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Aliphatic Di-N-Oxide Complexes; Cobalt(II), Nickel(II), and Chromium(III) Perchlorate Complexes of N,N,N′,N′-Tetramethylethylenediamine-N,N′-Dioxide

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The compound N,N,N′,N′-tetramethylethylenediamine-N,N′-dioxide, $TMEO_2$, has been synthesized and used to form complexes with chromium(III), cobalt(II), and nickel(II) perchlorates. The resulting coordination compounds have been characterized by elemental analyses, electronic and infrared spectra, conductance, and magnetic susceptibility measurements. The chromium compound has the formula $Cr(TMEO_2)_3(ClO_4)_3\cdot 3H_2O$ and is characterized as a tris six-coordinate distorted octahedral complex while the cobalt and nickel compounds have the formulas $Co(TMEO_2)_2(ClO_4)_2$ and $Ni(TMEO_2)_2(ClO_4)_2\cdot 5H_2O$ and are characterized as bis four-coordinate tetrahedral complexes. The chromium–$TMEO_2$ complex has a higher ligand field parameter, Dq, and a lower effective magnetic moment than other reported N-oxide complexes of chromium(III).

Introduction

Three review articles have appeared summarizing the extensive research on coordination complexes of amine N-oxides.[1–3] The vast majority of the work in this area has centered on complexes of aromatic amine N-oxides, especially substituted pyridine and quinoline N-oxides. Relatively little work has been done on aliphatic amine N-oxide complexes. A few reports of trialkylamine N-oxide complexes have appeared[1,4,5] along with one each on complexes of N,N-dimethylethylenediamine N-oxide,[6] $(CH_3)_2N(O)CH_2CH_2NH_2$, and N,N-dialkyl-2-aminoethanol N-oxides[7] such as $(CH_3)_2N(O)CH_2CH_2OH$. In addition, very few di-N-oxide ligands have been studied. There have been several reports on 2,2′-bipyridine-N,N′-dioxide complexes[1,8] and a few isolated reports of other aromatic di-N-oxides.[1] Consequently we have undertaken the study of the first aliphatic di-N-oxide ligand, N,N,N′,N′-tetramethylethylenediamine-N,N′-dioxide, $(CH_3)_2N(O)CH_2CH_2(O)N(CH_3)_2$, using chromium(III), cobalt(II), and nickel(II) perchlorates. It was of interest to investigate the relative effects of basicity and steric hindrance on the ability of this aliphatic di-N-oxide to function as a Lewis base. The ligand will hereafter be abbreviated as $TMEO_2$.

Experimental

Syntheses

N,N,N′,N′-tetramethylethylenediamine-N,N′-dioxide dihydrate

To 15.6 grams (0.13 mol) of N,N,N′,N′-tetramethylethylenediamine (Aldrich Chemical Company, 99%, used without further purification) in a 200 ml round-bottom flask cooled to about 0° C in an ice bath was slowly added 50 ml of 30% hydrogen peroxide (0.79 mol). The mixture was allowed to gradually warm to room temperature and let stand overnight. The volume was reduced using a rotory evaporator at temperatures below 80° C until a viscous syrup formed, then 25 ml of water were added and the volume was again reduced, producing a viscous syrup which crystallized upon standing at room temperature. The resulting white solid was washed with acetone and dried under vacuum at 100° C over phosphorus pentoxide, giving 13.9 grams of the hydrated product (56% yield).

Metal Complexes

The appropriate hydrated metal perchlorate (about 1.5 mmol) was dissolved in a minimum amount of methanol and then added to a solution of the hydrated ligand (about 3.2 mmol for cobalt and nickel, and about 4.7 mmol for chromium) dissolved in a minimum amount of methanol and a few ml of 2,2-dimethoxypropane. In the cobalt and chromium cases, precipitation was immediate while in the nickel case a viscous oil formed. In the latter case the solvent was decanted and the oil was triturated with anhydrous diethyl ether until crystallization occurred. The products were filtered, washed with ether, and dried under vacuum at 100° C for several hours over phosphorus pentoxide. Yields were 60–90%. CAUTION: *These complexes detonate near their decomposition points.*

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Physical Measurements

Infrared Spectra

Infrared spectra were obtained as Nujol mulls between sodium chloride disks on a Beckman IR-8 Infrared Spectrophotometer. Spectra were calibrated with known bands of polystyrene.

