with iron(II), while others formed complexes of iron(II), cobalt(II), nickel(II) and copper(II) of the type $[MLCl_2]$, in which the ligands are assumed to function as bi- or tridentates, with four- or five-coordination. The existence of polymeric structures in the solid state has not been definitely precluded.

During the present investigation complexes of iron(II), cobalt(II), nickel(II) and copper(II) with the tridentate ligand, 2-(α-pyridylmethyleneaminomethyl)-pyridine (PMP), were prepared and studied. This ligand contains the basic terpyridine linkage, -N=C-C=N-C-C=N-.

It has been definitely proven that, in the case of the cobalt(II) and nickel(II) complexes, two of the tridentate ligands (PMP) are coordinated to each metal ion, forming six-coordinate complexes. The stereochemistries of the iron(II) and copper(II) complexes are not definitely assigned.

The cobalt(II) complex, $[Co(PMP)_2]Cl_2$, was found to have a room temperature magnetic moment of 4.63 B.M. Spin-free octahedral cobalt(II), a $\underline{d}^7$ ion, has a $^4\underline{T}_{1g}$ ground state, which provides an orbital contribution to the magnetic moment. The value of the magnetic moment expected, based on this ground state, is 4.1 B.M. The larger value observed, which is in accord with the magnetic moments of many high-spin octahedral cobalt(II) complexes, can be explained on the basis of spin-orbit coupling which mixes in some of the higher levels having orbital angular momentum with the ground state.

Octahedral nickel(II), a $\underline{d}^8$ ion, has a $^3\underline{A}_{2g}$ ground state which provides no orbital contribution to the magnetic moment. The magnetic moment expected on the basis of this ground state is 2.8 B.M. The observed value, 3.08 B.M., is justified by the existence of higher levels having orbital angular momentum that can be mixed with the ground state <u>via</u> the mechanism of spin-orbit coupling.

The copper(II) complex has a room temperature magnetic moment of 2.15 B.M. This complex was found to be field strength dependent in that as the field strength was decreased, the value of the magnetic moment also decreased, thus indicating some form of metal-to-metal interaction.

Analytical data indicate that the complex is either four- or five-coordinate. The low conductances make it extremely difficult to determine whether the complex is of the type [MLCl]Cl, i.e. four-coordination with one chloride ion outside of the primary coordination sphere, or of the type $[MLCl_2]$, i.e. five-coordination with the conductivity values being due to a solvation reaction in which some of the chloride ions are replaced by solvent molecules. Because of the propensity of copper(II) complexes toward square-planar four-coordination and because of the existence of similar compounds prepared by Lions (17), this complex is assumed to be four-coordinate square-planar.

The metal-to-metal interaction could possibly arise through a direct copper-to-copper coupling mechanism, as in the copper(II) acetate complex (13), but ligand steric effects make this seem unlikely. A copper-to-chloride-to-copper coupling, a super-exchange phenomenon analogous to that found in systems such as FeO, CoO, or MnO, cannot be definitely excluded here.

A similar problem arises in the interpretation of the magnetic and analytical data of the iron (II) complex. High-spin octahedral iron(II) complexes normally have magnetic moments around 5.1 B.M., while the low-spin systems have moments around .5 B.M. The only four-coordinate square-planar iron(II) complex that has been well characterized is the phthalocyanine complex, which has a room temperature magnetic moment of 3.96 B.M. The room temperature magnetic moment of the iron(II) complex presently being studied was found to be 3.49 B.M. and is also field strength dependent. With the analytical data indicating four- or five-coordination, it is difficult to make a plausible stereochemistry assignment. If the complex is assumed to be four- or five-coordinate in solution, it could conceivably increase its coordination number to six in the solid state through the formation of chloride bridges, at the same time providing a mechanism for metal-to-metal interaction. However, this cannot be definitely concluded and the question must remain open.

For the cobalt(II) complex in solution, four absorption bands were observed: two in the ultra-violet region, at 2,475 A and 2,560 A, which were assigned to electronic transitions on the ligand, and two in the visible region, at 5,175 A and 5,550 A. In the solid state three absorption bands were observed: two in the visible region,

at 5,100 A and 5,500 A, and one in the near infrared region, at 10,600 A. The absorption maximum at 10,600 A (9,450 cm^{-1}) is assigned as the $^4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$ transition, thus giving a value of 1180 $cm.^{-1}$ for D_q. The absorption in the visible region from the solid state spectra and the solution spectra are assumed to arise from the same transitions. Thus the absorption at 5,500 A (18,200 $cm.^{-1}$) is assigned as the $^4T_{1g}(F) \longrightarrow {}^4A_{2g}(F)$ transition and the absorption at 5,100 A (19,600 $cm.^{-1}$) is assigned as the $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ transition (Figure 5).

