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Non-aqueous Coordination Phenomena—Complexes of Hexamethylphosphoramide. I. Preparation and Properties of Tetrahedral $[Zn\{PO[N(CH_3)_2]_3\}_4]^{+2}$, $[Co\{PO[N(CH_3)_2]_3\}_4]^{+2}$, and $[Ni\{PO[N(CH_3)_2]_3\}_4]^{+2}$ Compounds

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The ligand hexamethylphosphoramide forms some complexes of unusual stereochemistry and properties. Among these are the 1:4 adducts of $Zn(ClO_4)_2$, $Co(ClO_4)_2$, and $Ni(ClO_4)_2$. The preparation of these compounds is outlined and evidence indicating that these compounds contain tetrahedral cations is presented. At present, the nickel complex is the most nearly tetrahedral cationic complex of Ni(II) known. Approximate values of ligand field and electronic parameters are given for the Co(II) HMPA compound.

Introduction

In recent years it has been shown that tetrahedral Ni(II) complexes, though rare, do indeed exist. Venanzi[3] has prepared complexes of the type $NiX_2 \cdot 2(C_6H_5)_3P$ (X = halogen, NO_3) and has shown that these compounds contain tetrahedrally disposed Ni(II). Cotton and co-workers[4–8] have prepared mixed ligand complexes of the type $NiX_2 \cdot 2(C_6H_5)_3PO$ and $NiX_2 \cdot 2(C_6H_5)_3AsO$ (X = halogen, etc.). These have been reported to contain tetrahedral Ni(II). Gill and Nyholm[9] have prepared CoX_4^{2-} and NiX_4^{2-} complexes of the type $(R_4N)_2NiX_4$ and $(R_4N)_2CoX_4$ (X = halogen). These workers have reported the electronic spectra and have concluded that these ions are essentially tetrahedral.

The present study of the donor properties of $PO[N(CH_3)_2]_3$(HMPA) has produced complexes of this ligand with $Zn(ClO_4)_2$, $Ni(ClO_4)_2$, and $Co(ClO_4)_2$ which are tetrahedral. We believe the Ni(II) compound to be the first reported case of a new class of tetrahedral Ni(II) complexes, *i.e.*, tetrahedral *cationic* complexes. The only tetrahedral cationic complex previously proposed was reported in a study by Cotton,[8] in which $[\{(C_6H_5)_3PO\}_4Ni](ClO_4)_2$ was presented as tetrahedral. Later work by this same author[10] indicated that the complex is not tetrahedral and possibly possess D_{2d} symmetry.

Experimental

Preparation of Compounds. Tetrakis-(hexamethylphosphoramide)-cobalt(II) Perchlorate.—Five grams of $Co(ClO_4)_2 \cdot 6H_2O$ was treated with a 100% excess of 2,2-dimethoxypropane[11] for 2 hr. with stirring. The dehydration was endothermic and could be followed nicely by the resultant cooling of the reaction vessel. At the end of the dehydration period, a slight excess of hexamethylphosphoramide was added, whereupon the solution turned blue and a blue solid began to deposit in the vessel. After 2 hr., a 5:1 volume excess of anhydrous ether was added, causing precipitation. The mixture was filtered, washed under nitrogen, and dried overnight *in vacuo* over P_2O_5; yield, 40%. The solid was a fine blue powder, which when very dry was not appreciably deliquescent.

Anal. Calcd. for $Co(ClO_4)_2 \cdot 4PO[N(CH_3)_2]_3$: C, 29.57; H, 7.46; N, 17.25. Found: C, 29.76; H, 7.47; N, 17.09.

Tetrakis-(hexamethylphosphoramide)-cobalt(II) Tetraphenylborate.—$Co(ClO_4)_2 \cdot 4HMPA$ (0.7 g.) was dissolved in acetone. To this was added 0.68 g. of $NaB(C_6H_5)_4$ also dissolved in acetone. Anhydrous ether was added to complete precipitation. The light blue solid subsequently was treated in the same fashion as the perchlorate. The compound was non-hygroscopic; yield, 75%.

Anal. Calcd. for $Co\{B(C_6H_5)_4\}_2 \cdot 4PO[N(CH_3)_2]_3$: C, 61.14; H, 8.00; N, 11.89. Found: C, 60.09; H, 8.00; N, 11.45.

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[1] Universal Match Foundation Fellow.

[2] Abstracted in part from the Ph.D. Thesis of John T. Donoghue.

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

[4] F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961).

[5] D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *ibid.*, **83**, 4161 (1961).

[6] F. A. Cotton and D. M. L. Goodgame, *ibid.*, **82**, 5771 (1960).

