Cobalt(II) Complexes of Linear Pentadentate Schiff Base Ligands

R. H. NISWANDER, A. K. ST. CLAIR, S. R. EDMONDSON, and L. T. TAYLOR*

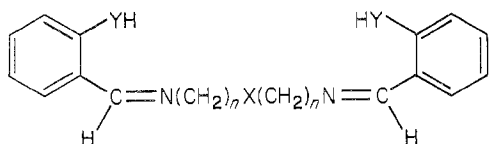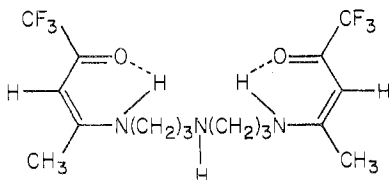Cobalt(II) complexes of linear potentially pentadentate ligands with donor sets of O_2N_3, O_2N_2S, O_3N_2, and O_2N_2P derived from salicylaldehyde and four different polyamines have been synthesized. Characterization *via* elemental analysis, infrared–visible spectra, mass spectra, and magnetic susceptibility has been accomplished. Tetrahedral high-spin complexes are produced when the donor sets are O_2N_2S and O_2N_2 wherein the ether oxygen and thioether sulfur atom are not coordinated. High-spin five-coordinate materials are produced when the donor sets are either O_2N_3 or O_2N_2P where the unique phenyl nitrogen or methyl phosphorus atom is coordinated. Reactivity in solution with oxygen is rapid for the five-coordinate compounds but considerably slower for the tetrahedral complexes. All materials are relatively stable in the solid state.

Introduction

Cobalt complexes formed from pentadentate Schiff base ligands have received limited study.[1] The first group of ligands of this type to be studied involved various substituted salicylaldehydes condensed with bis(3-aminopropyl)amine (DPT), Ia, or bis(3-aminopropyl)methylamine (MeDPT), Ib, in a 2:1 mole ratio, respectively.[2] The resulting cobalt(II) complexes were found to be high-spin five-coordinate structures. Similar ligands have been employed wherein *o*-mercaptobenzaldehyde was used instead of salicylaldehyde to give the donor set S_2N_3 (Ic, Id), rather than O_2N_3.[3] High-spin pentacoordination was again observed with these materials. The synthesis of a new pentadentate ligand derived from trifluoroacetylacetone and DPT, If, has been recently reported; however complexation with cobalt(II) was not attempted.[4] Investigations involving ligands of this basic type in which the central donor atom is varied have not been published except for the report regarding cobalt(II) complexes of the ligand derived from salicylaldehyde and bis(2-aminoethyl) sulfide (DAES),[5] Ie. Apparently the five-atom chain joining azomethine linkages is not long enough to allow coordination of the thioether sulfur because the complexes have properties characteristic of a tetrahedral geometry.


Ia, SALDPT, X = NH, Y = O, n = 3
b, SALMeDPT, X = NCH$_3$, Y = O, n = 3
c, TIBDPT, X = NH, Y = S, n = 3
d, TIBMeDPT, X = NCH$_3$, Y = S, n = 3
e, SALDAES, X = S, Y = O, n = 2

If, TFACDPT

We wish to describe our results concerning the preparation and characterization of cobalt(II) complexes formed from linear potentially pentadentate ligands derived from salicylaldehyde and bis(3-aminopropyl) ether (DAPE), bis(3-aminopropyl) sulfide (DAPS), bis(3-aminopropyl)methylphosphine (MeDAPP), and bis(3-aminopropyl)phenylamine (PhDPT). These compounds are represented in structure II
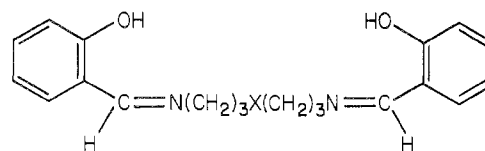
IIa, H$_2$SALDAPE, X = O
b, H$_2$SALDAPS, X = S
c, H$_2$SALMeDAPP, X = P(CH$_3$)
d, H$_2$SALPhDPT, X = N(C$_6$H$_5$)

and they illustrate a series of ligands where the central donor atom is varied.

