

hydrogen ion dissociation path, 35; and copper attack, 35. The observed ratios are 48, 2.8, and 14, respectively. Similarly, from calculations, the hydrogen ion dependent rate constant should be  $1.4 \times 10^3$  times larger than the simple first-order dissociation. The observed value is  $7.1 \times 10^2$  times larger. Comparison<sup>1,5</sup> can also be made between the iminodiacetate and the ethylenediaminetetraacetate systems. For the copper paths, a value of 1.2 is predicted for the ratio of ImDA:EDTA rate constants, and this value is observed. Agreement for the hydrogen ion dissociation path is not as good. A value of  $1 \times 10^4$  is predicted for the ratio of ImDA:EDTA rate constants and  $1.5 \times 10^3$  is observed.

The rate constants for the nickel iminodiacetate,

nitritotriacetate, and ethylenediaminetetraacetate systems can therefore be related on the basis of postulated intermediates formed prior to the transition state, and reasonable agreement is obtained between predicted and observed values. Moreover, it is reasonable that the above method of calculation can be applied to other nickel chelate systems capable of similar intermediate formation.

**Acknowledgment.**—This work was supported in part by the Research Committee of the Graduate School from funds supplied by the Wisconsin Alumni Research Foundation and by a grant from the National Science Foundation.

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## Transition Metal Ion Complexes of Trimethylamine N-Oxide

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Received February 8, 1965

The ligand trimethylamine N-oxide has been utilized in the synthesis of a series of complexes of transition metal perchlorates. X-Ray powder pattern, conductance, magnetic, solid and solution infrared, and electronic spectral data have been utilized to determine the stereochemistries of the complexes. The spectrochemical parameters  $Dq$  and  $\beta$  have been calculated for the chromium(III) and cobalt(II) complexes and the  $Dq$  values compared with those previously reported.

### Introduction

In recent years there have been a number of reports of transition metal complexes containing oxygen-coordinated ligands. These ligands have been utilized to form complexes of various stereochemistries, with tetrahedral, octahedral, square-planar, and intermediate cases having been reported. Ligands such as substituted and unsubstituted pyridine N-oxides,<sup>3-5</sup> dimethyl sulfoxide,<sup>5b,6</sup> amides,<sup>7-9</sup> phosphine oxides,<sup>10,11</sup> alcohols,<sup>12</sup> and hexamethylphosphoramide<sup>13</sup> are among the many which have been found to participate in the formation of stable transition metal ion complexes.

It was of interest to us to prepare some complexes of the ligand trimethylamine N-oxide, so that the structures and spectrochemical parameters of such complexes could be compared with those above. In this connection it should be noted that in all complexes except those of the alcohols there is a possibility for a  $\pi$ -bonding interaction involving the oxygen lone-pair electrons and the ligand atom adjacent to oxygen. This interaction can then remove electron density from the oxygen, thus decreasing its donor strength. Since this possibility is not present in trimethylamine N-oxide, a comparison of the coordination chemistry of this ligand with the aforementioned oxygen donors is therefore of interest.

A few complexes of trimethylamine N-oxide have been reported. Issleib and Kreibich<sup>14</sup> have reported complexes of trimethylamine N-oxide with cobalt halides and nitrates and manganese bromide. Cobalt chloride, bromide, or nitrate is reported to form complexes of the type  $\text{CoL}_2\text{X}_2$  (where L is the ligand  $(\text{CH}_3)_3\text{N}-\text{NO}$ ). Cobalt iodide forms the complex  $[\text{L}_3\text{CoI}]\text{I}$ , and the perchlorate forms  $[\text{CoL}_4](\text{ClO}_4)_2$ .

Kida<sup>15</sup> has reported the synthesis of complexes of cobalt, zinc, and cadmium nitrates—and also cobalt and zinc perchlorates—with trimethylamine N-oxide.

(1) Abstracted in part from the Ph.D. thesis of John T. Donoghue, University of Illinois, Urbana, Ill., 1963.

(2) N.S.F. Coop Fellow, 1964-1965.

(3) J. V. Quagliano, J. Fujita, G. Franz, D. J. Phillips, J. A. Walmsley, and S. Y. Tyree, *J. Am. Chem. Soc.*, **83**, 3770 (1961), and later papers.