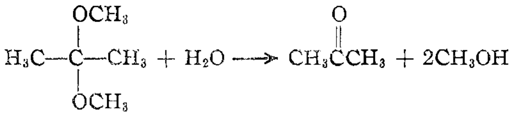
[7] D. M. L. Goodgame and F. A. Cotton, *ibid.*, **82**, 5774 (1960).

[8] F. A. Cotton, E. Bannister, R. Barnes, and R. H. Holm, *Proc. Chem. Soc.*, 158 (1959).

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

[10] F. A. Cotton and E. Bannister, *ibid.*, 1873 (1960).

[11] This compound reacts with H_2O according to the equation



$$H_3C-\overset{\displaystyle OCH_3}{\underset{\displaystyle OCH_3}{C}}-CH_3 + H_2O \longrightarrow CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_3 + 2CH_3OH$$

The reaction is presumably 95% complete in 1 hr. K. Starke, *J. Inorg. Nucl. Chem.*, **11**, 77 (1959).

Tetrakis-(hexamethylphosphoramide)-nickel(II) Perchlorate.—The details of the preparation were the same as for the Co(II) compound to the step in which excess ether was added. At this point a green oil separated from the reaction mixture. The mixture was allowed to stir for several minutes and the spent portion of ether then was decanted. This procedure was repeated, the oil growing darker with each successive extraction until its color was deep blue. The oil then was dissolved in nitromethane, followed by addition of a 10:1 volume excess of anhydrous ether. This treatment resulted in deposition of a deep blue, extremely deliquescent solid, which was filtered in a drybox, then stored for 48 hr. *in vacuo* over P_2O_5; yield, 94%.

Anal. Calcd. for $Ni(ClO_4)_2 \cdot 4PO[N(CH_3)_2]_3$: C, 29.58; H, 7.46; N, 17.25. Found: C, 29.75; H, 7.53; N, 17.27.

Tetrakis-(hexamethylphosphoramide)-zinc(II) Perchlorate.—After dehydrating $Zn(ClO_4)_2 \cdot 4H_2O$ in the manner already described addition of excess HMPA followed by addition of a 10:1 volume excess of ether yielded a white solid, which was washed 15 times with ether. The solid was dried *in vacuo* over H_2SO_4; yield, 99%.

Anal. Calcd. for $Zn(ClO_4)_2 \cdot 4PO[N(CH_3)_2]_3$: C, 29.37; H, 7.41; N, 17.14. Found: C, 29.73; H, 7.27; N, 17.00.

Conductance Measurements.—Measurements of the conductivities of nitromethane solutions of the complexes were obtained using an Industrial Instruments, Inc., bridge and a cell which previously had been calibrated with aqueous solutions of 0.01 *N* KCl. The results are summarized below.

	Concn. (*M*)	Λ Molar	Temp. (°C.)
$[Co(HMPA)_4](ClO_4)_2$	0.0105	178	30.4
$[Ni(HMPA)_4](ClO_4)_2$	.0049	184	25.0
$[Zn(HMPA)_4](ClO_4)_2$	.0020	180	26.5

X-Ray Powder Patterns.—X-Ray powder data were obtained utilizing cobalt $K\alpha_1$ radiation (λ = 1.78890 Å.) and a camera with rotating sample holder to minimize the effects of large particle size. It was not possible to grind the compounds since they decompose under heavy grinding. Under these conditions the patterns consisted of smooth arcs with relatively few spots to break the otherwise smooth appearance. Visual inspection of the diagrams reveals that all three patterns are indistinguishable. This observation is further supported by the data presented in Table II. From these data, it was concluded that $[Co(HMPA)_4](ClO_4)_2$ and $[Ni(HMPA)_4](ClO_4)_2$ are strictly isomorphous with $[Zn(HMPA)_4](ClO_4)_2$ and with each other.[12]

Spectral Measurements.—The infrared spectra for the free ligand and complexes gave the following phosphoryl frequencies, indicating coördination through oxygen. Due to strong perchlorate absorption in this region, in the case of the complexes, there is some uncertainty in these frequencies. The values should be regarded as upper limits for the P=O frequency. The infrared spectra definitely indicate the absence of water in these complexes.

	ν_{P-O} in cm.$^{-1}$
$PO[N(CH_3)_2]_3$ (smear)	1208
$[Co(HMPA)_4](ClO_4)_2$ (KBr)	1190
$[Co(HMPA)_4](ClO_4)_2$ (10% in CH_2Cl_2)	1188
$[Co(HMPA)_4](ClO_4)_2$ (Nujol)	1188
$[Zn(HMPA)_4](ClO_4)_2$ (Nujol)	1185
$[Ni(HMPA)_4](ClO_4)_2$ (KBr)	1193

Electronic solution spectra were obtained using a Cary (Model 14M) recording spectrophotometer. Solid reflectance spectra were obtained using the standard reflectance attachment with a Bausch and Lomb Spectronic 505 recording spectrophotometer with $MgCO_3$ as standard. All electronic spectral data are summarized in Table I and Fig. 1–3. The data obtained by several other workers for tetrahedral complexes are included in the table for comparison.

