

CONTRIBUTION FROM WM. A. NOYES CHEMISTRY LABORATORY,
UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS

Non-aqueous Coördination Phenomena—Complexes of Hexamethylphosphoramide. II. Pseudo-tetrahedral Complexes of Nickel(II) and Cobalt(II)

BY JOHN T. DONOGHUE¹ AND RUSSELL S. DRAGO

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In part I,² we reported tetrahedral cations formed by Ni(II) and Co(II) with the ligand hexamethylphosphoramide, OP[N(CH₃)₂]₃ (HMPA). In this paper we report adducts of Co(II) and Ni(II) halides and nitrates with this ligand, in which the anions from the original metal salts remain coördinated in the complexes. The compounds reported are treated in three general classes: CoX₂·2HMPA (X = halide), NiX₂·2HMPA, and M(NO₃)₂·2HMPA (M = Co, Ni, Cu). The preparations of these compounds are outlined. Conductivity, spectral, magnetic, and other data are interpreted to infer the structures of these compounds. From the data presented, it can be concluded that most of these compounds contain Co(II) and Ni(II) in tetrahedral environments.

Introduction

In an earlier article,² the unusual coördinating properties of hexamethylphosphoramide, OP[N(CH₃)₂]₃ (HMPA), were introduced. Coördination of this ligand to Ni(II) resulted in the isolation of the first tetrahedral cationic complex of this ion as the perchlorate salt. The spectral and magnetic characteristics of Ni(HMPA)₄⁺² are very similar to those of NiCl₄⁻². Data presented in this first article also indicated that HMPA and chloride ion occupy nearby positions in the spectrochemical series. It was therefore of interest to prepare complexes of this ligand with various nickel halides and to compare these products with other reported nickel complexes. Complexes of the cobalt halides and nitrate as well as nickel nitrate also were investigated.

It is felt that more data of this type must be accumulated to enable generalizations to be made concerning the essential factors leading to the different kinds of complexes which result. The variations in structures reported for some of these metal complexes will be reviewed briefly. In 1958, Venanzi reported³ the pseudo-tetrahedral (*i.e.*, C_{2v}) complex NiCl₂·2(C₆H₅)₃P. It also was reported that the bromo and iodo derivatives were most probably tetrahedral, while a thiocyanate derivative was found to be *trans*-planar. Similar complexes were prepared for the ligands (*p*-anisyl)₃P, (*p*-tolyl)₃P, and (C₆H₅)₂P(*n*-C₄H₉).^{4a} Complexes formed with nickel(II) halides by the ligands (*n*-C₄H₉)₂P-C₆H₅^{4b} and some aliphatic phosphines⁵ resulted in *trans*-planar complexes. These complexes studied by Venanzi generally are acknowledged to be the first genuinely demonstrated tetrahedral complexes of nickel(II).

Cotton and co-workers have described several tetrahedral complexes of cobalt(II) halides similar to those

described above: Co[(C₆H₅)₃P]₂X₂, Co[(C₆H₅)₃As]₂I- and [Co(C₆H₁₁)₃P]₂X₂.⁶ Complexes involving phosphine oxide and arsine oxide ligands coördinated to cobalt(II) and nickel(II) also have been investigated.⁶ Tetrahedral cobalt(II) complexes of the type CoL₂X₂ (where L = (C₆H₅)₃AsO or (C₆H₅)₃PO and X = halide) are reported. The nickel complexes [Ni(C₆H₅)₃PO]₂-X₂ and [Ni(C₆H₅)₃AsOX₂] are reported to contain tetrahedral nickel(II).

In contrast to the above type complex, it was found⁷ that nickel(II) chloride and cobalt(II) chloride formed complexes with dimethyl sulfoxide of the type: {Ni[(CH₃)₂SO]₆}NiCl₄ and {Co[(CH₃)₂SO]₆}[CoCl₄]. In view of the above described variations in structure, it was of interest to determine the formulation of the HMPA complexes formed with these metal halides.