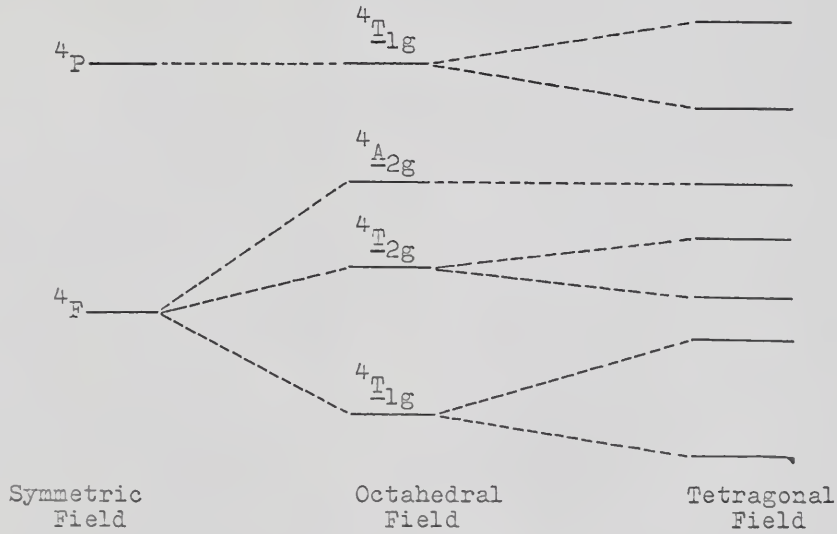

Fig. 5.--Energy states which arise from the ^4F and ^4P term states of a d^7 ion in a regular and tetragonally distorted octahedral field.

Using the value of $\underline{D}_q$ determined from the $^4\underline{T}_{1g}(F) \longrightarrow {}^4\underline{T}_{2g}(F)$ transition, the absorption values for the transitions $^4\underline{T}_{1g}(F) \longrightarrow {}^4\underline{A}_{2g}(F)$ and $^4\underline{T}_{1g}(F) \longrightarrow {}^4\underline{T}_{1g}(P)$ are calculated to be, respectively, 4,700 A (21,300 cm.$^{-1}$) and 4,450 A (22,500 cm.$^{-1}$). These calculations are based on transitions for regular octahedral complexes and no allowances are made for tetragonal distortion. Thus the validity of the assignments is not questioned because of the discrepancies between the calculated and observed values. Indeed, the absorption at 5,500 A agrees closely with that found at 5,530 A in the $[Co(terpy)_3]^{++}$ complex and assigned as the $^4\underline{T}_{1g}(F) \longrightarrow {}^4\underline{A}_{2g}(F)$ transition (19).

From the solution spectra of the nickel(II) complex three absorptions were observed: two in the ultra-violet region, at 2,500 A and at 2,620 A, which were assigned as charge-transfer bands, and one in the visible region at 5,800 A (17,300 cm.$^{-1}$). From the solid state spectra four absorptions were observed: two in the visible range, at 4,450 A (22,500 cm.$^{-1}$) and at 5,750 A (17,400 cm.$^{-1}$), and two in the near infrared region, at 8,100 A (12,350 cm.$^{-1}$) and at 9,700 A (10,300 cm.$^{-1}$). The band at 5,750 A from the solid state spectra and the band at 5,800 A from the solution spectra are assigned as the same transition.

If the absorption at 8,100 A is assigned as the $^3\underline{A}_{2g}(F) \longrightarrow {}^3\underline{T}_{2g}(F)$ transition, then a value of 1,235 cm.$^{-1}$

is found for D_q. The maximum at 9,700 A is assigned as the $^3A_{2g}(F) \longrightarrow {}^1E_g(D)$ transition, while the band at 5,800 A is assigned as the $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(F)$ transition. These observed values are only slightly lower than those of the $[Ni(dipy)_3]^{++}$ and $[Ni(terpy)_2]^{++}$ complexes (1,19,34). The absorption maximum at 4,450 A could only be tenuously assigned to the $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$ transition (Figure 6).