Magnetic Susceptibility Measurements.—Magnetic susceptibilities were measured using a Gouy magnetic balance. The Gouy tubes were calibrated using $Hg[Co(NCS)_4]$. The value of the susceptibility of this compound is given by Nyholm and Lewis.[13,14] The moments are room temperature values (30°) corrected for diamagnetism. The values for Pascal's constants were taken from Figgis and Lewis.[14]

Compound	χ_M × 10^6	Diamag. corrn. × 10^6	χ_M^1 × 10^6	μ_{eff} in B.M.
$Ni(ClO_4)_2 \cdot 4HMPA$	6041	550	6591	4.02 ± 0.04
$Co(ClO_4)_2 \cdot 4HMPA$	8077	550	8627	4.58 ± 0.04

The value for μ_{eff} (3.6 B.M.) for the Ni(II) compound is in the range predicted by Figgis[15] for Ni(II) in tetrahedral surroundings. Also, the moment is high enough so as to indicate very little contribution from a lower symmetry component. Introduction of say a C_{2v} or other lower symmetry component would lead to splitting of the ground state configuration with a resultant lower μ_{eff}.

Consideration of the data herein presented has led us to believe that the complexes of $Ni(ClO_4)_2$ and $Co(ClO_4)_2$ with $PO[N(CH_3)_2]_3$ are tetrahedral. Accordingly, we believe the Ni(II) compound to be the first member of a new series of Ni(II) complexes; a series of cationic tetrahedral Ni(II) species.

Results

The spectral data obtained and pertinent literature results are summarized in Table I. Table II contains X-ray powder diffraction data for $Co(HMPA)_4(ClO_4)_2$, $Ni(HMPA)_4(ClO_4)_2$, and $Zn(HMPA)_4(ClO_4)_2$.

Discussion

The conductance data in CH_3NO_2 establish the formulation of the compounds as $[M(HMPA)_4]$-

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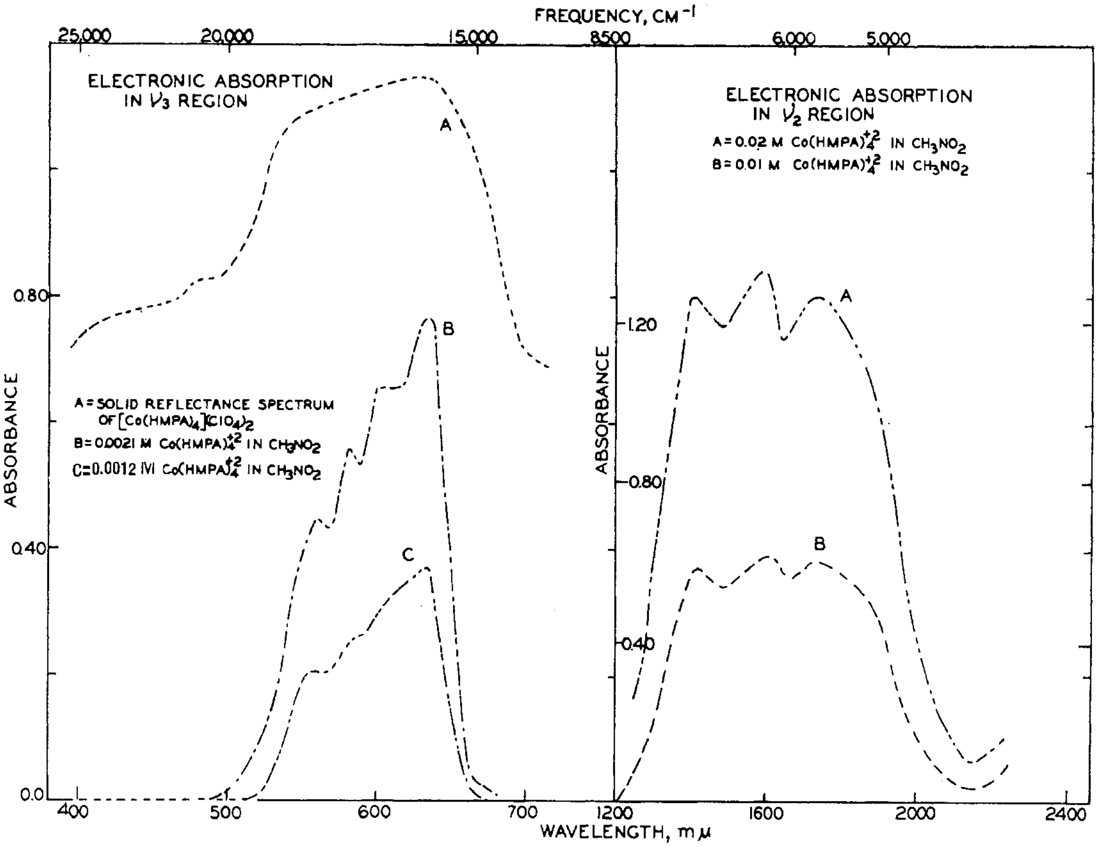
[12] The authors are indebted to Mr. George L. Morgan and Dr. C. E. Pfluger for assistance in obtaining and interpreting the powder data.