Experimental Section

DAPE was prepared by a catalytic hydrogenation similar to that reported by Modest, *et al.*[6] The preparation of DAPS by the Gabriel synthesis has been described elsewhere.[7] MeDAPP was prepared by the catalytic hydrogenation of bis(2-cyanoethyl)methylphosphine. The latter compound was synthesized according to Grayson, *et al.*[8] PhDPT was prepared by catalytically reducing bis(2-cyanoethyl)phenylamine which was prepared by allowing acrylonitrile to react with aniline.[9] All other chemicals were reagent grade or equivalent. All solvents used in the preparation of the complexes were deaerated with N$_2$.

Preparation of Co(SALDAPE). To a solution prepared by dissolving 2.44 g (0.02 mol) of salicylaldehyde in 25 ml of absolute ethanol was added 1.32 g (0.01 mol) of DAPE dissolved in 25 ml of absolute ethanol. The solution immediately turned yellow after which 0.8 g (0.02 mol) of NaOH was added. The resulting solution was warmed for 1 hr under nitrogen. To this mixture was added dropwise 2.49 g (0.01 mol) of Co(OAc)$_2$·4H$_2$O which was suspended in 75 ml of absolute ethanol. After refluxing for 2 additional hr the dark red-brown solution was reduced in volume by half and allowed to come to room temperature. An orange-yellow solid appeared after a while and was filtered under nitrogen and dried *in vacuo*, at room temperature for 12 hr.

Preparation of Co(SALDAPS). H$_2$SALDAPS (3.56 g or 0.01 mol), which had previously been prepared by allowing salicylaldehyde and DAPS to react in a 2:1 ratio in 95% ethanol, was dissolved in 100 ml of absolute ethanol. After addition of 0.02 mol of triethyl orthoformate, the mixture was refluxed for 0.5 hr. A solution prepared by dissolving 2.49 g (0.01 mol) of Co(OAc)$_2$·4H$_2$O in 60 ml of methanol was then added dropwise under nitrogen to the refluxing solution. Refluxing was continued for 1 hr during which time an orange-yellow material precipitated which was filtered under nitrogen and dried *in vacuo* at room temperature for 12 hr.

Preparation of Co(SALPhDPT). To a solution prepared by dissolving 2.44 g (0.02 mol) of salicylaldehyde in 50 ml of methanol was added 2.07 g (0.01 mol) of PhDPT dissolved in 20 ml of methanol. Co(OAc)$_2$·4H$_2$O (2.49 g, or 0.01 mol) dissolved in 50 ml of methanol was then added all at once to the resulting mixture which was maintained under nitrogen and at room temperature. After stirring for 2 hr, water was added dropwise to effect precipitation. The gold-colored precipitate was filtered, washed with 2-propanol, and dried at 100° *in vacuo* for 12 hr.

Table I. Analytical Data for the Cobalt(II) Complexes

Compd	% C		% H		% N	
	Calcd	Found	Calcd	Found	Calcd	Found
Co(SALDAPE)	60.46	60.22	5.58	5.30	7.05	7.18
Co(SALDAPS)	58.11	57.86	5.37	5.36	6.78	6.48
Co(SALPhDPT)	66.10	65.89	5.76	5.92	8.89	8.71
Co(SALMeDAPP)(H$_2$O)	56.63	56.24	6.11	6.12	6.29	6.06

Preparation of Co(SALMeDAPP). To 150 ml of a refluxing THF solution of 3.37 g (0.01 mol) of Co(SAL)$_2$·2H$_2$O was added dropwise from a syringe 1.62 g (0.01 mol) of MeDAPP. A few minutes after addition of the phosphine a brown precipitate appeared. The mixture was allowed to stand overnight after which the volume of the reaction solution was reduced by two-thirds. Filtration followed by washing with hexane and drying *in vacuo* at 150° was then accomplished. All operations were carried out under nitrogen. The product is a green powder which appears brown when highly illuminated and examined under a microscope.

