

TABLE I

THE CONCENTRATIONS (%) AND EQUILIBRIUM CONSTANTS FOR THE RACEMIC PAIRS IN THE REACTION MIXTURE $[\text{Co}(\pm)\text{pn}_3]\text{Cl}_3$

Racemic pairs	Isomer concn. (+)pn / (-)pn = 1	K_{20°	$\Delta G_{\text{obsd.}}$ kcal./mole	Isomer concn. (+)pn / (-)pn = 2
$\text{D}[\text{Co}(+)\text{pn}_3]^{3+}$, $\text{L}[\text{Co}(-)\text{pn}_3]^{3+}$	40.5	$\frac{\text{D}[\text{Co}(+)\text{pn}_3]^{3+}, \text{L}[\text{Co}(-)\text{pn}_3]^{3+}}{\text{D}[\text{Co}(+)\text{pn}_2(-)\text{pn}]^{3+}, \text{L}[\text{Co}(-)\text{pn}_2(+)\text{pn}]^{3+}} = 1$	0.0	48.5
$\text{D}[\text{Co}(+)\text{pn}_2(-)\text{pn}]^{3+}$, $\text{L}[\text{Co}(-)\text{pn}_2(+)\text{pn}]^{3+}$	40.3	$\frac{\text{D}[\text{Co}(+)\text{pn}_2(-)\text{pn}]^{3+}}{\text{L}[\text{Co}(+)\text{pn}_2(-)\text{pn}]^{3+}} = 2.4$	-0.52	36.0
$\text{D}[\text{Co}(+)\text{pn}(-)\text{pn}_2]^{3+}$, $\text{L}[\text{Co}(-)\text{pn}(+)\text{pn}_2]^{3+}$	16.5	$\frac{\text{D}[\text{Co}(+)\text{pn}(-)\text{pn}_2]^{3+}, \text{L}[\text{Co}(-)\text{pn}(+)\text{pn}_2]^{3+}}{\text{D}[\text{Co}(-)\text{pn}_3]^{3+}, \text{L}[\text{Co}(+)\text{pn}_3]^{3+}} = 6.1$	-1.1	12.3
$\text{D}[\text{Co}(-)\text{pn}_3]^{3+}$, $\text{L}[\text{Co}(+)\text{pn}_3]^{3+}$	2.7			3.2

$K = 0.92$ (found 1.07). Also, if it is assumed that the energy difference between conformations is ~ 0.5 kcal./mole, then the calculated values for the equilibrium constant are 0.58 and 0.89 for (+)pn/(-)pn = 1 and (+)pn/(-)pn = 2, respectively. From the agreement between the observed and calculated equilibrium ratios it would seem that the conformational factor and the statistical factor, where relevant, are the two principal contributions in determining the isomer ratios.

Experimental

Reaction Mixture.—Cobalt(II) chloride 6 hydrate (71 g.), HCl (60 ml., 5 *N*), and (\pm)-propylenediamine (74 g.) in water (1.5 l.) were oxidized in a stream of air in the presence of charcoal (30 g.) for 12 hr. The solution was filtered and made slightly acid with HCl, evaporated to dryness, and the dry *luteo* product finely powdered (125 g.).

Separation of the Isomers.—Whatman cellulose powder (500 g.) suspended in 1-butanol (water satd.) was packed in a column (14 in./3 in.). The *luteo* product (2 g.) in wet butanol (400 ml.) and HCl (1 ml., 10 *N*) was heated to 35° to effect dissolution and dry butanol (200 ml.) then added. This solution was adsorbed on the column and eluted with butanol (500 ml. of water satd.) and HCl (10 ml., 10 *N*). The fractions were extracted with water and evaporated to dryness at 40°. The procedure was repeated until sufficient sample was obtained for resolution (10 g.). The sample was then recrystallized from water with acetone.

D-(+)-Bis-(+)-propylenediamine(-)-propylenediaminecobalt(III) Iodide.—Fraction 2 (10 g.) was dissolved in warm water (50 ml.), $\text{Ag}_2(+)$ -tartrate (9 g.) added, and the mixture shaken for 10 min. Methanol was then added to the filtered solution and $\text{D}(+)\text{[Co}(+)\text{pn}_2(-)\text{pn}]\text{Cl}(+)\text{tartrate}$ crystallized out. The diastereoisomer was recrystallized several times from aqueous methanol to constant rotation $[\alpha]_{\text{D}} + 91^\circ$.