[13] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

[14] B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins (ed.), Interscience, New York, N. Y., 1960, p. 403.

[15] B. N. Figgis, *Nature*, **182**, 1568 (1958).



A. B.

Fig. 1A.—Electronic absorption spectra of [Co(HMPA)$_4$](ClO$_4$)$_2$ in the ν_3 region: curve A, diffuse reflectance spectrum of solid compound, ordinate in arbitrary units; curve B, spectrum of 0.0021 *M* solution in CH$_3$NO$_2$; curve C, .0011 *M*. Fig. 1B.—Electronic absorption spectra of nitromethane solutions of [Co(HMPA)$_4$](ClO$_4$)$_2$ in ν_2 region: curve A, 0.02 *M* solution; curve B, 0.01 *M*.

(ClO$_4$)$_2$ complexes. Infrared data indicate that the oxygen atom of HMPA is the donor site for all three metals. The spectral, magnetic, and X-ray data support the assignment of tetrahedral structures for all three cations. The similarity of the spectrum of Ni(HMPA)$_4^{+2}$ to that of NiCl$_4^{2-}$, of established tetrahedral structure, is evident in Fig. 2A and 2B. This is a very strong indication of similarity in structure for these two species. Magnetic moment data also support the contention that this ion is tetrahedral. The Co(II) and Zn(II) compounds which are not expected to show distortion from pure T$_d$ symmetry give X-ray powder diagrams which indicate strict isomorphism of these compounds and the Ni(II) derivative. This would indicate that any distortion from pure T$_d$ symmetry in the latter complex is not large.

Crystal field theory predicts that Ni(II) in a tetrahedral field must distort. On the other hand, Liehr argues that if spin orbit coupling is considered (as needs be for Ni(II) in tetrahedral fields) the ground state for Ni(II) is A$_1$ and hence is non-degenerate, so Jahn–Teller forces need not be operable. Also, the next state is at least 300 cm.$^{-1}$ removed, so large pseudo Jahn–Teller distortion should not be observed.[16] So according to the latter, tetrahedral Ni(II) without serious distortion is possible.

The data herein presented would indicate that our complex of Ni(II) does not belong to one of the specific point groups (*i.e.*, D$_{2d}$) which ordinarily are associated with distorted tetrahedral geometry. We submit on the basis of its apparent similarity to NiCl$_4^{2-}$ that, like the latter ion, it belongs to the point group T$_d$, exhibiting only slight distortion from pure tetrahedral symmetry. Support for this contention is lent by the obviously great similarity in the spectra of NiCl$_4^{-2}$ and Ni(HMPA)$_4^{+2}$ on the one hand and the greatly different spectrum of Ni(PO(C$_6$H$_5$)$_3$)$_4^{+2}$ on