Experimental

CoX₂·2HMPA Compounds (X = Cl, Br, I, NCS).—Five g. of anhydrous CoX₂ was dissolved in 20 ml. of A.R. acetone and excess HMPA added. The mixture was allowed to stir for 2 hr. Precipitation was accomplished by adding a 10:1 volume excess of low boiling (30–60°) petroleum ether. The solids were filtered, washed fifteen times with petroleum ether, and dried *in vacuo* over H₂SO₄; yields ranged from 50–80%.

Anal. Calcd. for CoCl₂·2HMPA: C, 29.52; H, 7.46; N, 17.22. Found: C, 29.73; H, 7.51; N, 16.91. Calcd. for CoBr₂·2HMPA: C, 24.97; H, 6.30; N, 14.56. Found: C, 25.30; H, 6.28; N, 14.34. Calcd. for Co(NCS)₂·2HMPA: C, 31.51; H, 6.81; N, 21.01. Found: C, 31.69; H, 6.69; N, 20.73. Calcd. for CoI₂·2HMPA: C, 21.47; H, 5.42; N, 12.52. Found: C, 21.61; H, 5.64; N, 12.74.

Molecular weights for the dichloro derivative in benzene and toluene were found to be 477 and 498. The calculated value for a monomer is 488.

NiX₂·2HMPA (X = Cl, Br, I).—Five g. of anhydrous nickel halide was dissolved in excess HMPA by heating to greater than 100°. The temperature was maintained for 1 hr. to expel water from the reactants. The reaction mixture then was poured into 150 ml. of low petroleum ether and allowed to cool. The crystals were collected, washed fifteen times with petroleum ether, and dried *in vacuo* over H₂SO₄ for 48 hr; yields varied from 70–90%.

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(7) D. W. Meek, D. K. Straub, and R. S. Drago, *J. Am. Chem. Soc.*, **82**, 6013 (1960), and references contained therein.

(1) Universal Match Foundation Fellow. Abstracted in part from the Ph.D. Thesis of John T. Donoghue.

(2) J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **1**, 866 (1962).

(3) L. M. Venanzi, *J. Chem. Soc.*, 719 (1958).

(4) (a) M. C. Browning, R. F. B. Davies, D. J. Morgan, E. Sutton, and L. M. Venanzi, *ibid.*, 4816 (1961); (b) C. R. Coussmaker, M. H. Hutchinson, J. R. Mellor, L. E. Sutton, and L. M. Venanzi, *ibid.*, 2075 (1961).

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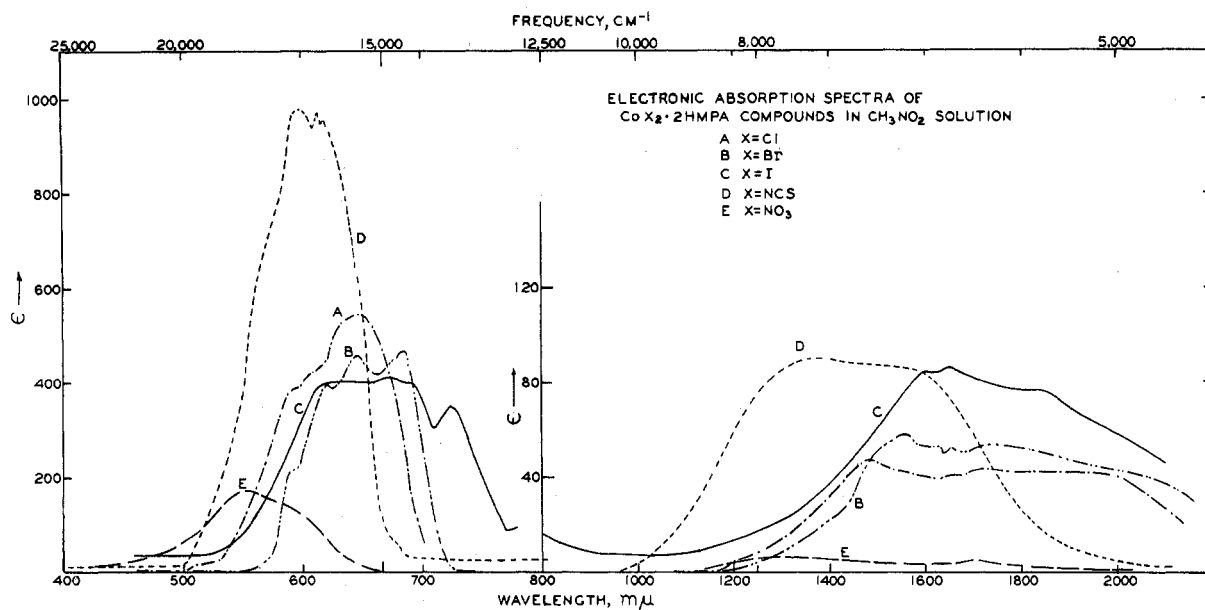