Nuclear Magnetic Resonance Spectra

Nuclear magnetic resonance spectra were obtained in D_2O or $CDCl_3$ on a Varian EM 360 60 MHz Nuclear Magnetic Resonance Spectrometer. TMS was used as either an external or internal reference.

Electronic Absorption Spectra

Electronic absorption spectra were obtained as Nujol mulls on filter paper using Cary Model 14 and Beckman DB-GT Spectrophotometers.

Magnetic Susceptibility

Magnetic susceptibility measurements were obtained at 295° K and at 7000 gauss by the Gouy method using an instrument constructed from an Ainsworth balance and an Ealing electromagnet. The compound $HgCo(SCN)_4$ was used as calibrant and diamagnetic corrections were made using Pascal's constants.

Molar Conductance

Molar conductance measurements were made in nitromethane solution using a General Radio Company 650-A Impedance Bridge.

Elemental Analyses

Carbon, hydrogen, and nitrogen analyses were performed by M–H–W Laboratories, Garden City, Michigan.

Results and Discussion

The ligand $TMEO_2$ was isolated as a dihydrate from the reaction of hydrogen peroxide and N,N,N′,N′-tetramethylethylenediamine and confirmed by elemental analyses (Table I) and nmr spectroscopy. The nmr spectrum of the amine in $CDCl_3$ consists of singlets at δ, 2.23 and δ, 2.40 with relative areas of three to one, while the spectrum of the product in D_2O shows singlets at δ, 3.27 and δ, 3.86 with relative areas of three to one. The $TMEO_2$ product is quite hygroscopic and a singlet of variable intensity at δ, 4.76 is observed unless the nmr spectrum is recorded immediately after dehydration.

Attempts to prepare the corresponding di-N-oxide of N,N,N′,N′-tetramethylmethylenediamine, $(CH_3)_2N(O)CH_2(O)N(CH_3)_2$, under a variety of conditions met with failure. Less than a two percent yield of an off-white product with empirical formula C_2H_4NO was obtained (calculated: C 41.37%, H 6.94%, N 24.13%; experimental: C 41.20%, H 6.92%, N 24.18%). The nmr spectrum of the amine starting material in $CDCl_3$ consists of singlets at δ, 2.23 and δ, 2.72 with relative areas of six to one, while the spectrum of the product in D_2O shows singlets at δ, 3.80 and δ, 7.98 with relative areas of three to one. As with $TMEO_2$, unless the compound is dehydrated just prior to recording the spectrum a singlet of variable intensity at δ, 4.72 is also observed. The analytical and nmr data suggest the structure of the product is $CH_3N(O){=}CH{-}CH{=}(O)NCH_3$. No further work was done with this compound due to the low yields.

Coordination complexes of $TMEO_2$ with chromium (III), cobalt(II), and nickel(II) perchlorates were prepared using metal-to-ligand mol ratios ranging from 1:2 to 1:4. The purest products were obtained when the ratios were 1:2 for cobalt or nickel and 1:3 for chromium. The analytical data are presented in Table I. The chromium and nickel complexes detonate near their decomposition points. Infrared spectra of all three complexes show a broad single band about 1090 cm^{-1} (Table II) assigned as the ν_3 vibration of tetrahedral perchlorate ions.[9] Molar conductance values in nitromethane solution (Table II) are in the range indicative of 2:1 electrolytes for the cobalt and nickel complexes.[4,10] These infrared and conductance data suggest that the perchlorate groups are not coordinated to the metal ion in the solid state or in solution.

TABLE I. Elemental Analyses and Physical Data.