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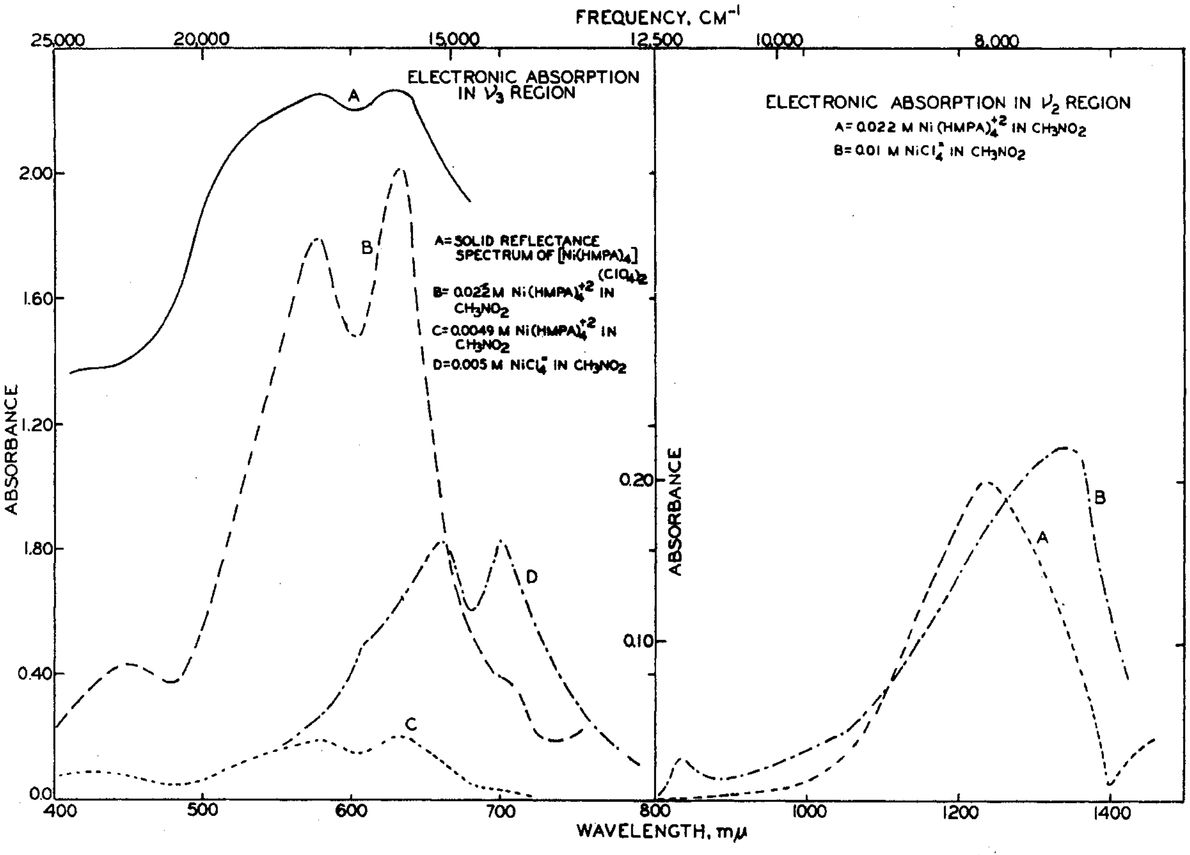
(16) A. D. Liehr, 137th National Meeting of A.C.S., April 5–14, 1960, Cleveland, Ohio.



A. B.

Fig. 2A.—Electronic absorption spectra of [Ni(HMPA)$_4$](ClO$_4$)$_2$ and NiCl$_4^{-2}$ in ν_3 region: curve A, diffuse reflectance spectrum of [Ni(HMPA)$_4$](ClO$_4$)$_2$; curve B, spectrum of 0.022 *M* HMPA complex in CH$_3$NO$_2$; curve C, spectrum of 0.0049 *M* HMPA complex in CH$_3$NO$_2$; curve D, spectrum of 0.005 *M* NiCl$_4^{-2}$ in CH$_3$NO$_2$ estimated from work of Gill and Nyholm.[9] Fig. 2B.—Electronic absorption spectra of nitromethane solutions of [Ni(HMPA)$_4$](ClO$_4$)$_2$ and NiCl$_4^{2-}$ in ν_2 region: curve A, 0.022 *M* HMPA complex; curve B, spectrum of 0.01 *M* NiCl$_4^{2-}$ estimated from work of Cotton.[5]

the other. The latter ion is thought to have a D$_{2d}$ configuration.[8,10]

In Fig. 1, 2, and 3 it is evident that a change in concentration of the complexes in CH$_3$NO$_2$ has a very pronounced effect on $\epsilon_{\max}$, particularly for the Ni(II) complex. Similar behavior was noted by other investigators[5,9,17,18] for CoCl$_4^{2-}$ and NiCl$_4^{2-}$. It is thought that this is due to disturbance solvation equilibria in CH$_3$NO$_2$. It is of interest to note in Fig. 2 that, for the concentrated Ni(II) solution, absorption at 450 mμ now has become detectable and significant. It is far less obvious at lower concentration because of the low molar absorptivities of these bands. Also, in the more concentrated solution, a shoulder appears at 715 mμ and a new band appears at 758 mμ. It is thought that absorption at these wave lengths possibly is due to solvated octahedral or tetragonal species. The 450-mμ peak does not appear in the reflectance spectrum, but does appear in solution. The peaks at 715 and 758 mμ are not evident for solutions of lower concentration but the intensities grow as the concentration of the complex in solution increases. These results are summarized in Fig. 3. As we add free ligand, increasing its concentration in solution, absorption at 582 and 633 mμ diminishes and that at 450 mμ increases until in the extreme case, absorption at 582 and 633 mμ vanishes. At this point the 450-mμ peak attains its maximum $\epsilon_{\max}$ value.

These observations are thought to indicate the possible presence of a species in solution which is other than four-coördinate. It is thought that this might partially explain the low observed $\epsilon_{\max}$ values for the 582 and 633 mμ peaks compared to those of NiCl$_4^{-2}$. The presence of six-

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(17) S. Buffagini and T. M. Dunn, *Nature*, **188**, 937 (1960).