Figure 1.

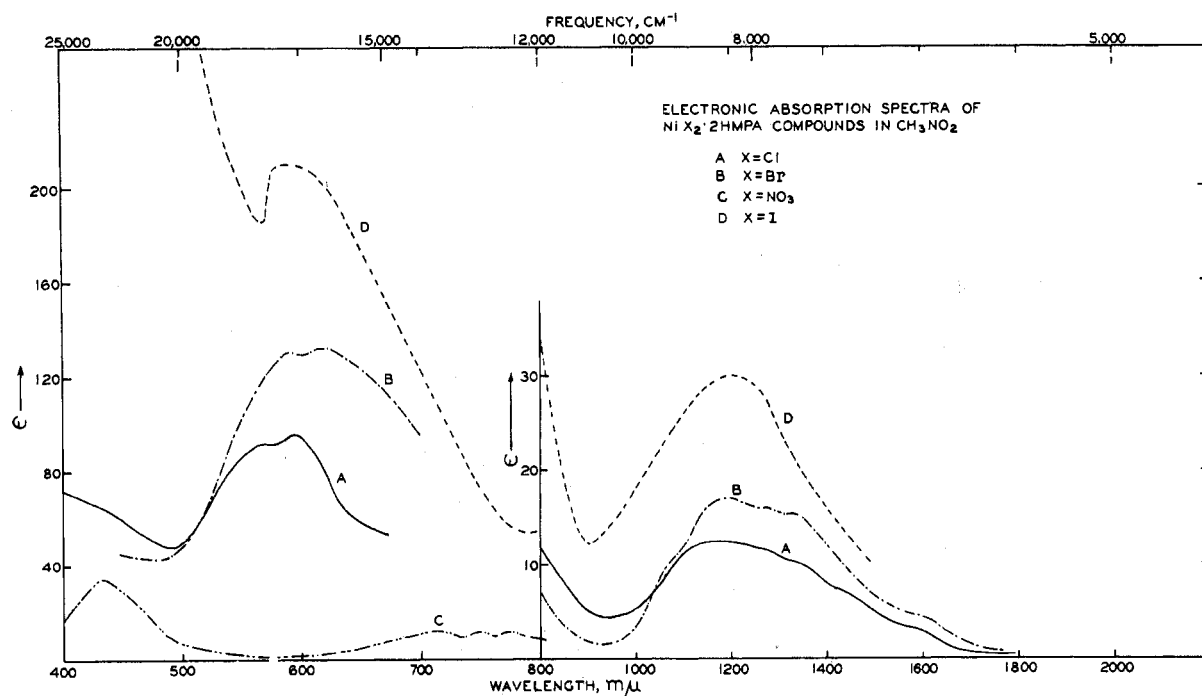


Figure 2.