Physical Measurements. Elemental analyses were performed using a Perkin-Elmer Model 240 C, H, and N analyzer. Mass spectra were obtained using an Hitachi Perkin-Elmer RMU-7 double-focusing mass spectrometer. Each sample was placed on a solid inlet probe and maintained at an appropriate temperature below the point of sample decomposition. Infrared spectra were obtained on a Perkin-Elmer Model 621 and a Beckman 20AX recording spectrophotometer over the region 5000–400 cm^{-1}. Samples were prepared as Nujol mulls. Magnetic susceptibility data were obtained by the Faraday method at room temperature and at several different magnetic fields. Uv–visible–near-ir spectra were measured with a Cary 14 recording spectrophotometer. Solids and solutions were examined as Nujol mulls and in 1.0 cm quartz cells respectively.

Results and Discussion

Cobalt(II) complexes of four potentially pentadentate ligands possessing donor sets of O$_2$N$_3$, O$_2$N$_2$S, O$_3$N$_2$, and O$_2$N$_2$P have been synthesized. Analytical data for these materials, Table I, indicate the general empirical formula [CoL] where L is the appropriate pentadentate ligand. Co(SALMeDAPP) could only be obtained as the monohydrate since all attempts at removing this water were unsuccessful. In the solid state all the cobalt(II) complexes appear to be quite stable since oxygenated and nonoxygenated material have identical physical and chemical properties. Aerated solutions of Co(SALPhDPT) and Co(SALMeDAPP)(H$_2$O) quickly discolor whereas solutions of Co(SALDAPE) and Co(SALDAPS) are relatively stable to oxygen.

The proposed formulation for these compounds is supported by both infrared and mass spectral data. The mass spectrum of each complex is characterized by an intense molecular ion, which is the most abundant ion in the spectrum, as well as relatively abundant doubly charged parent molecular ions. No polymeric species were detected in any spectrum which suggests that either the complexes are monomeric or any polymers are destroyed upon sublimation or upon electron impact such that no polymeric ions are collected in the spectrometer. Only Co(SALMeDAPP)(H$_2$O) exhibits infrared absorption above approximately 3000 cm^{-1}. The broad band centered at *ca.* 3250 cm^{-1} is assigned to the symmetric and asymmetric O–H stretching vibrational modes of water. The infrared spectra of all compounds display a strong absorption band in the region 1595–1610 cm^{-1} assignable to C=N stretching mode. In those cases where the free ligand was isolated (*i.e.*, H$_2$SALDAPE and H$_2$SALDAPS) a shift of 25–30 cm^{-1} to lower energy was observed in the position of this band on complexation with cobalt suggesting metal azomethine nitrogen interaction.

The C–O–C stretching frequency of Co(SALDAPE) at 1110 cm^{-1} occurs at exactly the same position in the free ligand. This observation lends evidence to the postulate that the ether oxygen is not coordinated or sufficiently perturbing the metal ion. On the contrary, analogous nickel(II) complexes show

a slight shift between the complex and free-ligand C–O–C frequencies.[10] A much more dramatic shift is observed when a comparison is made between free DAPE and pseudooctahedral [Ni(DAPE)$_2$]X$_2$ wherein the C–O–C shift on complexation is 65 cm^{-1} to lower energy.[11] The weak C–S–C stretching frequency in Co(SALDAPS) is obscured by other absorptions which prohibited a similar comparison from being made. Yet ionization potential data *via* mass spectrometry[12] support the idea that the ether and thioether linkages are cobalt bound. It would be expected that the ionization potentials should approximate those of Co(SALHTDA), III, however,
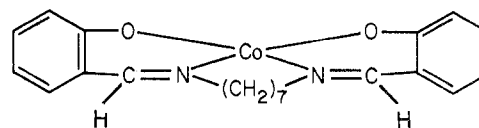
III

the IP's of Co(SALDAPE) and Co(SALDAPS) are significantly lower. The explanations for the differences in interpretation of the data are not obvious although a slightly different structure in the gas phase relative to the solid phase could account for such a discrepancy.