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

TABLE I

ELECTRONIC ABSORPTION SPECTRA OF SOME TETRAHEDRAL COMPLEXES

Compound	Medium	$\lambda_{\max}$, mμ	ν_3, cm.$^{-1}$	$\lambda_{\max}$, mμ	ν_2, cm.$^{-1}$	Reference
$Co(ClO_4)_2 \cdot 4HMPA$	0.0021 *M* in CH_3NO_2	633 (374)[b]	15,800			*a*
		605 (302)	16,550			
		583 (268)	17,150			
		561 (210)	17,825			
		549 (sh)	18,200			
$Co(ClO_4)_2 \cdot 4HMPA$	0.02 *M* in CH_3NO_2			1400 (64)[b]	7150	*a*
				1590 (67)	6300	
				1710 (63)	5850	
$[Co(N_3)_4]^{2-}$	CH_3NO_2 soln.	618 (430)	16,180	1365 (150)	7330	19
		660 (760)	15,150	1480 (157)	6760	
		690 (800)	14,490	1675 (122) 1725 (116)	5970 5800	
$CoCl_4^{2-}$	0.0005 *M* in CH_3NO_2	693 (653)	14,400			9
		668 (580)	14,950			
		635 (419)	15,750			
		613 (sh)	16,300			
		593 (122)	16,850			
$Ni(ClO_4)_2 \cdot 4HMPA$	0.022 *M* in CH_3NO_2	450 (17)	22,200			
		582 (77.1)	17,200			
		633 (90.9)	15,800	1250 (9.0)	8000	*a*
		715 (sh)	14,000			
		758 (8.0)	13,175			
$Ni(ClO_4)_2 \cdot 4HMPA$	Solid, reflectance	~580	17,250			*a*
		~630	15,875			
$Ni(ClO_4)_2 \cdot 4HMPA$	0.005 *M* in CH_3NO_2	415 (sh)	24,100			*a*
		582 (38)	17,200			
		633 (42)	15,800			
$[Ni((C_6H_5)_3PO)_2I_2]$	0.01 *M* in acetone	714 (136)	14,000	~1360 (19.2)	7370	5
		800 (sh)	12,500			
$[Ni((C_6H_5)_3PO)_2Cl_2]$	Solid, reflectance	~615	16,275			5
		~700	14,300			
$NiCl_4^{2-}$	0.005 *M* in CH_3NO_2	610 (sh)	16,400			9
		660 (167)	15,150			
		700 (167)	14,300			
$[CH_3(C_6H_5)_3P]_2NiCl_4$	0.01 *M* in CH_3NO_2	658 (140)	15,200	1315 (18)	7620	5
		703 (134)	14,220	1160 (18)	8620	

[a] Designates this work. [b] Numbers in parentheses represent molar extinction coefficients at band maxima.

coördinate species also explains why the new peaks which appear in concentrated CH_3NO_2 solutions increase so markedly in intensity as free ligand concentration increases. A similar effect was observed as a function of time. $\epsilon_{\max}$ at the assigned tetrahedral peaks was found to decrease with time, whereas the intensities of the new bands were enhanced. As a general practice, spectra were recorded within 10 min. after preparation of a solution.

Cotton[19] has made approximate calculations of crystal field parameters for Co(II) complexes, utilizing the following relations, derived from the results of Tanabe and Sugano.[20]

$$\nu_1 = \Delta$$

$$\nu_2 = 1.5\Delta + 7.5B^1 - Q$$

$$\nu_3 = 1.5\Delta + 7.5B^1 + Q \qquad (1)$$

$$Q = {}^1/_2[(0.6\Delta - 15B^1)^2 + 0.64\Delta^2]^{1/2}$$

Δ = ligand field strength modulus, B^1 = effective value of Racah interelectronic repulsion integral.

In a field of tetrahedral symmetry, the ^4F ground state of Co(II) is split to give $^4A_2$, $^4T_2$, and $^4T_1(F)$. There is also a $^4T_1(P)$ state originating from ^4P in the free ion. Following Cotton,[17] the frequencies of the transitions $^4A_2 \rightarrow {}^4T_2$, $^4A_2 \rightarrow {}^4T_1(F)$, and $^4A_2 \rightarrow {}^4T_1(P)$ are designated ν_1, ν_2, and ν_3, respectively.

Low[21] has shown that each of the three upper states are split by spin orbit coupling, giving splitting in the two T_1 states (eq. 2).

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[19] F. A. Cotton and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 1777 (1961).

[20] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753 (1954).