Anal. Calcd. for $\text{NiCl}_2 \cdot 2\text{HMPA}$: C, 29.53; H, 7.45; N, 17.22. Found: C, 29.44; H, 7.49; N, 17.07. Calcd. for $\text{NiBr}_2 \cdot 2\text{HMPA}$: C, 24.98; H, 6.30; N, 14.57. Found: C, 24.71; H, 6.57; N, 14.33. Calcd. for $\text{NiI}_2 \cdot 2\text{HMPA}$: C, 21.49; H, 5.43; N, 12.53. Found: C, 21.68; H, 5.64; N, 12.16.

Nitrato Complexes.—These compounds were prepared by dehydrating the hydrated nitrate with 2,2-dimethoxypropane as previously described.² An excess of ligand then was added and the mixture allowed to stir. Precipitation was accomplished by adding a 10:1 excess of low petroleum ether; yields were 90% or better.

Anal. Calcd. for $\text{Co}(\text{NO}_3)_2 \cdot 2\text{HMPA}$: C, 26.62; H, 6.72; N, 20.70. Found: C, 26.95; H, 6.79; N, 20.56. Calcd. for $\text{Ni}(\text{NO}_3)_2 \cdot 2\text{HMPA}$: C, 26.63; H, 6.72; N, 20.70. Found: C, 26.92; H, 6.77; N, 20.33. Calcd. for $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{HMPA}$: C, 26.40; H, 6.66; N, 20.53. Found: C, 26.24; H, 6.68; N, 20.28.

Conductance Measurements.—Measurements of the conductivities of nitromethane solutions of these complexes were obtained as previously described.² The results are indicated in Table I.

Spectral Measurements.—Electronic spectra of nitromethane

TABLE I

Compound	Concn., M	Temp., °C.	Λ_{inolar}
$\text{CoCl}_2 \cdot 2\text{HMPA}$	0.001	27.0	1.41
$\text{CoBr}_2 \cdot 2\text{HMPA}$.0005	26.0	1.44
$\text{CoI}_2 \cdot 2\text{HMPA}$.0003	27.0	1.15
$\text{Co}(\text{NCS})_2 \cdot 2\text{HMPA}$.001	27.0	1.84
$\text{Co}(\text{NO}_3)_2 \cdot 2\text{HMPA}$.0020	27.0	1.15
$\text{NiCl}_2 \cdot 2\text{HMPA}$.001	25.4	1.32
$\text{NiBr}_2 \cdot 2\text{HMPA}$.0005	25.4	1.03
$\text{NiI}_2 \cdot 2\text{HMPA}$.0005	25.4	2.12
$\text{Ni}(\text{NO}_3)_2 \cdot 2\text{HMPA}$.0005	28.0	3.10

TABLE II
SPECTRAL DATA FOR $\text{CoX}_2 \cdot 2\text{HMPA}$, $\text{NiX}_2 \cdot 2\text{HMPA}$, AND
 $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{HMPA}$