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(5) (a) W. E. Hatfield, Y. Muto, H. B. Jonassen, and J. S. Paschal, *Inorg. Chem.*, **4**, 97 (1965); (b) D. W. Meek, R. S. Drago, and T. S. Piper, *ibid.*, **1**, 285 (1962).

(6) D. W. Meek, D. K. Straub, and R. S. Drago, *J. Am. Chem. Soc.*, **82**, 6013 (1960), and the papers referenced therein.

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(10) F. A. Cotton and E. Bannister, *J. Chem. Soc.*, 1873, 1878 (1960).

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(12) V. I. Imhof and R. S. Drago, *Inorg. Chem.*, **4**, 427 (1965).

(13) (a) J. T. Donoghue and R. S. Drago, *ibid.*, **1**, 866 (1962); (b) *ibid.*, **2**, 572 (1963); (c) *ibid.*, **2**, 1158 (1963).

(14) K. Issleib and A. Kreibich, *Z. anorg. allgem. Chem.*, **313**, 338 (1961).

(15) S. Kida, *Bull. Chem. Soc. Japan*, **36**, 712 (1963).

It was reported that nickel, chromium, and copper salts could not be obtained.

### Experimental

**Preparation of Complexes.**— $(\text{CH}_3)_3\text{NO}\cdot 2\text{H}_2\text{O}$  was prepared by the oxidation of  $(\text{CH}_3)_3\text{N}$  with  $\text{H}_2\text{O}_2$  according to the procedure of Meisenheimer<sup>16</sup> or was obtained commercially from the K. and K. Chemical Co. The compound was isolated from the preparation as a hygroscopic white solid in 69% yield.

*Anal.* Calcd.: C, 32.40; H, 11.81; N, 12.60. Found: C, 31.86; H, 11.49; N, 12.35.

The complexes were prepared in the following manner. The dihydrate of trimethylamine N-oxide was dehydrated by its reaction with 2,2-dimethoxypropane.<sup>7</sup> The dehydration was carried out in either 2-propanol or methanol. Anhydrous solutions of transition metal perchlorates in either 2-propanol or methanol were similarly prepared. Mixing of the two solutions generally caused instantaneous precipitation. The precipitation process was completed by adding a large excess of anhydrous ether. Occasionally oils were formed from this process. Crystallization was then induced by dissolution in nitromethane and reprecipitation from more dilute solutions. The solids were collected by filtration, washed with isopropyl alcohol and ether, and then dried *in vacuo* over sulfuric acid or phosphorus pentoxide for 48 hr. Yields were from 75 to 90%. All of the complexes are slightly hygroscopic.

*Anal.* Calcd. for  $[\text{Co}[(\text{CH}_3)_3\text{NO}]_4](\text{ClO}_4)_2$ : C, 25.81; H, 6.51; N, 10.04. Found: C, 25.57; H, 6.30; N, 9.87.

*Anal.* Calcd. for  $[\text{Ni}[(\text{CH}_3)_3\text{NO}]_4](\text{ClO}_4)_2$ : C, 25.82; H, 6.52; N, 10.05. Found: C, 25.35; H, 6.32; N, 9.87.

*Anal.* Calcd. for  $[\text{Cu}[(\text{CH}_3)_3\text{NO}]_4](\text{ClO}_4)_2$ : C, 25.60; H, 6.46; N, 9.95. Found: C, 25.19; H, 6.60; N, 9.54.

*Anal.* Calcd. for  $[\text{Mn}[(\text{CH}_3)_3\text{NO}]_4](\text{ClO}_4)_2$ : C, 26.00; H, 6.55; N, 10.11. Found: C, 25.68; H, 6.24; N, 9.77.

*Anal.* Calcd. for  $[\text{Zn}[(\text{CH}_3)_3\text{NO}]_4](\text{ClO}_4)_2$ : C, 25.52; H, 6.44; N, 9.92. Found: C, 25.02; H, 6.36; N, 10.16.

*Anal.* Calcd. for  $[\text{Cr}[(\text{CH}_3)_3\text{NO}]_6](\text{ClO}_4)_3$ : C, 26.98; H, 6.81; N, 10.49. Found: C, 25.97; H, 6.94; N, 10.00.