[21] R. Stahl-Brada and W. Low, *Phys. Rev.*, **113**, 775 (1959)

TABLE II

X-RAY POWDER PATTERN DATA, COBALT $K\alpha_1$ X-RAYS, EXPOSURE TIME 12 HR.[a]

$[Zn(HMPA)_4](ClO_4)_2$			$[Ni(HMPA)_4](ClO_4)_2$			$[Co(HMPA)_4](ClO_4)_2$		
θ_{hkl} (degrees)	d_{hkl} (Å.)	Intensity	θ_{hkl} (degrees)	d_{hkl} (Å.)	Intensity	θ_{hkl} (degrees)	d_{hkl} (Å.)	Intensity
5.56	9.23	s	5.41	9.49	s	5.57	9.22	s
6.67	7.70	w	6.67	7.70	w	6.75	7.61	w
7.41	6.93	vs	7.37	6.97	vs	7.41	6.93	vs
7.86	6.54	m	8.02	6.41	m	7.98	6.44	m
8.92	5.77	s	8.84	5.82	s	8.88	5.79	s
9.45	5.45	m	9.45	5.45	m	9.50	5.42	m
9.86	5.23	s	9.95	5.18	s	9.95	5.18	s
10.64	4.84	m	10.72	4.81	m	10.72	4.81	m
11.21	4.60	w	11.26	4.58	w	11.21	4.60	w
11.91	4.33	w	11.99	4.31	w	11.95	4.32	w
12.40	4.17	vvw	12.48	4.14	vvw	12.48	4.14	vvw
12.97	3.99	vvw	12.97	3.99	vvw	12.97	3.99	vvw
13.42	3.85	s	13.47	3.84	s	13.38	3.87	s
14.28	3.63	m	14.28	3.63	m	14.24	3.64	m
15.35	3.38	m	15.39	3.37	m	15.27	3.40	m
16.13	3.22	vw	16.25	3.24	vw	16.21	3.20	vw
16.82	3.13	vvw	16.74	3.11	vvw	16.78	3.10	vvw

[a] Abbreviations: d_{hkl} and θ_{hkl} are the familiar parameters defined in the modified Bragg relation $\lambda = 2d_{hkl} \sin \theta_{hkl}$; s designates strong, w—weak, m—medium, v—very; intensities were estimated visually.

$$T_1\left\{\begin{array}{l} -\frac{9}{4}\lambda' \\ \\ +\frac{6}{4}\lambda' \\ \\ +\frac{15}{4}\lambda' \end{array}\right. \begin{array}{l} \\ > \frac{15}{4}\lambda' \\ \\ > \frac{9}{4}\lambda' \\ \\ \end{array} \qquad (2)$$

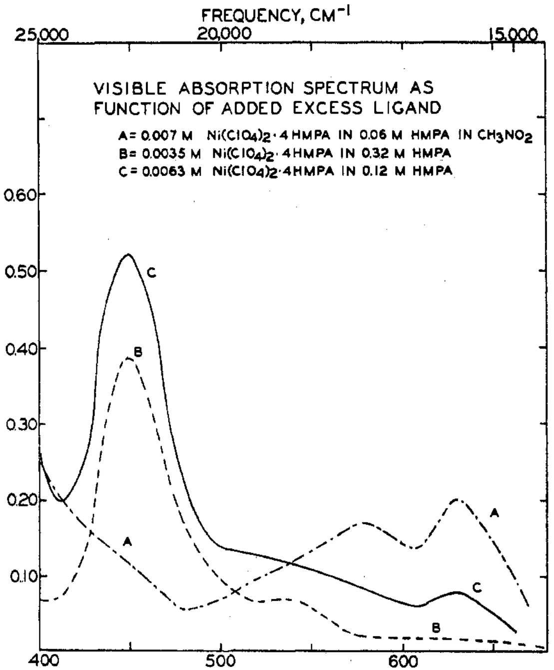

Fig. 3.—Visible absorption spectrum of $[Ni(HMPA)_4](ClO_4)_2$ as a function of added excess ligand in nitromethane: curve A, 0.007 *M* complex in 0.06 *M* HMPA; curve B, 0.0035 *M* complex in 0.32 *M* HMPA; curve C, 0.0063 *M* complex in 0.12 *M* HMPA.

TABLE III

SPECTRAL AND ELECTRONIC PARAMETERS FOR TETRAHEDRAL Co(II) COMPLEXES

	$Co(ClO_4)_2\cdot 4HMPA^a$	$[Co(N_3)_4]^{2-b}$	$[Co(NCO)_4]^{2-b}$
ν_2, cm.$^{-1}$	6590	6,750	7,150
ν_3, cm.$^{-1}$	16,150	14,900	16,100
Δ, cm.$^{-1}$	3640	3,920	4,150
B^1, cm.$^{-1}$	774	658	720
$\beta = (B^1/B^c)$	0.800	0.680	0.745
μ, B.M.	4.45 ± 0.05	4.47 ± 0.05	4.32 ± 0.05
λ^1, cm.$^{-1}$	150 ± 20	146 ± 20	115 ± 20

[a] This work. [b] See ref. 19. [c] Free ion value = 967 cm.$^{-1}$.