Anal. Calcd. for $\text{Co}(\text{C}_3\text{H}_{10}\text{N}_2)_3\text{ClC}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH}$: C, 31.88; H, 8.20; N, 14.88. Found: C, 31.56; H, 7.7; N, 14.59.

It was treated with a little HCl (10 *N*) and the complex chloride was precipitated with acetone and recrystallized from aqueous

ethanol; $[\alpha]_{\text{D}} + 125^\circ$, $[\alpha]_{578} + 160^\circ$, $[\alpha]_{546} + 380^\circ$. The chloride was converted to the iodide by adding excess LiI to an aqueous solution of the chloride and the specific rotations for the complex iodide were $[\alpha]_{\text{D}} + 80^\circ$, $[\alpha]_{578} + 100^\circ$, and $[\alpha]_{546} + 246^\circ$.

The pn was extracted after decomposing the complex with Na_2S_2 and gave $[\alpha]_{\text{D}} + 11.5^\circ$ in benzene.

Anal. Calcd. for $[\text{Co}(\text{C}_3\text{H}_{10}\text{N}_2)_3]\text{I}_3$: C, 16.33; H, 4.57; N, 12.70. Found: C, 16.37; H, 4.98; N, 12.46.

L-(-)-Bis(-)-propylenediamine-(+)-propylenediaminecobalt(III) Iodide.—The filtrate from the diastereoisomer above was reconverted to the chloride (5.2 g.) and then to the chloride(-)-tartrate with $\text{Ag}_2(-)$ -tartrate (4.6 g.). The pure diastereoisomer $\text{L}[\text{Co}(-)\text{pn}_2(+)\text{pn}]\text{Cl}(-)\text{tartrate}$, $[\alpha]_{\text{D}} - 90^\circ$, was obtained as above.

The iodide obtained from an aqueous solution of the diastereoisomer with LiI gave $[\alpha]_{\text{D}} - 78^\circ$, $[\alpha]_{578} - 100^\circ$, and $[\alpha]_{546} - 240^\circ$ and the extracted pn had a specific rotation $[\alpha]_{\text{D}} - 11.2^\circ$.

Anal. Calcd. for $[\text{Co}(\text{C}_3\text{H}_{10}\text{N}_2)_3]\text{I}_3$: C, 16.33; H, 4.57; N, 12.70. Found: C, 16.32; H, 4.60; N, 12.35.

Relative Concentrations of the Fractions.—A sample of the reaction mixture prepared at 20° was spread in a strip on Whatman 3 MM chromatography paper and eluted overnight with a 1-butanol-H₂O-HCl (60:30:10) mixture. The three fractions which separated were cut out and the complex eluted off the paper with water. The relative concentrations were then measured spectrophotometrically at 470 m μ .

fract. 1, $\text{D}[\text{Co}(+)\text{pn}_3]\text{Cl}_3$, $\text{L}[\text{Co}(-)\text{pn}_3]\text{Cl}_3$, fastest moving, 40.0–41%

fract. 2, $\text{D}[\text{Co}(+)\text{pn}_2(-)\text{pn}]\text{Cl}_3$, $\text{L}[\text{Co}(-)\text{pn}_2(+)\text{pn}]\text{Cl}_3$, 40.5–40%

fract. 3, $\text{D}[\text{Co}(+)\text{pn}(-)\text{pn}_2]\text{Cl}_3$, $\text{L}[\text{Co}(-)\text{pn}(+)\text{pn}_2]\text{Cl}_3$, $\text{D}[\text{Co}(-)\text{pn}_3]\text{Cl}_3$, $\text{L}[\text{Co}(+)\text{pn}_3]\text{Cl}_3$, slowest moving, 19.5–19%

The second set of values was obtained by repeating the whole procedure on another sample.

The reaction mixture prepared using (-)pn/(+)pn = 2 gave the following concentrations: fraction 1, 48.5%; fraction 2, 36.0%; fraction 3, 15.5%.