Compound	Medium	ν_3 $\lambda_{\text{max}}, \text{m}\mu$	ν_2 $\lambda_{\text{max}}, \text{m}\mu$
$\text{CoCl}_2 \cdot 2\text{HMPA}$	Solid, reflectance	432	
		475	
		498	
		600 (sh)	
$\text{CoCl}_2 \cdot 2\text{HMPA}$	0.002 M in CH_3NO_2	656	
		515 (sh)	
		590 (sh)	1450 (43)
		605 (sh)	1700 (42)
		650 (545)	1850 (42)
$\text{CoBr}_2 \cdot 2\text{HMPA}$	Solid, reflectance	407	
		440	
		480 (sh)	
		510	
		590 (sh)	
		640	
		655	
		690	
$\text{CoBr}_2 \cdot 2\text{HMPA}$	0.002 M in CH_3NO_2	590 (sh)	1490 (55) ^a
		620 (400) ^a	1700 (53)
		647 (450)	2000 (42)
		672 (440)	
$\text{CoI}_2 \cdot 2\text{HMPA}$	Solid, reflectance	415	
		460	
		520	
		570-700	
		630 (sh)	
$\text{CoI}_2 \cdot 2\text{HMPA}$	5×10^{-4} M in CH_3NO_2	655 (404)	1580 (79)
		725 (330)	1620 (82)
		760 (sh)	1800 (74)
		805 (120)	
		490	
$\text{Co}(\text{NCS})_2 \cdot 2\text{HMPA}$	Solid, reflectance	565 (sh)	
		585	
		630	
		650 (sh)	
$\text{Co}(\text{NCS})_2 \cdot 2\text{HMPA}$	0.001 M in CH_3NO_2	565 (sh)	
		605 (980)	1300 (81)
		616 (960)	1590 (sh)
		622 (950)	
		630 (sh)	
$\text{Co}(\text{NO}_3)_2 \cdot 2\text{HMPA}$	Solid, reflectance	540-600	
$\text{Co}(\text{NO}_3)_2 \cdot 2\text{HMPA}$	0.001 M in CH_3NO_2	568 (170)	
$\text{NiCl}_2 \cdot 2\text{HMPA}$	Solid, reflectance	460	
		590	
		610	
$\text{NiCl}_2 \cdot 2\text{HMPA}$	0.0025 M in CH_3NO_2 ^b	400	1150 (12)
		575 (sh)	1410 (sh)
		596 (95)	1590 (sh)
$\text{NiBr}_2 \cdot 2\text{HMPA}$	Solid, reflectance	480	
		610 (sh)	
		670	
$\text{NiBr}_2 \cdot 2\text{HMPA}$	0.005 M in CH_3NO_2 ^b	400	1230 (14)
		610 (130)	1300 (sh)
$\text{NiI}_2 \cdot 2\text{HMPA}$	Solid, reflectance	402	
		436	
		442	
		460	
		510	
		535	
		640	
		700	
$\text{NiI}_2 \cdot 2\text{HMPA}$	0.01 M in acetone ^b	420 (>1200)	1190 (29)
		585 (215)	

TABLE II (Continued)

Compound	Medium	ν_3 $\lambda_{\text{max}}, \text{m}\mu$	ν_2 $\lambda_{\text{max}}, \text{m}\mu$
$\text{Cu}(\text{NO}_3)_2 \cdot 2\text{HMPA}$	Solid, reflectance	<400	
		>700	
$\text{Cu}(\text{NO}_3)_2 \cdot 2\text{HMPA}$	0.01 M in CH_3NO_2	378 (110)	
		750 (55)	
$\text{Ni}(\text{NO}_3)_2 \cdot 2\text{HMPA}$	Solid, reflectance	~440	
		>700	
$\text{Ni}(\text{NO}_3)_2 \cdot 2\text{HMPA}$	0.01 M in CH_3NO_2	<360	
		435 (33)	
		710 (10)	
		746 (10)	
		775 (sh)	

^a Numbers in parentheses designate apparent molar extinction coefficients at band maxima. ^b These solutions develop opalescence upon standing due to deposition of anhydrous nickel halides.

solutions of the compounds were obtained with a Cary (Model 14M) recording spectrophotometer. Solid reflectance spectra were obtained using a standard reflectance attachment with a Bausch and Lomb Spectronic 505 recording spectrophotometer. Blocks of MgCO_3 were used as the standard. Electronic spectral data are tabulated in Table II and summarized in Fig. 1 and 2.

Infrared Data.—The phosphoryl frequencies of the free ligand and the complexes have been determined; these are presented in Table III. The data are interpreted in terms of oxygen being the donor site of the ligand in all cases studied. The infrared spectra definitely indicate the absence of water in the complexes.