**Infrared Spectra.**—Infrared spectra of solid mulls of the ligand and its transition metal complexes were obtained using a Perkin-Elmer Model 21 recording infrared spectrophotometer with sodium chloride optics. Nitromethane solution spectra of the complexes (Eastman Spectrograde, dried over molecular sieves) were also obtained (using a Perkin-Elmer Model IR 521 with IR-tran cells), to determine if free ligand was present in solution.

**Electronic Spectra.**—Electronic spectral data of solutions and Nujol mulls of the complexes in the 300–2200  $m\mu$  range were obtained with a Cary Model 14M recording spectrophotometer. The solids were preground in a Wig-L-Bug grinder and then mullied in Nujol to give a stiff mull. The mulls were then applied to pieces of Whatman No. 1 filter paper and run against filter paper soaked in Nujol as a reference.<sup>17</sup> Diffuse reflectance spectra of the solid powders were obtained using a Bausch and Lomb Spectronic 505 recording spectrophotometer in conjunction with a standard reflectance attachment. The range covered by this integrating sphere is 400–700  $m\mu$ . Blocks of  $\text{MgCO}_3$  were used as the standard of white reflectance. The spectral data for the complexes are given in Table I.

Spectra of the complexes in methylene chloride could not be obtained due to the insolubility of the complexes in this solvent. The complexes are, however, readily soluble in nitromethane (with the exception of manganese, which is only slightly soluble) and these data, along with the reflectance and solid mull data, are presented in Table I.

**Magnetic Susceptibility Measurements.**—Measurements of the magnetic susceptibilities of the solid powders of the complexes were measured by the Gouy technique. The electromagnet employed in this apparatus has been described previously.<sup>7</sup>

The standard employed for susceptibility measurements was  $\text{Hg}[\text{Co}(\text{NCS})_4]$ .<sup>18</sup> The results are given in Table II.

TABLE I  
ELECTRONIC SPECTRAL DATA FOR COMPLEXES OF  
TRIMETHYLAMINE N-OXIDE

Complex	Medium	$\lambda_{\text{max}}$ , $m\mu$	$\epsilon$	
$[\text{Cr}[(\text{CH}_3)_3\text{NO}]_6](\text{ClO}_4)_3$	Solid, reflectance	<400		
		405		
		605		
	Solid, mull	<330		
		406		
		585		
$[\text{Co}[(\text{CH}_3)_3\text{NO}]_4](\text{ClO}_4)_2$	$9.98 \times 10^{-3} M$ in $\text{CH}_3\text{NO}_2$	376	96.9 <sup>d</sup>	
		585	26.1	
	Solid, reflectance	575		
		Solid, mull	575	
		1065		
	$[\text{Ni}[(\text{CH}_3)_3\text{NO}]_4](\text{ClO}_4)_2$	$4.73 \times 10^{-3} M$ in $\text{CH}_3\text{NO}_2$	537 sh <sup>a</sup>	
567			217	
$1.0 \times 10^{-2} M$ in $\text{CH}_3\text{NO}_2$		1090	66.3	
		1405	48.5	
$[\text{Cu}[(\text{CH}_3)_3\text{NO}]_4](\text{ClO}_4)_2$		$2.7 \times 10^{-4} M$ in acetone <sup>b</sup>	568	224
			Solid, reflectance	<400
	Solid, mull	555		
		605		
		395		
		550		
$[\text{Cr}[(\text{CH}_3)_3\text{NO}]_6](\text{ClO}_4)_3$	$3.32 \times 10^{-3} M$ in $\text{CH}_3\text{NO}_2$	373	88.8 <sup>d</sup>	
		667	22.0	
	Solid, reflectance	1000–1100 <sup>c</sup>		
		<400		
		700		
		Solid, mull	<350	
$1.25 \times 10^{-2} M$ in $\text{CH}_3\text{NO}_2$	815			
	634	144		

<sup>a</sup> sh, shoulder. <sup>b</sup> Solubility difficulties prevented other spectral data in acetone; due to the low solubility of the complex and the low extinction coefficients in the infrared, no definite assignments could be made on the broad absorption band in the near-infrared. <sup>c</sup> Too broad to determine  $\lambda_{\text{max}}$  or  $\epsilon$ . <sup>d</sup> Since nitromethane cuts off at approximately 370  $m\mu$ , these extinction coefficients are only approximately accurate; since nitromethane *vs.* air does not peak in this area, the  $\lambda_{\text{max}}$  values are thought to be accurate, however.