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[CONTRIBUTION FROM THE EVANS AND MCPHERSON CHEMICAL LABORATORIES, THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO]

The Reactions of Coordinated Ligands. VII. Metal Ion Control in the Synthesis of Chelate Compounds Containing Pentadentate and Sexadentate Macrocyclic Ligands

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The metal ion mediation of the Schiff base condensation reactions between 2,6-diacetylpyridine and two polyethylenepolyamines, triethylenetetraamine, and tetraethylenepentamine, has led to the synthesis of unique complexes containing macrocyclic chelate ligands that are, respectively, pentadentate and sexadentate. The ligands have been prepared in their highly crystalline spin-paired iron(III) complexes. The complexes have been characterized through magnetic, conductance, and spectral measurements.

Introduction

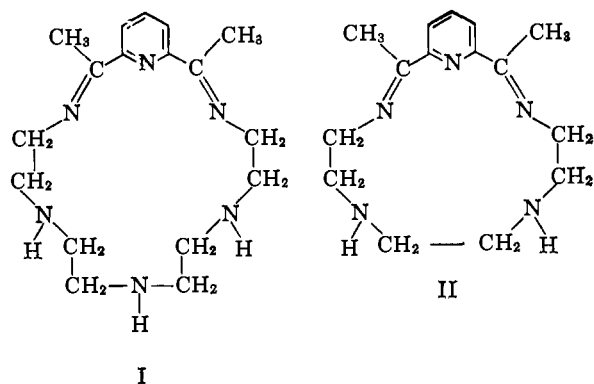
During the past few years, a number of dramatic examples have served to illustrate the ability of a metal ion to serve as a template in the course of reactions that

lead to the formation of macrocyclic organic ligands. Prime examples from these Laboratories have involved the reaction of alkyl dihalides with α -diketobis(mercaptoethylimine)nickel(II) complexes² and the cyclic

(1) C. F. Kettering Fellow, The Ohio State University.

(2) M. C. Thompson and D. H. Busch, *Chem. Eng. News*, **40**, No. 38, 57 (1962).

tetramerization of *o*-aminobenzaldehyde in the presence of a metal ion.³ Others have reported the reaction of bis(dimethylglyoximate)nickel(II) with boron trifluoride^{4,5} or triphenylboron leading to replacement of the hydrogen bridge with BX_2^+ , and the mixed Schiff base-aldehyde condensation of acetone with nickel-ethylenediamine complexes.⁶ All these processes produce tetradentate macrocyclic ligands best suited to the formation of planar structures. The compounds reported here constitute the first examples of completely cyclized ligands bound to a metal ion in more than four positions. The ligands are 2,16-dimethyl-3,6,9,12,15,21-hexaazabicyclo[15.3.1]heneicosa-1-(21),-2,15,17,19-pentaene (we shall call this ligand A, structure I), and 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene (structure II, ligand B).



The compounds $[Fe^{III}(A-H)]I_2$ (bronze crystals) and $[Fe^{III}B(OH)](ClO_4)_2$ (coral crystals) are formed by the slow addition of the amine to the previously formed (solution) complex of iron(II) with 2,6-diacetylpyridine. Oxidation of the iron(II) accompanies the condensation reaction. It is significant that a purple solution similar to that usually associated with the iron(II) di- or trimethine chromophores⁷ forms initially in both cases. The purple color is replaced by the bright green or coral colors of the products as air oxidation of the iron proceeds. The resulting iron(III) complexes are more readily isolated than the iron(II) precursors and the former have therefore been used to characterize these ligands. The compositions of the materials are shown by analytical data.

The magnetic moments for the iron atoms in $[Fe(A-H)]I_2$ and $[FeB(OH)](ClO_4)_2$, as reported in Table I, reveal that the spin-paired states are present in both cases. μ_{eff} has been determined at two field strengths to eliminate the possibility of ferromagnetic impurities. The low spin states might be expected in view of the multiply connected nature of the ligand and the presence, therein, of the powerful trimethine grouping.

TABLE I
MAGNETIC SUSCEPTIBILITIES, MAGNETIC MOMENTS, AND MOLAR CONDUCTANCES OF THE COMPLEXES

Compound	—Magnetic properties—		Molar conductance	
	$\chi_M \times 10^{-6}$	μ_{eff}	$T, ^\circ C.$	χ_M, ohm^{-1}
$[Fe(A-H)]I_2$	1205	1.90	30	228
$[FeB(OH)](ClO_4)_2$	1188	1.86	31	220

The molar conductances of the compounds (Table II) are consistent with their formulation as di-univalent electrolytes.