The calculated magnetic moment for each cobalt complex is listed in Table II. The experimental values appear to rule out a low-spin square-planar or high-spin octahedral stereochemistry for any of these materials; however, they fall well within the range expected for tetrahedral and high-spin five-coordinate complexes. Co(SALHTDA) is reported[13] to be tetrahedral with μ_{eff} = 4.68 BM while Co(SALDPT) is known[2] to be five-coordinate with μ_{eff} = 4.41 BM.

The electronic spectra of the cobalt(II) complexes are presented in Table III and Figures 1 and 2 and these data offer the most convincing evidence concerning the geometry of these complexes. Spectra were measured on solid samples as Nujol mulls and as pyridine solutions. Although these complexes represent a series of compounds in which the central donor atom is varied, all materials are not stereochemically identical as judged from their visible spectra. The compounds readily fall into two groups (*i.e.*, H$_2$SALDAPE and H$_2$SALDAPS in one group and H$_2$SALPhDPT and H$_2$SALMeDAPP in another group).

The near-infrared and visible spectra of Co(SALDAPE) and Co(SALDAPS), Figure 1, correspond very favorably with the spectra of known pseudotetrahedral species. Bis(*N*-phenylsalicylaldiminato)cobalt(II) has been shown by spectral as well as by crystallographic evidence to have a pseudotetrahedral geometry.[14] Figure 1 reveals that the similarity of our spectra and the spectrum of Co(SALNPh)$_2$ is striking. Replacement of the ether or thioether linkage with a methylene carbon group produces no significant spectral changes. Therefore based on the available ir, magnetic susceptibility, and near-ir–visible spectral data, a tetrahedral geometry for Co(SALDAPE) and Co(SALDAPS) can be concluded wherein the ether oxygen and thioether sulfur atom are not coordinated, IVa. A polymeric tetrahedral complex appears unlikely since these materials are relatively soluble in several nondonor solvents. In contrast, the analogous nickel(II) complexes have been shown to be polymeric nontetrahedral materials.[15]

It is known that [Co(trenMe$_6$)Br]Br has a trigonal-bipyramidal structure[16] and the difference in the electronic

Table II. Magnetic Properties of the Cobalt(II) Complexes in the Solid State at Room Temperature

| Compd	$10^6\chi_M,^a$ cgsu	$\mu_{eff},^b$ BM	Compd	$10^6\chi_M,^a$ cgsu	$\mu_{eff},^b$ BM
Co(SALDAPE)	7900	4.33	Co(SALPhDPT)	7890	4.35
Co(SALDAPS)	7780	4.30	Co(SALMeDAPP)(H$_2$O)	8450	4.47

^{a} Molar susceptibilities have been corrected for diamagnetic ligands. ^{b} μ_{eff} was found to decrease only slightly with increasing field strength.