TABLE III

Compound	Medium	$\nu_{\text{P=O}}$, cm^{-1}
$\text{PO}[\text{N}(\text{CH}_3)_2]_3$	Smear	1208
$\text{CoCl}_2 \cdot 2\text{HMPA}$	Nujol	1193
$\text{CoBr}_2 \cdot 2\text{HMPA}$	Nujol	1193
$\text{CoI}_2 \cdot 2\text{HMPA}$	Nujol	1193
$\text{Co}(\text{NCS})_2 \cdot 2\text{HMPA}$	Nujol	1190
$\text{Co}(\text{NO}_3)_2 \cdot 2\text{HMPA}$	Nujol	1191
$\text{NiCl}_2 \cdot 2\text{HMPA}$	Nujol	1193
$\text{NiBr}_2 \cdot 2\text{HMPA}$	Nujol	1191
$\text{NiI}_2 \cdot 2\text{HMPA}$	Nujol	1188
$\text{Ni}(\text{NO}_3)_2 \cdot 2\text{HMPA}$	Nujol	1198
$\text{Cu}(\text{NO}_3)_2 \cdot 2\text{HMPA}$	Nujol	1188

Magnetic Measurements.—The room temperature magnetic susceptibilities of the complexes were measured by the Gouy method utilizing a Newport (Type C) electromagnet. The Gouy tubes were calibrated using solid $\text{Hg}[\text{Co}(\text{NCS})_4]$ as standard, as described by Figgis and Nyholm.^{8,9} The calibrations were checked by determinations of the susceptibility of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The moments given in Table IV, corrected for diamagnetic

TABLE IV

Compound	$10^3 \chi_M$	10^3 (dia. mag. contribn.)	$10^3 \chi_M'$	μ_{eff} , B.M.
$\text{CoCl}_2 \cdot 2\text{HMPA}$	8836	313	9149	4.72 ± 0.04
$\text{CoBr}_2 \cdot 2\text{HMPA}$	9453	334	9787	4.88 ± 0.04
$\text{CoI}_2 \cdot 2\text{HMPA}$	9508	362	9870	4.91 ± 0.04
$\text{Co}(\text{NCS})_2 \cdot 2\text{HMPA}$	8528	335	8863	4.66 ± 0.04
$\text{NiCl}_2 \cdot 2\text{HMPA}$	6388	313	6701	4.03 ± 0.04
$\text{NiBr}_2 \cdot 2\text{HMPA}$	6247	334	6581	4.00 ± 0.04
$\text{NiI}_2 \cdot 2\text{HMPA}$	6125	362	6487	3.98 ± 0.04
$\text{Co}(\text{NO}_3)_2 \cdot 2\text{HMPA}$	8115	311	8426	4.52 ± 0.04
$\text{Cu}(\text{NO}_3)_2 \cdot 2\text{HMPA}$	1008	311	1319	1.79 ± 0.06
$\text{Ni}(\text{NO}_3)_2 \cdot 2\text{HMPA}$	4583	311	4894	3.47 ± 0.04

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contributions⁹ (but not for temperature independent paramagnetism), are room temperature (30°) values.

Discussion

The reduction of the P=O stretching frequencies in the compounds as compared with the value in the free ligand supports the contention that complex formation occurs through the oxygen on the ligand molecule. The infrared spectra of Nujol mulls of the complexes indicate the absence of water. The conductivities for the complexes in nitromethane solutions are far lower than those reported for typical electrolytes,¹⁰ so it appears that the complexes are all non-electrolytes. Monomeric structures also would seem to be indicated. This latter contention is supported by molecular weight values found for $\text{CoCl}_2 \cdot 2\text{HMPA}$ in benzene and toluene, which are reported in the Experimental section. It was not possible to obtain molecular weights for the nickel compounds, since solutions of these complexes rapidly decompose.

The spectra of the cobalt derivatives (shown in Fig. 1 and summarized in Table II) show the characteristic long visible wave length absorption (ν_3) which usually is found for tetrahedral Co(II) compounds. They also exhibit the multi-component absorption in the 1000 to 2000 $\text{m}\mu$ range (ν_2) found for Co(II) in tetrahedral surroundings. The absorption intensities are very much higher than those normally observed for octahedral complexes¹⁰ of Co(II). As reported earlier,² the intensities of absorption are strongly dependent on the concentration of the complex in solution. References to several observations of similar nature by several other workers are given in reference 2.