TABLE II  
MAGNETIC SUSCEPTIBILITY DATA (25°) FOR COMPLEXES OF  
TRIMETHYLAMINE N-OXIDE

Complex	$10^6 \chi$	$10^6 \chi_M$	$\mu_{\text{eff}}$ , B.M.
$[\text{Co}[(\text{CH}_3)_3\text{NO}]_4](\text{ClO}_4)_2$	8457	8675 <sup>b</sup>	4.54 ± 0.04 <sup>a</sup>
$[\text{Ni}[(\text{CH}_3)_3\text{NO}]_4](\text{ClO}_4)_2$	5912	6130 <sup>b</sup>	3.86 ± 0.05
$[\text{Mn}[(\text{CH}_3)_3\text{NO}]_4](\text{ClO}_4)_2$	11002	11220 <sup>b</sup>	5.29 ± 0.04
$[\text{Cr}[(\text{CH}_3)_3\text{NO}]_6](\text{ClO}_4)_3$	5830	6048 <sup>b</sup>	3.84 ± 0.04
$[\text{Cu}[(\text{CH}_3)_3\text{NO}]_4](\text{ClO}_4)_2$	1463	1681 <sup>b</sup>	2.00 ± 0.06

<sup>a</sup> The magnetism ( $\mu = 4.12$  B.M.) of the cobalt complex has been previously reported.<sup>14</sup> <sup>b</sup> A diamagnetic correction of  $218 \times 10^{-6}$  was made for compounds of divalent metal ions; the correction was  $327 \times 10^{-6}$  for the chromium(III) compound.

(16) J. Meisenheimer, *Ann.*, **397**, 286 (1913).

(17) R. H. Lee, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, **3**, 1278 (1964).

(18) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960, pp. 400–454; B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

**X-Ray Diffraction Patterns.**—X-Ray powder diagrams were obtained using copper  $K\alpha_1$  radiation,  $\lambda$  1.54050 Å., and a camera with a rotating sample holder. The samples were not ground because of the possibly explosive nature of the perchlorates. The values of  $d_{hkl}$  for all complexes except those of the chromium complex are reported in Table III.

TABLE III  
X-RAY POWDER PATTERN DATA, COPPER  $K\alpha_1$  X-RAYS, EXPOSURE TIME 12 HR.<sup>a</sup>

[Zn[(CH <sub>3</sub> ) <sub>3</sub> NO] <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>		[Co[(CH <sub>3</sub> ) <sub>3</sub> NO] <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>		[Mn[(CH <sub>3</sub> ) <sub>3</sub> NO] <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	
$d_{hkl}$ , Å.	Int.	$d_{hkl}$ , Å.	Int.	$d_{hkl}$ , Å.	Int.
7.58	s	7.64	s	8.67	s
6.57	m	6.59	vw	7.69	s
5.99	m	6.01	w	...	...
5.39	vs	5.46	s	5.41	vs
...	...	5.00	w	...	...
4.48	s	4.49	m	4.53	s
...	...	...	...	4.23	m
4.19	w	...	...	4.15	w
3.94	w	3.97	w	3.95	m
3.76	w	3.76	w	3.79	m
3.56	w	...	...	3.58	m
				3.17	vw
				3.11	m
[Ni[(CH <sub>3</sub> ) <sub>3</sub> NO] <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>		[Cu[(CH <sub>3</sub> ) <sub>3</sub> NO] <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>			
8.81	s	7.76	vs	2.84	m
5.14	s	6.57	m	2.55	m
4.58	s	5.49	vvs	2.46	m
4.21	s	4.93	m	2.35	m
3.73	w	4.49	s	2.22	m
3.15	vw	4.19	m	2.10	s
		3.91	s	2.01	w
		3.50	s	1.94	w
		3.21	s		

<sup>a</sup> Abbreviations:  $d_{hkl}$  values are obtained from the Bragg equation  $\lambda = 2d_{hkl} \sin \theta_{hkl}$ ; s designates strong; w, weak; m, medium; v, very; intensities were estimated visually.