(3) G. A. Melson and D. H. Busch, *Proc. Chem. Soc.*, 223 (1963).

(4) G. N. Schrauzer, *Chem. Ber.*, **95**, 1438 (1962).

(5) D. Thierig and F. Umland, *Angew. Chem.*, **74**, 388 (1962).

(6) D. A. House and N. F. Curtis, *J. Am. Chem. Soc.*, **84**, 3248 (1962).

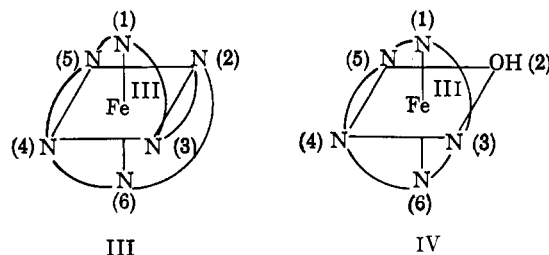
(7) D. H. Busch and J. C. Bailar, Jr., *ibid.*, **78**, 1137 (1956).

TABLE II
ELECTRONIC SPECTRA OF THE COMPLEXES^a

Band	$[Fe(A-H)]I_2$		$[FeB(OH)](ClO_4)_2$	
	$\bar{\nu}, \text{cm.}^{-1}$	ϵ_{max}	$\bar{\nu}, \text{cm.}^{-1}$	ϵ_{max}
ν_1	9,850	7.93	11,430	3.6
	10,740	6.80		
ν_2	16,950	79.3	(?)	
ν_3	20,390	202	20,580	79.3
	21,390	293	21,510	85.8
ν_4	26,850	6,050	27,400	4680
	$\approx 32,260$	6,390		
ν_5	$\approx 35,970$	7,810	36,360	7870
ν_6	44,840	46,300

^a Extinction coefficients are given on a molar basis.

Infrared spectra reveal the absorptions expected for structures I and II. A single N-H stretching frequency suggests the presence of secondary, but not primary, amine groups. The $>C=N-$ functions appear at 1645 and 1655 cm.^{-1} for $[Fe(A-H)]I_2$ and $[FeB(OH)](ClO_4)_2$, respectively. The usual modes of the substituted pyridine ring⁸ are observed in both cases. However, major significance must be attached to the fact that the infrared spectra are devoid of any evidence for the presence of either a ketonic carbonyl or a primary amine group. This and the presence of the $C=N$ stretching band provide assurance that the required Schiff base linkages have formed. This result combined with the established stoichiometry, highly crystalline nature, and the normal molar conductances of solutions of the materials lead to the conclusion that the complexes are those expected and not polymeric materials such as those observed by Lions and Martin.⁹ Since the spin state of the iron atom clearly indicates the ligands to be powerful ones, it is reasonable to conclude, further, that the ligands are cyclic and bound as indicated schematically in structures III and



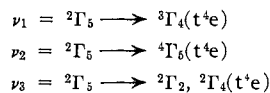
IV. The N atoms at position (1) in structures III and IV are the pyridine nitrogen atoms. The donors (N) adjacent to the pyridine ring, in the (3) and (5) positions, must be coplanar with that ring because of the structures of the ligands (structures I and II).

In the case of the sexadentate complex, this requires the three secondary amine groups to occupy the (2), (6), and (4) positions. Thus, the grouping $-N-CH_2CH_2-N-CH_2CH_2-N-$ is strung along an octahedral edge. This structure is highly strained; but the distortion of the bond angles of the nitrogen atom (2° amine) at position (6) toward the trigonal angle of 120° greatly relieves this strain. Such a distortion may lead to increased acidity on the part of the proton originally on this nitrogen atom. This provides a rationalization for the fact that this ligand coordinates as an anion, producing a divalent cation, rather than the trivalent species that might otherwise have been expected. Potentiometric titration reveals that the complex is too weak a base to be protonated in dilute aqueous solution. This provides additional support for the proposed structure.

(8) C. H. Kline, Jr., and J. Turkevich, *J. Chem. Phys.*, **12**, 300 (1944).