Table III. Electronic Spectra of the Cobalt(II) Complexes

Compd	Solvent	Band maxima, cm^{-1}					
Co(SALDAPE)	Nujol	7,800	11,400	17,100	21,500	26,000	
Co(SALDAPS)	Nujol	8,300	11,100	17,200	19,400	21,500	26,000
Co(SALPhDPT)	Nujol	5,820	14,600				
Co(SALMeDAPP)(H$_2$O)	Nujol	6,750	13,100	17,230			
Co(SALPhDPT)	Pyridine	9,950	17,700				
Co(SALMeDAPP)(H$_2$O)	Pyridine	10,000	16,260				
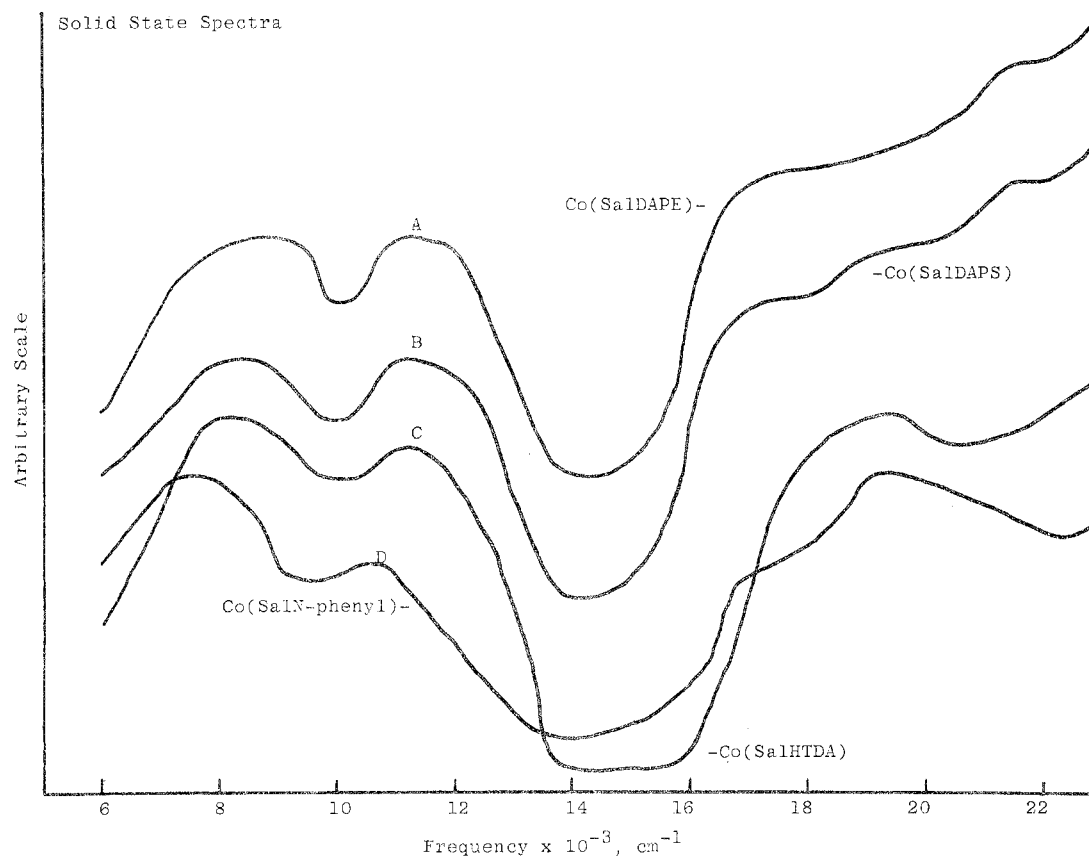
Figure 1. Near-infrared spectra of Co(SALDAPE) (A), Co(SALDAPS) (B), Co(SALHTDA) (C), and Co(SALNPh)$_2$ (D) in the solid state.