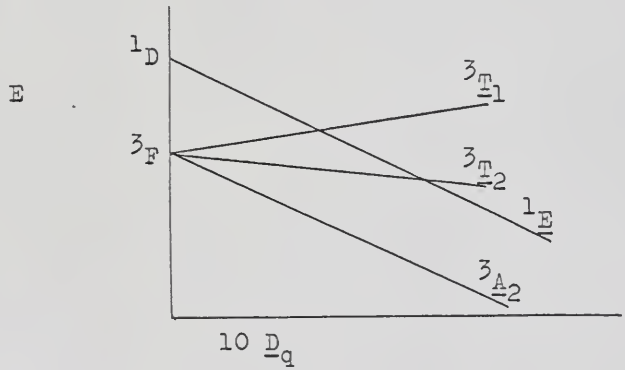

Fig. 6.--Partial energy level diagram for a d^8 ion in an octahedral field, showing the triplet states and the lowest singlet state.

From the spectra of the iron(II) complex six absorptions were observed: one at 2,665 A, from the ultraviolet solution spectra, and assigned as an electronic transition on the ligand; three from the visible solution

spectra, at 3,520 A (28,400 cm.$^{-1}$), at 4,800 A (20,800 cm.$^{-1}$) and at 5,750 A (17,400 cm.$^{-1}$); and two from the solid state visible spectra, at 4,850 A (20,600 cm.$^{-1}$) and at 5,900 A (16,950 cm.$^{-1}$). The absorptions at 4,800 A from the solution spectra and 4,850 A from the solid state spectra were assigned as the same transition. There is some doubt as to whether the absorptions at 5,750 A from the solution spectra and 5,900 A from the solid state spectra arise from the same transition. In the absorption spectra of the $[Fe(H_2O)_6]^{++}$ complex, a band composed of two maxima is found at 10,000 cm.$^{-1}$ and 12,000 cm.$^{-1}$, which is identified as the $^5\underline{T}_{2g}(D) \longrightarrow {}^5\underline{E}_g(D)$ transition (Figure 7), split because of a Jahn-Teller effect (21,26). Since the ligand field of PMP is greater than that of water, the absorptions are expected to occur at higher values. Thus the absorptions at 5,750 A and 5,900 A are tentatively assigned as the $^5\underline{T}_{2g}(D) \longrightarrow {}^5\underline{E}_g(D)$ transition, while the remaining peaks are supposedly the transitions $^5\underline{T}_{2g}(D) \longrightarrow {}^3\underline{T}_{1g}(D)$, $^3\underline{T}_{2g}(D)$,... . These are not identified with certainty, in part because of the indefinite assignment of the stereochemistry of the complex.

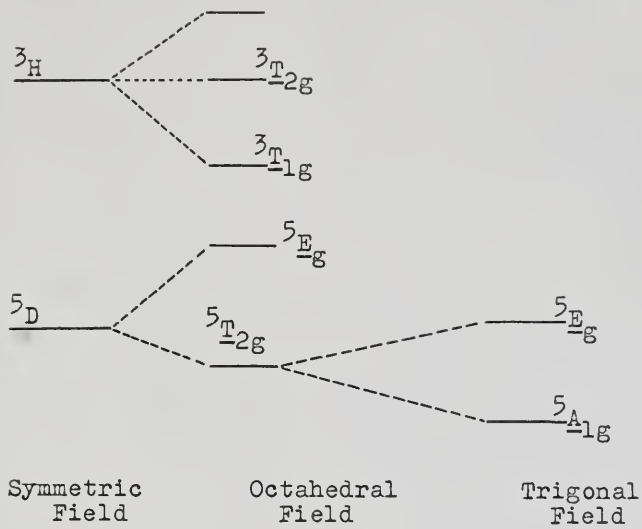

Fig. 7.--Energy states which arise from the ^3H and ^5D term states of a d^6 ion in a regular and trigonally distorted octahedral weak field.

For the copper(II) complex in solution, five absorption bands were observed: two in the ultra-violet region, at 2,500 A and 2,900 A, which were assigned as electronic transitions on the ligand, and three in the visible region, at 3,730 A (26,800 cm.$^{-1}$), 3,900 A (25,600 cm.$^{-1}$) and at 5,050 A (19,800 cm.$^{-1}$). In the solid state spectra one absorption band was observed at 5,050 A and this band and the band from the solution spectra at 5,050 A are assigned as the same transition.