(9) F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, **79**, 2733 (1957).

Although the symmetries of these complexes are quite low, it might be expected that their electronic spectra would conform approximately to the prescription for spin-paired d^5 in O_h symmetry.¹⁰ The absorption spectrum of $[\text{Fe}(\text{A-H})]_2$ (Table II) in aqueous solution consists of a doublet of low extinction coefficient centered at 10,290 cm^{-1} , a single weak band at 16,950 cm^{-1} , and a second doublet centered at 20,890 cm^{-1} . These are followed by four very intense bands at lower wave lengths. Using $\Delta = 2525 \text{ cm}^{-1}$, $B = 832 \text{ cm}^{-1}$, and $C = 2700 \text{ cm}^{-1}$ ($C/B = 3.3$), the energies of the first three bands agree very well with the assignments



Assignments of these d-d transitions are further supported by the intensities of the bands. The value of Dq (2525 cm^{-1}) is reasonable in view of the accepted value of 3495 cm^{-1} for $\text{Fe}(\text{CN})_6^{3-}$.^{10,11}

Although the spectrum of $[\text{FeB}(\text{OH})]^{2+}$ resembles that of $[\text{Fe}(\text{A-H})]^{2+}$, failure to observe ν_2 renders assignments less satisfying. However, values of $B = 754 \text{ cm}^{-1}$, $C = 2451 \text{ cm}^{-1}$ ($\gamma = 3.25$), and $Dq = 2500 \text{ cm}^{-1}$ provide a reasonable fit (Table II).

Among the most serious doubts attending the inference of structures III and IV, as presented here, is the great strain in the chelate rings in the sexadentate structure proposed (III). From scale models, it might be anticipated that the failure of the sixth metal-ligand bond to form would greatly relieve this strain, thus leading to concern for the possible existence of a pentadentate structure. Under these circumstances, an OH^- ion might fill the sixth position of the iron(III) atom in the case of the derivative of ligand A, as well as for that of ligand B. Differences in optical spectra provide the strongest evidence in opposition to this alternate structural assignment, for $[\text{FeA}(\text{OH})]^{2+}$ and $[\text{FeB}(\text{OH})]^{2+}$ should certainly have extremely similar electronic spectra if they differed only in this way. In contrast, the much more complicated spectrum of $[\text{Fe}(\text{A-H})]^{2+}$ argues for the decreased symmetry expected to attend sexadentate coordination in that case. Further, the iron(III) complex of ligand A exhibits a somewhat greater splitting parameter, as required by structure III rather than the alternate structure mentioned.¹²

These materials provide further illustration of the function of a metal ion as a template during the course of a reaction leading to the production of new ligands that are well suited for strong complexing.^{13,14} The fact that both the ketone and the amine with which it reacts contain effective donor atoms that are not involved in the condensation process may be of significance in this system, for α -diketones have not proven to be so cooperative under similar conditions.¹⁵ The

(10) C. S. Naiman, *J. Chem. Phys.*, **35**, 323 (1961).

(11) A. V. Kiss, J. Abraham, and I. Hegedüs, *Z. anorg. allgem. Chem.*, **244**, 98 (1940).

(12) The ultimate resolution of the question of the structure of the sexadentate complex must await the results of a definitive X-ray structure determination in progress in the laboratory of Dr. E. B. Fleischer, University of Chicago.

(13) M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 213 (1964).

(14) D. H. Busch, *Advances in Chemistry Series*, No. 37, American Chemical Society, Washington, D. C., 1963, p. 1.

(15) M. C. Thompson, G. A. Melson, and D. H. Busch, unpublished results.

nitrogen atom of the pyridine ring of the 2,6-diacetylpyridine and the secondary amines of the polyethylene-polyamine may serve to position the components on the metal ion template during the course of the final ring closure.

Experimental

Materials.—2,6-Diacetylpyridine was obtained from Aldrich Chemical Co. and the polyamines from Carbide and Carbon Chemicals Co. Both were used as received. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory.