spectra of this compound and that of Co(SALDPT) and Co(SALMeDPT) has been postulated to arise from differences in their five-coordinate geometries.[2] X-Ray structures of Ni(SALDPT) and Ni(SALMeDPT) have shown these compounds to be intermediate between a trigonal bipyramid and square pyramid[17] with trans rather than cis phenolic oxygen atoms. Differences in the X-ray powder photographs of Ni(SALDPT) and Co(SALDPT) have been attributed to subtle differences in the packing of molecules in the crystal rather than to substantial changes in the stereochemistries of the complexes.[2] Supporting evidence for the trans arrangement in complexes of the "SALDPT type" is found in the recently performed X-ray study of [Co^{III}(SALDPT)(1-methylimidazole)]Br wherein the cobalt(III) is nearly octahedral and the quinquedentate ligand adopts a trans configuration.[18]
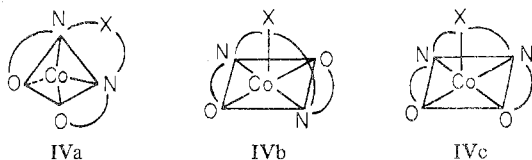
The similarity of the spectrum of Co(SALPhDPT) to the spectra of both Co(SALDPT) and Co(SALMeDPT) must be taken as an indication of geometry similarity. See Figure 2. Although a weaker donor is evidenced by the shift of each band maximum to lower energy, the tertiary aryl nitrogen atom is apparently forced into coordination by the trans structure of the complex, IVb, rather than the cis structure, IVc.

On the other hand, Co(SALMeDAPP)(H$_2$O) appears to have a somewhat different structure as revealed by the visible spectrum, Figure 2. Back-bonding to the phosphorus atom may result in a less distorted structure. The similarity in its spectrum to that of [Co(trenMe$_6$)Br]Br suggests a more trigonal-bipyramidal structure. The infrared and visible spectral data support the contention that H$_2$O is a water of crystallization.

One major difference between Co(SALPhDPT) and Co(SALMeDAPP)(H$_2$O) as a group and Co(SALDPT) and Co(SALMeDPT) as a group is their behavior in pyridine. The latter group exhibits the same spectra in the solid state as well as in pyridine, whereas in pyridine the former group gives different spectra characteristic of six-coordinate pseudooc-
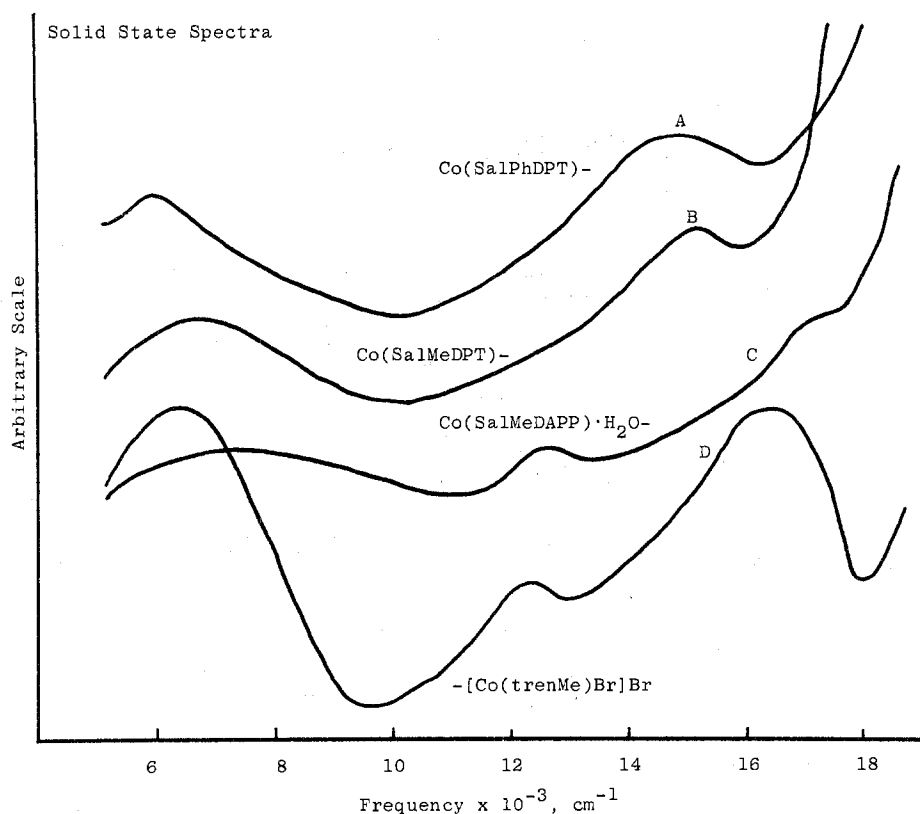