**Conductance Measurements.**—Measurements of the conductivities of nitromethane solutions of the complexes were obtained using an Industrial Instruments, Inc., Model RC16B2 conductivity bridge and a cell which had previously been calibrated with aqueous solutions of 0.01 N KCl. These results are presented in Table IV.

TABLE IV  
CONDUCTANCES IN CH<sub>3</sub>NO<sub>2</sub> SOLUTIONS

Complex	Concn., M	$\Lambda_{molar}$	Temp., °C.
[Cr[(CH <sub>3</sub> ) <sub>3</sub> NO] <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	$1.96 \times 10^{-3}$	247 (253) <sup>a</sup>	24.6
[Co[(CH <sub>3</sub> ) <sub>3</sub> NO] <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	$3.24 \times 10^{-3}$	170 (178)	25.0
[Ni[(CH <sub>3</sub> ) <sub>3</sub> NO] <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	$3.66 \times 10^{-3}$	159 (184)	25.4
[Cu[(CH <sub>3</sub> ) <sub>3</sub> NO] <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	$5.08 \times 10^{-3}$	161 (184)	25.0
[Zn[(CH <sub>3</sub> ) <sub>3</sub> NO] <sub>4</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	$5.10 \times 10^{-3}$	154 (184)	26.0

<sup>a</sup> The values in parentheses are those previously reported<sup>13a,c</sup> for the analogous hexamethylphosphoramide complexes.

## Results

The electronic spectral data for several of the complexes are presented in Table I, the magnetic data in Table II, the powder diffraction data in Table III, and the conductances in Table IV.

## Discussion

In several cases, the data obtained permit us to make fairly conclusive structural assignments for the species present in solution and in the solid state. Infrared

spectra obtained on Nujol mulls of the complexes showed a single broad band around 1100 cm.<sup>-1</sup> which was assigned to the  $\nu_3$  vibration of tetrahedral perchlorate. Coordinated perchlorate is eliminated, since coordination through the oxygen of perchlorate lowers the symmetry of this group from T<sub>d</sub> to C<sub>3v</sub>, thus splitting this peak into two broad peaks.<sup>19,20</sup> Thus in the solid state the coordination numbers are six for chromium and four for the other metal ions.

As previously reported,<sup>15</sup> the N–O stretching vibration of (CH<sub>3</sub>)<sub>3</sub>NO undergoes very little change upon coordination to a metal ion. Nitromethane solvent absorption masks the  $\nu_3$  region of perchlorate absorption. Thus, in contrast to the behavior of some tetramethylguanidine complexes,<sup>21</sup> it is not possible to say from infrared data alone whether or not free ligand is present in nitromethane solution. Conductance data eliminate perchlorate coordination in the solution, for the values obtained are within the accepted range for 3:1 (chromium) and 2:1 electrolytes in nitromethane.

The electronic spectrum observed for the chromium complex is similar to that observed for other six-coordinate chromium complexes.<sup>5b,7,13c</sup> The shift of about 20–30 m $\mu$  in the band positions in solution as compared to the solid could be due to the presence of crystal lattice forces in the solid.

The purple color and magnetic moment of the cobalt complex are prime indications of its tetrahedral stereochemistry. The high extinction coefficients in both nitromethane and acetone solutions and the similarity (except for slight shifts) of the solution and solid spectra also point to a tetrahedral structure in both solid and solution phases. The powder diffraction pattern is nearly identical with that of the zinc complex, although neither of these patterns (or for that matter those of the nickel and manganese complexes) shows a large number of well-defined lines. Since the samples were not ground due to their possibly explosive character, it is possible that inhomogeneous particle sizes are the cause of the effect. The manganese compound also possesses a powder pattern nearly identical with that of zinc, and since the infrared data show no coordinated perchlorates in the solid form, this compound is also assumed to be tetrahedral.

The structures of the nickel and copper compounds cannot be determined in as straightforward a manner. The situation is further complicated by the fact that the species present in solution are not the same as those in the solid phase. In the case of nickel, in which reflectance and mull spectra agree as to the peak positions, a new peak—fully 65 m $\mu$  from any in the solid—appears in nitromethane solution.