An interesting observation is apparent from comparison of the reflectance spectra of these compounds with the nitromethane spectra. Several high energy (low intensity) peaks disappear as a result of the solution process. There seems to be no appreciable change in the lower energy peaks. These observations would tend to indicate some minor change has occurred in the ligand field in the solution process. Nevertheless, the solution spectra are still in accord with a predominantly hemihedric cubic field about the Co(II), upon which is superposed a contribution for a lower symmetry C_{2v} component. On the basis of the spectra, it is concluded that the compounds are pseudo-tetrahedral.^{9,11}

The magnetic moments of the solid compounds, given in the Experimental section, are in accord with the previous conclusions. The observed regular increase in moments upon proceeding from the chloro to the iodo compound is in accord with ligand field theory. The ground state of Co(II) in a tetrahedral field is a singlet and a ground state orbital contribution is not expected. However, the first excited state is a triplet and can give rise to an orbital contribution if mixed in. The separation between these states (Δ) decreases

from chloride to iodide and thus the orbital contribution is expected to increase in this order as is observed for the HMPA complexes. The spectral and magnetic properties of these compounds are similar to those found for complexes of cobalt(II) which have been characterized as pseudo-tetrahedral.^{9,11}

Studies on the HMPA complexes of nickel halides enable one to draw some interesting conclusions relative to the structure of these compounds. The infrared and conductivity data are similar to those found for the Co(II) complexes and it is probable that these complexes are also monomeric. The spectra of these compounds exhibit long wave length absorption and absorption intensities very much higher than those normally associated with centrosymmetric Ni(II).¹⁰ The chloro and bromo derivatives show singlet or doublet peaks of very small multiplet separation, and the overall results would seem to indicate essentially tetrahedral stereochemistry in these complexes. Thus it can be concluded that the average field approximation¹² is valid and thus the ligand field is essentially cubic with a small C_{2v} perturbation superimposed on the T_d field. The iodo compound shows a strong peak at longer visible wave lengths and a very strong peak at shorter wave lengths, similar to the results observed for NiI_4^{-2} .¹⁰ It is thought possible that in this compound the C_{2v} contribution to the field is more significant than in the other cases studied. The same effects of concentration on absorption intensity as mentioned for the cobalt(II) compounds are found in the spectra of the Ni(II) complexes.

The magnetic moment data are interesting in that the values would seem to indicate very large orbital contributions to the total moment. It has been suggested that an inverse relationship exists between the magnitude of the orbital contribution and the magnitude of distortion from pure tetrahedral symmetry.¹³ If such is the case, the moments of the HMPA complexes tend to show that distortions from regular symmetry in these compounds are indeed small. Since the moments of these compounds are essentially identical within experimental error, no conclusions relative to the respective magnitudes of distortion are warranted on magnetic grounds. In contrast to these moments are those reported by Venanzi⁹ for $\text{NiX}_2 \cdot 2\text{P}(\text{C}_6\text{H}_5)_3$ in which the distortions are known to be quite large ($\mu \sim 3$ B.M.). Cotton^{14,15} reports values for $\text{NiX}_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ ($\mu \sim 4$ B.M.) which are similar to those of $\text{NiX}_2 \cdot 2\text{HMPA}$ and it thus appears that deviations from T_d symmetry in both these sets of complexes are very small.

Studies on the nitrate complexes revealed some interesting results. The conductivity data suggest that the nitrate ions are located within the coordination spheres of Co(II), Ni(II), and Cu(II), respectively, in these compounds. The Cu(II) compound gives a

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(10) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(11) F. A. Cotton, O. D. Faut, D. M. L. Goodgame, and R. H. Holm, *J. Am. Chem. Soc.*, **83**, 1780 (1961).

magnetic moment which would seem to preclude the possibility of tetrahedral Cu(II). The spectrum (Table II) is in accord with those of known planar Cu(II) complexes, though a highly distorted tetragonal complex involving bidentate nitrate groups cannot be positively rejected. The compound gives a spectrum similar to that of $\text{Cu}(\text{NO}_3)_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ for which square planar geometry has been assumed.¹⁶ The ϵ values are greater by a factor of ten than those¹⁷ for $\text{Cu}(\text{NO}_3)_4^{-2}$, implying a square planar or highly distorted tetragonal structure for $\text{Cu}(\text{HMPA})_2(\text{NO}_3)_2$.