From the spectra of $[Cu(dipy)_3]^{++}$ a band is reported at 14,700 cm.$^{-1}$ (22), while a slightly lower value is reported from the $[Cu(terpy)_2]^{++}$ spectra (19,22). No absorptions in this region were observed from the spectra of the copper(II) complex presently being studied. Because of the Jahn-Teller effect, no regular octahedral copper(II) complexes are expected to exist (33) and, indeed, it is generally found that the $^2\underline{E}_g$ and $^2\underline{T}_{2g}$ levels are split into two components each (Figure 8), which give rise to three transitions (10,12,20). On this basis the absorptions observed in the visible region of the spectrum are assigned as transitions $^2\underline{B}_{1g} \longrightarrow {}^2\underline{A}_{1g}$ $^2\underline{B}_{2g}$ $^2\underline{E}_g$. This is in agreement with the proposed four-coordinate square-planar configuration of the copper(II) complex.

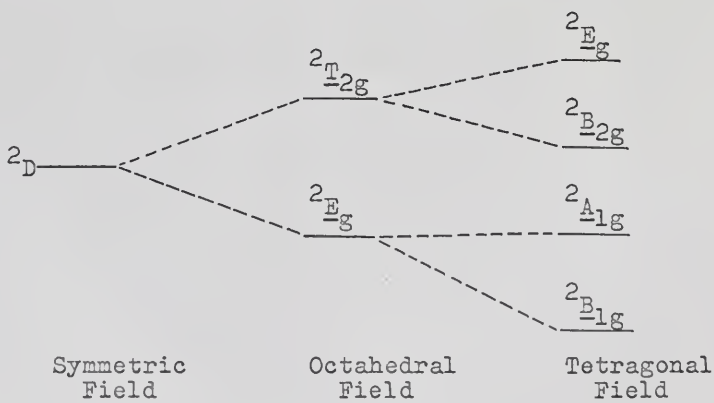

Fig. 8.--Energy states which arise from the ^2D term state of a d^9 ion in a regular and tetragonally distorted octahedral field.

The present investigation of these complexes suggests a number of areas in which future work must be done before a better understanding of the magnetic and spectral behavior of iron(II) and copper(II) complexes can be gained. The magnetic susceptibilities of these complexes in solution, and the magnetic properties of single crystals, should be thoroughly investigated. A detailed x-ray diffraction study should be made. There is a tremendous amount of work yet to be done in connection with spectral characterizations, especially those of iron(II) complexes.

SUMMARY

The syntheses of the iron(II), cobalt(II), nickel(II) and copper(II) chloride complexes of the tridentate ligand 2-(α-pyridylmethyleneaminomethyl)pyridine (PMP) are reported. The cobalt(II) and nickel(II) complexes are six-coordinate and of the type $[ML_2]Cl_2$ while the iron(II) and copper(II) complexes, in solution, are presumed to be four- or five-coordinate, that is $[MLCl]Cl$ or $[MLCl_2]$.

The solid state magnetic susceptibility of each of these complexes was determined as a function of temperature. It was demonstrated that each of the complexes follows the Curie-Weiss law, but that the magnetic moment of the iron(II) and copper(II) complexes were found to be field strength dependent. The room temperature magnetic moments of the cobalt(II) and nickel(II) complexes are those expected for high-spin octahedral complexes whereas the moment exhibited by the copper(II) complex was that expected for either a square-planar or an octahedral complex. The moment exhibited by the iron(II) complex is consistent with neither of these stereochemistries and indicates a significant degree of metal-to-metal interaction.

Definite assignments were made for the absorptions of the cobalt(II), nickel(II) and copper(II) complexes in the ultra-violet, visible, and near infrared regions of the spectra. Only tentative assignments could be made for the absorption maxima of the iron(II) complex. These assignments correspond to $\underline{D}_q$ values that are within the range expected for complexes formed by these ions with terpyridine-like ligands. Definite assignments of the iron(II) complex are difficult because of the uncertainty surrounding its stereochemistry.