The spectral data on the solid are similar to those reported for solutions of [Ni(HMPA)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub><sup>13a</sup> in CH<sub>3</sub>NO<sub>2</sub> and also to results from solution and reflectance

(19) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

(20) Two broad peaks for coordinated perchlorate have recently been observed in this laboratory with Ni(py)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>, Co(py)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub>, Fe(py)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub> (where py = pyridine), and Ni(An)<sub>4</sub>(ClO<sub>4</sub>)<sub>2</sub> (where An = aniline).

(21) R. Longhi and R. S. Drago, *Inorg. Chem.*, **4**, 11 (1965).

tance data for  $\text{Ni}(\text{HMPA})_2\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ).<sup>13b</sup> The magnetic moment of this complex is higher than that of  $[\text{Ni}[(\text{C}_6\text{H}_5)_3\text{PO}]_4](\text{ClO}_4)_2$  (3.51 B.M.)<sup>22</sup> but lower than that of  $[\text{Ni}(\text{HMPA})_4](\text{ClO}_4)_2$  (4.02 B.M.).<sup>13a</sup> This lowering might indicate some distortion from a tetrahedral environment around the nickel ion. Our X-ray powder pattern for the nickel complex has only six observable lines, and although it shows some similarity to that of the zinc complex, there is not enough agreement to conclude that the two patterns are identical. Thus it is proposed that the nickel complex in the solid has a distorted tetrahedral structure.

The color change which occurs on dissolution (from light purple to a light yellow-green), along with the resultant change in the absorption spectra, indicates a possible six-coordinate species in the solution. The formation of a six-coordinate species would not be surprising, since nickel(II) is known to prefer an octahedral or tetragonal configuration as opposed to tetrahedral. Even in the case of  $[\text{Ni}(\text{HMPA})_4](\text{ClO}_4)_2$ ,<sup>13a</sup> shown to be a tetrahedral nickel complex, dissolution of the complex in nitromethane containing excess ligand produces bands in the spectrum indicative of octahedral or tetragonal nickel.

The copper complex in the solid phase has a different structure from those of the other complexes, as shown by its powder pattern. This pattern has the largest number of lines, and also the largest number of intense lines. Absorption for tetrahedral copper complexes in the near-infrared region (5000–7000  $\text{cm}^{-1}$  or 1400–2000  $\text{\AA}$ .) is predicted by theory.<sup>23</sup>

Absorption in the near-infrared region is not found in this complex. This theory also predicts no visible absorption for tetrahedral copper, and none is found for this complex. The absorption bands seen in the reflectance spectrum are the beginnings of absorptions which maximize in the very near-infrared (815  $m\mu$ ) and ultraviolet (350  $m\mu$ ) regions. The magnetic moment for the compound is of little use in determining its structure, since there is little difference in magnitude among the various configurations in copper complexes. Since the mull spectrum is different from that of  $[\text{Cu}(\text{HMPA})_4](\text{ClO}_4)_2$ <sup>13c</sup> or  $[\text{Cu}(\text{TMG})_4](\text{ClO}_4)_2$ <sup>21</sup> (TMG = tetramethylguanidine), believed to be tetrahedral (with possible small distortions), it seems most likely that the copper complex is close to square-planar with possible distortions toward a  $D_{2d}$  configuration.

Dissolution of the complex in nitromethane causes a color change (from light green to a dark yellow-green), probably because of solvent coordination.

**Calculation of Spectrochemical Parameters,  $Dq$  and  $\beta$ .**—The electronic spectra of the chromium and cobalt complexes have permitted calculation of the spectrochemical parameters,  $Dq$  and  $\beta$ . The procedure em-

ployed for chromium, which has previously been reported,<sup>7</sup> produced a value (in nitromethane solution) for  $Dq$  of 1710  $\text{cm}^{-1}$  and for  $\beta$  of 0.75. This value of  $Dq$  is fairly high in comparison with those values which have been reported previously:  $\text{NH}_3$  (2160) >  $\text{H}_2\text{O}$  (1740) >  $(\text{CH}_3)_3\text{NO}$  (1710) >  $\text{CH}_3\text{CONH}_2$  (1645)<sup>7</sup> >  $(\text{CH}_3)_2\text{SO}$  (1580)<sup>5b</sup> >  $\text{C}_5\text{H}_5\text{NO}$  (1540)<sup>5b</sup> ~  $\text{HMPA}$  (1540)<sup>13c</sup> >  $\text{DMA}$  (1520).<sup>7</sup>