Compound	%C		%H		%N		Color	Decomposition Point, °C
	calc.	expr.	calc.	expr.	calc.	expr.		
$C_6H_{16}N_2O_2 \cdot 2H_2O$	39.11	39.59	10.94	11.15	15.21	15.67	White	139–140
$Co(C_6H_{16}N_2O_2)_2(ClO_4)_2$	26.00	25.73	5.82	5.75	10.11	9.77	Purple	184–187
$Ni(C_6H_{16}N_2O_2)_2(ClO_4)_2 \cdot 5H_2O$	22.37	22.41	6.57	5.91	8.70	8.14	Yellow	169–170[a]
$Cr(C_6H_{16}N_2O_2)_3(ClO_4)_3 \cdot 3H_2O$	25.39	25.39	6.41	6.25	9.90	9.69	Green	163–165[b]

[a] Detonates at 183° C. [b] Detonates at 165° C.

TABLE II. Conductance, Magnetic, Infrared and Electronic Spectral Data.

Compound	Infrared Data[a]		Molar Conductance[b] Λ_M	Magnetic Data[c] μ_{eff}	Electronic Spectral Data[d] Absorption Maxima
	ν_{NO}	ν_{ClO}			
$TMEO_2$	965	–	–	–	–
$Co(TMEO_2)_2(ClO_4)_2$	967	1092	190	4.51	507sh, 563, 970br, 1330br
$Ni(TMEO_2)_2(ClO_4)_2 \cdot 5H_2O$	967	1083	149	3.70	412, 700sh, 771, 1270br
$Cr(TMEO_2)_3(ClO_4)_3 \cdot 3H_2O$	962	1085	–	3.33	425sh[e], 552

[a] Nujol mull spectra; all values in cm^{-1}; ν_{ClO} is for perchlorate. [b] For $1.0 \times 10^{-3} M$ solutions in nitromethane; values in $cm^2mho\ mol^{-1}$; chromium complex not sufficiently soluble. [c] Determined at 295° K; all values in Bohr Magnetons. [d] Nujol mull spectra; all values in nm; sh = shoulder, br = broad. [e] Shoulder on ultraviolet absorption peak.

It has been found that the ν_{NO} stretching frequency, found in the 900–1000 cm^{-1} region, for aliphatic amine N-oxide ligands undergoes little change upon coordination.[4–7] This is in contrast to significant decreases in the ν_{NO} frequency, occuring in the 1200–1300 cm^{-1} region, upon coordination of most of the aromatic amine N-oxides.[1, 11] The infrared data for the complexes reported here (Table II) are in agreement with these observations.

The relative steric effects of various aromatic N-oxide ligands toward metal perchlorates have been noted. For example, cobalt and nickel perchlorate complexes of 4-substituted pyridine and quinoline N-oxides are six-coordinate,[1] while those of bulkier ligands such as acridine-, 2-methylquinoline-, 2-methylpyridine-, and 2,6-dimethylpyridine N-oxides are four- or five-coordinate.[1, 12] The chromium(III) perchlorate complexes with each of these ligands, however, are six-coordinate.[1, 13] Steric effects also occur in aliphatic amine N-oxide complexes. For example only four trimethylamine N-oxide ligands coordinate to cobalt and nickel perchlorates, while again chromium perchlorate supports six coordination.[4] Three of the bidentate mono N-oxide $(CH_3)_2N(O)CH_2CH_2NH_2$ ligands were found to coordinate to nickel(II), iron(III), and cobalt(III) perchlorates, while the cobalt(II) perchlorate complex could not be prepared in pure form.[6] The steric effect of $TMEO_2$ is expected to be greater than that for $(CH_3)_2N(O)CH_2CH_2NH_2$ due to the presence of two additional methyl groups, yet less than that of two isolated trimethylamine N-oxides since two of the methyl groups have been "joined." The stoichiometries of the resulting $TMEO_2$ complexes are indicative of significant steric interaction in that only bis complexes form in the case of cobalt and nickel. A tris chromium complex is formed with $TMEO_2$ but six-coordination is most often the case for chromium (III) even when severe steric interactions occur.