The compound $\text{Co}(\text{NO}_3)_2 \cdot 2\text{HMPA}$ gives a spectrum which exhibits a single visible band of intermediate intensity ($\epsilon \sim 175$), somewhat lower than intensities normally associated with tetrahedral Co(II). However, the magnetic moment of the compound given in the Experimental section would seem to preclude possible octahedral coordination although a highly distorted tetragonal structure involving chelate or bridging nitrate cannot be eliminated. Similar effects have been noted for other Co(II) complexes in which NO_3^- is a ligand. It was concluded that these complexes were tetrahedral.¹⁶⁻¹⁸ The compound $\text{Ni}(\text{NO}_3)_2 \cdot 2\text{HMPA}$, a yellow solid, exhibits an absorption spectrum very much different from those normally associated with tetrahedral Ni(II). The spectrum shows several bands

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of low intensity suggestive of centrosymmetric Ni(II). Two possibilities exist here. The complex could be tetragonal due to bidentate nitrate groups¹⁷ or could be a radically distorted tetrahedral (*i.e.*, D_{2d}) structure. The spectrum of the compound is very similar to that reported for $\text{Ni}(\text{NO}_3)_2 \cdot 2(\text{C}_6\text{H}_5)_3\text{PO}$ ¹⁶ for which a D_{2d} structure has been suggested. The spectra of both of these compounds agree qualitatively with predictions of the appearance of the spectrum for Ni(II) in a ligand field of D_{2d} symmetry.^{19,20} Once again, the possibility of tetragonal coordination cannot be completely dismissed.

On the basis of evidence presented in earlier sections, it is concluded that the compounds: $\text{CoX}_2 \cdot 2\text{HMPA}$ ($X = \text{Cl}, \text{Br}, \text{I}, \text{NCS}, \text{NO}_3$) contain Co(II) in pseudo-tetrahedral (C_{2v}) environments and the compounds $\text{NiX}_2 \cdot 2\text{HMPA}$ ($X = \text{Cl}, \text{Br}, \text{I}$) contain Ni(II) in the same geometrical arrangement. $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{HMPA}$ is thought to be a planar complex while Ni(II) in $\text{Ni}(\text{NO}_3)_2 \cdot 2\text{HMPA}$ probably experiences a pseudo- D_{2d} ligand field.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, NORTH CAROLINA

The Chemistry of Metal Chelate Rings. IV. Electrophilic Substitution of Optically Active Tris-acetylacetonates¹⁻³

By JAMES P. COLLMAN, ROBERT P. BLAIR, ROGER L. MARSHALL, AND LAIRD SLADE

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The tris-acetylacetonates of chromium(III), cobalt(III), and rhodium(III) were resolved by chromatography on a 16-ft. column of *D*-lactose hydrate. The optically active chelates were subjected to a variety of electrophilic substitution reactions including chlorination, bromination, thiocyanogenation, nitration, and acetylation. In each instance, the substituted chelates were found to be optically active, suggesting that the chelate rings are not ruptured during electrophilic substitution. The optical stabilities of the cobalt and rhodium chelates were examined. Several of the cobalt chelates were found to racemize during crystallization whereas the rhodium chelates exhibited remarkable optical stability.

Introduction

During the past three years, experiments in these and other laboratories have demonstrated that several metal acetylacetonates and related chelate systems undergo a variety of electrophilic substitutions of the central carbon of the chelate rings in the manner of an aromatic

system.⁴⁻¹² By such processes, the inert tris-acetyl-

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(3) Part of this work is taken from the Ph.D. dissertation of Robert P. Blair, 1961, and from the Ph.D. dissertation of Roger L. Marshall, 1962, University of North Carolina.

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