It is interesting to note that toward octahedral chromium(III), trimethylamine N-oxide is a better donor than  $(\text{CH}_3)_2\text{SO}$ , HMPA, and pyridine N-oxide. In all three of these donors, electron density can be removed from oxygen by  $\pi$ -bonding to the neighboring atom, thus decreasing the donor properties of the oxygen. In the case of pyridine N-oxide, the fact that the oxygen is attached to an  $\text{sp}^2$  nitrogen which is more electronegative than the  $\text{sp}^3$  nitrogen in trimethylamine N-oxide also tends to decrease the donor properties of pyridine N-oxide relative to trimethylamine N-oxide.

The procedure employed for the cobalt complex has already been described.<sup>13a</sup> The values for  $\nu_2$  and  $\nu_3$  are found by utilizing a center of gravity method for weighing the various contributions to the bands. Utilizing values of  $\nu_2 = 8210 \pm 30 \text{ cm}^{-1}$ ,  $\nu_3 = 17,790 \pm 50 \text{ cm}^{-1}$ , and  $\mu_{\text{eff}} = 4.54 \pm 0.04 \text{ B.M.}$ , calculated values of  $\Delta = 4780 \pm 20 \text{ cm}^{-1}$ ,  $B' = 777 \pm 7 \text{ cm}^{-1}$ ,  $\beta (B'/B) = 0.80 \pm 0.01$ , and  $\lambda = 200 \pm 15 \text{ cm}^{-1}$  are obtained for the complex. The error limits for the calculated values are obtained by utilizing values of the measured quantities with maximum error limits in the calculations.

The value of  $\Delta$  obtained in this case ( $4780 \pm 20 \text{ cm}^{-1}$ ) is one of the higher values reported thus far for complexes involving tetrahedral cobalt. Other values reported have included: benzimidazole (5100  $\text{cm}^{-1}$ ),<sup>24</sup> dimethylacetamide (4900  $\pm 100 \text{ cm}^{-1}$ ),<sup>9</sup> tetramethylguanidine (4460  $\pm 20 \text{ cm}^{-1}$ ),<sup>21</sup> thiocyanate (4450  $\text{cm}^{-1}$ ),<sup>25</sup> hydroxide (4230  $\text{cm}^{-1}$ ),<sup>11</sup> cyanate (4150  $\text{cm}^{-1}$ ),<sup>26</sup> azide (3920  $\text{cm}^{-1}$ ),<sup>26</sup> triphenylphosphine oxide (3680  $\text{cm}^{-1}$ ),<sup>11</sup> hexamethylphosphoramide (3440  $\pm 90 \text{ cm}^{-1}$ ),<sup>13a,27</sup> chloride ( $\sim 3100 \text{ cm}^{-1}$ ),<sup>11,28</sup> bromide ( $\sim 2850 \text{ cm}^{-1}$ ),<sup>11,28</sup> iodide ( $\sim 2650 \text{ cm}^{-1}$ ).<sup>11,28</sup>

**Acknowledgment.**—The authors wish to thank the Chemistry Branch of the Atomic Energy Commission for their generous support of this research through Contract No. AT(11-1)758.

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(27) The value for HMPA is different from that reported. This value has been recalculated using the center of gravity of the intensities of the bands—instead of the averaging procedure employed previously—so that the result can be compared with the other data calculated by this procedure. Error limits are estimated by calculating  $\Delta$  and  $\beta$  for various combinations of the maximum and minimum error limits of the band frequencies. A  $\beta$  value of  $0.84 \pm 0.02$  results from this calculation. Previous values given<sup>13a</sup> were  $\Delta = 3640$  and  $\beta = 0.80$ .

(28) These values are approximate ones, since the tetrahedral cobalt(II) ions have been studied in many situations, with various values of  $\Delta$  having been determined for each situation.

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