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APPENDICES

APPENDIX I

Calibration of Field Strength as a Function of Current

The strength of the magnetic field was standardized by using a 29 per cent $NiCl_2$ solution, water, and solid nickel ammonium sulfate-6-hydrate. The gram susceptibility of the $NiCl_2$ solution is dependent on the mole function of $NiCl_2$ in the solution (36):

$$\chi_g = [\frac{10,030}{T} p + 0.720(1-p)] \times 10^{-6} \text{ erg gauss}^{-2} .$$

The susceptibility of the water is reported to be 0.72×10^{-6} erg gauss^{-2}(36) and χ_g for $Ni(NH_4)_2(SO_4)_2 \cdot 6H_2O$ is reported to be (4)

$$[\frac{3174}{T + 2.5} - 0.30] \times 10^{-6} \text{ erg gauss}^{-2} .$$

TABLE 14

FIELD STRENGTH AS A FUNCTION OF CURRENT AS DETERMINED WITH WATER

Amperage	H (gauss)
4.0	6693
3.8	6504
3.6	6558
3.4	6558
3.2	6140
3.0	5950
2.8	5577
2.6	5157
2.4	4879
2.2	4775
2.0	4123

TABLE 15

FIELD STRENGTH AS A FUNCTION OF CURRENT AS DETERMINED WITH NICKEL AMMONIUM SULFATE-6-HYDRATE

Amperage	H (gauss)
4.0	6848
3.8	6656
3.6	6458
3.4	6253
3.2	6025
3.0	5771
2.8	5459
2.6	5148
2.4	4848
2.2	4461
2.0	4123

TABLE 16

AVERAGE FIELD STRENGTH AS A FUNCTION OF CURRENT

Amperage	H (gauss)
4.0	6770
3.8	6580
3.6	6508
3.4	6405
3.2	6082
3.0	5860
2.8	5518
2.6	5152
2.4	4863
2.2	4618
2.0	4123

APPENDIX II

TEMPERATURE DEPENDENT DIAMAGNETIC CORRECTIONS FOR A QUARTZ GOUY TUBE

Several quartz Gouy tubes were prepared and found to be slightly diamagnetic. The following data were obtained by using a magnetic field of approximately 6770 gauss.

TABLE 17

TEMPERATURE DEPENDENT DIAMAGNETIC CORRECTIONS FOR A QUARTZ GOUY TUBE

T°K	$1/T \times 10^3$	Δ_g
88.04	11.36	-0.00313
100.24	9.98	-0.00285
148.84	6.72	-0.00270
177.54	5.63	-0.00268
221.44	4.52	-0.00271
314.64	3.18	-0.00269
359.40	2.78	-0.00270

APPENDIX III

The complexes were corrected for diamagnetism by using Pascal's constants.

TABLE 18

PASCAL'S CORRECTIONS FOR DIAMAGNETISM

C_6H_5	-55.5×10^{-6} c.g.s
C_6H_5N	-49.2
C	- 6.0
N (open chain)	- 5.6
Cl	-20.1
C=N	8.2
H	- 2.9
O	- 4.6
Fe	-12.8
Co	-12.8
Ni	-12.8
Cu	-12.8

APPENDIX IV

Conductances of certain compounds were determined in tetrahydrofuran solution and used as standards.

TABLE 19

SPECIFIC CONDUCTANCES AT 25°C

Compound	Concentration (moles per liter)	k ($ohm^{-1}cm.^{-1}$)
KCl	1×10^{-3}	15.3
$CoCl_2$	1×10^{-3}	42.8
$MnCl_2$	1×10^{-3}	46.4
$CoBr_2$	1×10^{-3}	41.0

APPENDIX V

Molecular weights of certain compounds were determined in tetrahydrofuran solution and used as standards.

TABLE 20

MOLECULAR WEIGHTS

Compound	Values (a.m.u.)	
	Calculated	Observed
KCl	75	82
$CoCl_2$	130	145
$MnCl_2$	126	137
$CoBr_2$	219	240

BIOGRAPHICAL SKETCH

James Leroy Petrofsky was born March 2, 1938, at Jacksonville, Texas. After attending Pendorff Grade School, Laurel, Mississippi, he entered Jones County Agricultural High School, Ellisville, Mississippi, and was graduated in May, 1955. In June, 1959, he received the degree of Bachelor of Science from Mississippi College, Clinton, Mississippi. In September, 1959, he entered the Graduate School of the University of Florida and in February, 1962, he received the degree of Master of Science. From that time until December, 1964, he held a graduate assistantship in the Department of Chemistry.

This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 19, 1964

E. Ruffin Jones
Dean, College of Arts and Sciences

Dean, Graduate School

Supervisory Committee:

R. C. Stoufer
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