IVa   IVb   IVc

Figure 2. Near-infrared spectra of Co(SALPhDPT) (A), Co(SALMeDPT) (B), Co(SALMeDAPP)(H$_2$O) (C), and [Co(trenMe$_6$)Br]Br (D) in solid state.

tahedral species, Table III. No doubt a pyridine molecule completes the hexacoordinate structure.

In conclusion the length of the donor-containing chain joining azomethine groups certainly influences the extent to which the central donor may coordinate; however, even with sufficient chain flexibility a relatively poor donor like an ether or thioether linkage apparently will not coordinate. It is open to question as to whether this behavior is due to the poor coordinative affinity of the central bridging atom or due to the reluctance of the bridging chain of H$_2$SALDAPE and H$_2$SALDAPS to span trans positions. Since the chain of each pentadentate ligand is seven atoms in length and amines and phosphines are better ligands than ethers and thioethers, the best explanation for this different behavior appears to lie in the coordinating ability of the central donor. Whether the fifth donor group is in fact coordinated affects the reactivity of these materials with small molecules. Preliminary results suggest that the tetrahedral complexes will not react with dioxygen or alkyl substrates whereas the five-coordinate materials are very promising in this regard.

Registry No. Co(SALDAPE), 52279-51-3; Co(SALDAPS), 52279-54-6; Co(SALPhDPT), 53385-24-3; Co(SALMeDAPP), 53385-25-4.

References and Notes

(1) C. Furlani, *Coord. Chem. Rev.*, **3**, 141 (1968).
(2) L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, **88**, 5180 (1966).
(3) I. Bertini, L. Sacconi, and G. P. Speroni, *Inorg. Chem.*, **11**, 1323 (1972).
(4) W. N. Wallis and S. C. Cummings, *Inorg. Chem.*, **13**, 988 (1974).
(5) S. R. Edmondson, W. M. Coleman, and L. T. Taylor, *Inorg. Chem.*, **12**, 1191 (1973).
(6) M. Israel, J. S. Rosenfield, and E. J. Modest, *J. Med. Chem.*, **7**, 710 (1964).
(7) L. W. Lane and L. T. Taylor, *J. Coord. Chem.*, **2**, 295 (1973).
(8) M. Grayson, P. T. Keough, and G. A. Johnson, *J. Amer. Chem. Soc.*, **81**, 4803 (1959).
(9) J. T. Braunholtz and F. C. Mann, *J. Chem. Soc.*, 1817 (1953).
(10) A. K. St. Clair, M.S. Thesis, Virginia Polytechnic Institute and State University, 1972.
(11) A. G. King and L. T. Taylor, *J. Inorg. Nucl. Chem.*, **33**, 3057 (1971).
(12) L. T. Taylor and J. G. Dillard, *Inorg. Chem.*, **13**, 2620 (1974).
(13) H. Weigold and B. O. West, *J. Chem. Soc. A*, 1310 (1967).
(14) L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *J. Amer. Chem. Soc.*, **82**, 3246 (1962); E. Frasson and C. Panattoni, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **116**, 154 (1961).
(15) R. H. Niswander and L. T. Taylor, unpublished results.
(16) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966).
(17) M. DiVaira, P. L. Orioli, and L. Sacconi, *Inorg. Chem.*, **10**, 553 (1971).
(18) L. G. Marzilli, T. J. Kistenmacher, P. A. Marzilli, and L. A. Epps, *Inorg. Chem.*, **13**, 2089 (1974).