(2,16-Dimethyl-3,6,9,12,15,21-hexaazabicyclo[15.3.1]heptacosane-1(21),2,15,17,19-pentaene-9-ato)iron(III) Diiodide, $[\text{Fe}(\text{A-H})]_2$.—Finely ground 2,6-diacetylpyridine (6.52 g., 0.04 mole) was added to 7.88 g. of iron(II) chloride 4-hydrate (0.04 mole) dissolved in 250 ml. of distilled water. The appearance of a pink color indicates complex formation between the diketone and the iron(II) in solution. After stirring for 15 min. and heating to 40°, 7.36 g. of tetraethylenepentamine (0.04 mole) was added very slowly with stirring. A purple color characteristic of complexes of iron(II) with imine-type nitrogens appeared at this point. The mixture was stirred for 10 min. and 10 drops of 16 *M* HCl was added to retard the formation of $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. The solution was maintained at approximately 50° with constant stirring for 24 hr. At this point, a brown material ($\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$) was removed by filtration and 20 g. of potassium iodide was added to the solution. The bronze filtrate was concentrated in the presence of air at room temperature until the separation of bronze needles was observed. The crystals were isolated by filtration, washed with cold methanol, and dried *in vacuo* over P_2O_5 overnight, yield 2.92 g. (11%).

Anal. Calcd. for $[\text{Fe}(\text{A-H})]_2$: C, 32.66; H, 4.35; N, 13.45; I, 40.61. Found: C, 32.67; H, 4.76; N, 13.18; I, 40.48.

Hydroxy-(2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]-octadeca-1(18),2,12,14,16-pentaene)iron(III) Perchlorate, $[\text{FeB}(\text{OH})](\text{ClO}_4)_2$.—Finely ground 2,6-diacetylpyridine (3.26 g., 0.02 mole) was added with stirring to 3.98 g. of iron(II) chloride 4-hydrate (0.02 mole) dissolved in 60 ml. of distilled water, followed by 2.92 g. of triethylenetetramine, and, finally, 5 drops of 16 *M* HCl. The purple solution was filtered and 7.0 g. of solid $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ was added immediately. Air was bubbled through the solution of 36 hr. Upon initiation of the air flow, a coral-colored solid began to form. Following the treatment described, this coral product was removed by filtration and recrystallized from 1:1 (v./v.) ethanol-water by dissolving at 45° and cooling. The product was dried *in vacuo* over P_2O_5 overnight, yielding 3.05 g. (28%).

Anal. Calcd. for $[\text{FeB}(\text{OH})](\text{ClO}_4)_2$: C, 33.05; H, 4.44; N, 12.85; Cl, 13.01. Found: C, 33.42; H, 4.21; N, 12.91; Cl, 12.80.

Magnetic Measurements.—Magnetic moments were obtained at room temperature by the Gouy method, using mercury(II) tetrathiocyanatocobaltate(II) as a standard. Diamagnetic corrections for the ligands and anions were obtained by the use of Pascal's law with the aid of tabulated constants^{16,17} and values measured for ligands containing similar functional groups.¹⁸ For ligand A-H, the derived value of the molar susceptibility is -190.6×10^{-6} while that for ligand B is -161.3×10^{-6} .

Conductivity Measurements.—Molar conductances were measured using an Industrial Instruments, Inc., Model RC-16B conductivity bridge and a cell with a constant of 1.95 ohm^{-1} . The measurements were made at a bridge frequency of 1000 c.p.s. in doubly distilled water employing 10^{-3} *M* solutions of the compounds. Results are compiled in Table I.

Electronic Spectra.—Ultraviolet, visible, and near-infrared spectra were obtained with a Cary Model 14 recording spectrophotometer, using matched cells of 1 cm. or 5 cm. length. Water was used as the solvent and solutions of appropriately varied concentrations were employed in order to observe the several absorption bands of the complexes.

Infrared Spectra.—The infrared spectra were determined with a Perkin-Elmer Model 21 recording spectrophotometer equipped with sodium chloride optics. Spectra were obtained both on samples in compressed KBr pellets and in Nujol mulls.

Acknowledgment.—The financial support of the National Institutes of Health is gratefully acknowledged.

(16) P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience, New York, N. Y., 1956.

(17) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," ed. by J. Lewis and R. G. Wilkins, Interscience, New York, N. Y., 1960.

(18) P. E. Figgis and D. H. Busch, *J. Am. Chem. Soc.*, **82**, 820 (1960).