The structures of the $TMEO_2$ complexes have been deduced from electronic spectra and magnetic susceptibility measurements. These data for the cobalt and nickel compounds (Table II) are very similar to those reported for the trimethylamine N-oxide complexes which have previously been characterized as having tetrahedral structures.[4] The electronic spectrum of the chromium complex of $TMEO_2$ is typical of a six-coordinate species, however the effective magnetic moment of 3.33 B. M. is lower than the 3.84 B.M. value found for the trimethylamine N-oxide complex,[4] and, for that matter, those for other N-oxide complexes (3.8 to 4.1. B.M.).[14–16] The effective magnetic moment of the chromium–$TMEO_2$ complex is essentially independent of temperature in the 278–318° K range.

There are a number of binuclear hydroxo-bridged chromium(III) complexes with magnetic moments in the 1.8 to 3.5 B.M. range, indicative of magnetically condensed systems.[17] However the $Cr(TMEO_2)_3(ClO_4)_3 \cdot 3H_2O$ stoichiometry does not easily lend itself to interpretations involving hydroxo or aquo bridges. An alternative explanation for the low magnetic moment seems to center on a loss of degeneracy in the t_{2g} d-orbitals due to a ligand field symmetry lower than O_h. Since the $TMEO_2$ ligands are bidentate, the effective symmetry of the CrO_6 moiety may be closer to D_3, which would cause the triply degenerate orbitals to split. If the distortion were severe enough, a d^3 doublet-quartet spin state equilibrium might account for the somewhat lower magnetic moment. Whereas one might expect to see the effects of such distortion in the electronic spectrum as each spectroscopic state would theoretically be split into two components ($^4T_{2g}$ in O_h to ^4E and $^4A_1$ in D_3; $^4T_{1g}$ in O_h to ^4E and $^4A_2$ in D_3), it has been noted that this splitting may not always be resolved in the broad bands.[18] The absorption band assigned to the $^4A_{2g} \rightarrow {}^4T_{2g}$ electronic transition for the chromium(III) complex of the bidentate ligand bipyridine N,N′-dioxide is split into two components,[8] however the spectrum of the $TMEO_2$ complex does not exhibit such splitting. Splitting is also not observed in the spectrum of the chromium(III) complex of the bidentate picolinic acid N-oxide, even though this complex has still lower symmetry.[16]

The fact that chromium forms six-coordinate complexes with a wide variety of N-oxide ligands provides a consistent means of comparing ligand field strengths via the ligand field parameter Dq. This parameter is obtained directly from the energy of the $^4A_{2g} \rightarrow ^4T_{2g}$ transition as this transition energy equals 10 Dq. The Dq value of $TMEO_2$ is 1812 cm^{-1}, the highest of any N-oxide complex of chromium yet reported. The indicated spectrochemical series for N-oxide ligands toward chromium(III) is: $TMEO_2$. (1812)> picolinic acid N-oxide (1755)[16]>trimethylamine N-oxide (1710)[4]> quinoline N-oxide (1618)[15]> 2-methylquinoline N-oxide (1610)[13]> acridine N-oxide (1590)[13]>pyridine N-oxide (1587, 1539)[14,19]> bipyridine-N,N′-dioxide (1585)[8]> 2,6-dimethylpyridine N-oxide (1570)[13]> 2-methylpyridine N-oxide (1540).[13] In making such comparisons one generally considers the effects of basicity, steric hindrance, and metal–ligand π-bonding interactions. The π-bonding effects should make significant contributions to Dq only for the aromatic cases. These interactions, however, cannot compensate for the markedly larger basicities of the aliphatic N-oxides (for example, pK_a is 4.65 for trimethylamine N-oxide[20] *versus* −1.7 to 2.0 for the various aromatic N-oxides[1]). As steric effects increase, Dq is expected to decrease and this is generally borne out in that the bulky aromatic N-oxides have the lower values. Thus it is expected that Dq for $TMEO_2$ would be higher than for trimethylamine N-oxide. The high Dq value of $TMEO_2$ further illustrates the importance of chelation even though it involves a seven-membered ring when five-membered aliphatic systems are generally considered most stable. Similar chelate effects have been observed in comparing the Dq values for various monodentate ligands with those for corresponding bidentate ligands. For example, Dq for the chromium complex of N,N-dimethylacetamide[21] is 1517 cm^{-1} as compared to the 1690 cm^{-1} value for N,N,N′,N′-tetramethylmalonamide;[22] Dq for the nickel complex of dimethylsulfoxide[19] is 773 cm^{-1} as compared to 860 cm^{-1} for 2,5-dithiahexane-2,5-dioxide.[23] The relatively high Dq value for the chromium complex of picolinic acid N-oxide also suggests the importance of the chelate effect involving a six-membered ring while the chelate effect of the seven-membered bipyridine-N,N′-dioxide bidentate system is somewhat obscured by the disagreement in reported Dq values for the pyridine N-oxide complex of chromium.