The pertinent frequency data for the transitions represented by ν_2 and ν_3 are presented in Table I and Fig. 1A and 1B for the complex $Co(ClO_4)_2\cdot 4HMPA$.

We assign ν_2 at 6660 cm.$^{-1}$ and ν_3 at 16,400 cm.$^{-1}$. These assignments yield the values listed in Table III. From Δ and μ_{eff} one can obtain a value for the spin orbit coupling constant, λ',[19,22,23] from eq. 3.

$$\mu_{obs.} = \mu_{s.o} - \frac{15.56\lambda'}{\Delta} = 3.89 - \frac{15.56\lambda'}{\Delta} \qquad (3)$$

λ' is the effective value of the spin orbit coupling constant.

The value for λ' is included in Table III. In the calculation, an uncertainty of 200 cm.$^{-1}$ is allowed in Δ and 0.05 B.M. in μ_{eff}.

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(22) F. A. Cotton and R. H. Holm, *J. Chem. Phys.*, **31**, 788 (1959).

(23) F. A. Cotton and R. H. Holm, *ibid.*, **32**, 1168 (1960).

From the data in Table III, it is concluded that the position of $PO[N(CH_3)_2]_3$ in the spectrochemical series relative to N_3^- and NCO^- is: $Cl^- \sim PO[N(CH_3)_2]_3 < N_3^- < NCO^-$.

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Complexes Derived from Strong Field Ligands. XIII. The Complexes of β-Mercaptoethylamine with Nickel(II), Palladium(II), Cobalt(II), and Cadmium(II)

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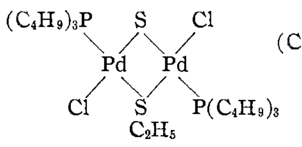
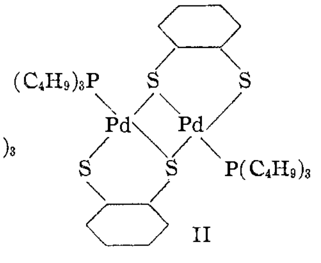
β-Mercaptoethylamine forms two distinct types of compounds with transition metal ions. One type is represented by the well defined monomeric complexes bis-(β-mercaptoethylamine)-nickel(II) and bis-(β-mercaptoethylamine)-palladium(II), ML_2. Nickel(II) and palladium(II) also form a second compound, $[M(ML_2)_2]Cl_2$. The nickel(II) trimer is diamagnetic, indicating that all three nickel atoms are contained in planar coördination polygons. The trimer exhibits the usual properties of a salt and is readily prepared from aqueous solution, either by reaction of the ligand and metal ion or by the solubilization of NiL_2 with nickel chloride. A structure involving a third nickel atom utilizing to full advantage the strong donor properties of two *cis*-NiL_2 molecules is consistent with the preparation and properties of this compound. A cobalt(II) trimer, $[Co(CoL_2)_2]Cl_2$, which exhibits a magnetic moment of 2.49 B.M. per cobalt(II) atom, has been isolated. A cadmium(II) complex also has been isolated and has been assigned the formulation $[Cd\{Cd(NH_2CH_2CH_2S)_2\}_2][CdCl_4]$.

Introduction

One of the most distinguishing properties associated with the mercaptide group is its ability to react readily with many metals to form complexes containing sulfur bridges. The initial investigations involving compounds of this class were carried out by Chatt and Mann,[1] who prepared dichlorobis-(tri-*n*-butylphosphine)-μ-ethylthiolodipalladium(II) (structure I) and bis-(tri-*n*-butylphosphine)-μ-bis-(*o*-phenylenedithiolo)-dipalladium(II) (structure II).



I



II

The fact that the former compound and the platinum(II) analog[2] can be isolated in both *cis* and *trans* forms is a measure of the stability of the mercaptide bridge when compared to the chlorine-bridged analog which forms only the stable *trans* isomer. The great stability of the coördinated mercaptide group also is apparent from the inability of these compounds to undergo reactions with strong donor ligands. In contrast to this behavior, the chloro-bridge is quite labile in the presence of the same ligands. Recently, bridged compounds of platinum(II) and palladium(II) have been reported for *o*-methylthiobenzenethiol, 3-dimethylarsinepropane-1-thiol, 3-ethylthiopropane-1-thiol, and *o*-aminobenzenethiol.[3,4]

Jensen has observed this same bridge-forming tendency for the nickel(II) complex with ethyl mercaptan, which he established to be a diamagnetic polymetallic complex.[5] The formation of polymeric species is prevalent for mercaptan ligands in the absence of other donor atoms of comparable strength. The influence of an additional donor atom, which fulfills this requirement, upon the extent of bridging in mercaptan com-

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[4] S. E. Livingstone, *ibid.*, 1989 (1956).
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