References

1 N.M. Karayannis, L.L. Pytlewski and C.M. Mikulski, *Coord. Chem. Rev., 11,* 93 (1973).
2 R.G. Garvey, J.H. Nelson and R.O. Ragsdale, *Coord. Chem. Rev., 3,* 375 (1968).
3 M. Orchin and P.J. Schmidt, *Coord. Chem. Rev., 3,* 345 (1968).
4 R.S. Drago, J.T. Donoghue and D.W. Herlocker, *Inorg. Chem., 4,* 836 (1965).
5 S. Kida, *Bull, Chem. Soc. Japan, 36,* 712 (1963).
6 J.T. Summers and J.V. Quagliano, *Inorg. Chem., 3,* 1767 (1964).
7 M. Okamura and S. Kida, *J. Inorg. Nucl. Chem., 36,* 1413 (1974).
8 S.K. Madan and W.E. Bull, *J. Inorg. Nucl. Chem., 26,* 2211 (1964).
9 W.E. Bull and L.E. Moore, *J. Inorg. Nucl. Chem., 27,* 1341 (1965).
10 N.S. Gill and R.S. Nyholm, *J. Chem. Soc., London,* 3997 (1959).
11 L.C. Nathan and R.O. Ragsdale, *Inorg. Chim. Acta, 10,* 177 (1974).
12 J.H. Nelson, "Donor Properties of Aromatic Amine Oxides", *Ph.D. Thesis,* University of Utah, Salt Lake City, Utah, 1968.
13 L.C. Nathan, "Some Transition Metal Complexes of Substituted Aromatic Amine N-Oxides", *Ph.D. Thesis,* University of Utah, Salt Lake City, Utah, 1971.
14 R. Whyman, W.E. Hatfield and J.S. Paschal, *Inorg. Chim. Acta, 1,* 113 (1967).
15 L.C. Nathan and R.O. Ragsdale, *Inorg. Chim. Acta, 3,* 473 (1969).
16 A.B.P. Lever, J. Lewis and R.S. Nyholm, *J. Chem. Soc., London,* 5262 (1962).
17 D.J. Hodgson, "The Structural and Magnetic Properties of First-Row Transition-Metal Dimers containing Hydroxo, Substituted Hydroxo and Halogen Bridges", *Progress in Inorganic Chemistry,* Vol. 19, S.J. Lippard, Editor, Interscience, New York, 1975
18 R.L. Carlin, Editor, *Transition Metal Chemistry,* Vol. 5, Marcell Dekker, New York, 1969, p. 30.
19 D.W. Meek, R.S. Drago and T.S. Piper, *Inorg. Chem., 1,* 285 (1962).
20 E. Ochiai, *Aromatic Amine Oxides,* Elsevier, New York, 1967, p. 8.
21 R.S. Drago, D.W. Meek, M.D. Joesten and L. LaRoche, *Inorg. Chem., 2,* 124 (1963).
22 W.E. Bull and R.G. Ziegler, *Inorg. Chem., 5,* 689 (1966).
23 S.K. Madan, C.M. Hull and L.J. Herman, *Inorg. Chem., 7,* 491 (1968).