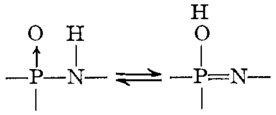
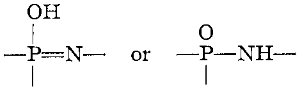


$$-\underset{|}{\overset{\overset{\displaystyle O}{\uparrow}}{P}}-\overset{\overset{\displaystyle H}{|}}{N}- \rightleftharpoons -\underset{|}{\overset{\overset{\overset{\displaystyle H}{\displaystyle O}}{|}}{P}}{=}N-$$

Certainly the hydrogen is readily replaceable and is ionic in solution. In the solid state, however, it is possible one could observe one or the other of the tautomers or perhaps their equilibrium mixture. Inspection of Fig. 1, containing portions of the infrared absorption spectra of tetraphenyl imidodiphosphate (I), of partially deuterated tetraphenyl imidodiphosphate (I-D), of the silver derivative of tetraphenyl imidodiphosphate (I-Ag), and of tetraphenyl N-methyl imidodiphosphate (V), shows that, first, in I there is a sharp band at 1420 cm.$^{-1}$ which is not present in V and is thus related to the system containing hydrogen, either as



$$-\underset{|}{\overset{\overset{\displaystyle OH}{|}}{P}}{=}N- \quad \text{or} \quad -\underset{|}{\overset{\displaystyle O}{P}}-NH-$$

secondly, this band is considerably weaker in I-D than in I, and thus can be attributed to N—H rather than P═N. If the P═N structure were present, one would expect this band to be as strong in I-D as in I. Finally, this band is missing from the spectrum of the silver derivative and the N-methyl derivative of I.

The formation of the N-methyl derivative by replacement of silver by methyl iodide is probably not proof for the location of the silver atom on nitrogen, since methyl could attack nitrogen to form the activated complex or transient intermediate even if silver were on oxygen. The structure of the tetraphenyl N-methylimidodiphosphate was established unequivocably by the proton n.m.r. where a triplet was found for the methyl hydrogens because of splitting with the two phosphorus nuclei.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
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The Donor Properties of N,N-Dimethylethylenediamine N-Oxide

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The reaction of N,N-dimethylethylenediamine N-oxide (DMEO) with a number of transition and post transition metal salts has been investigated. Coordination compounds were obtained of the types: $[M(DMEO)X_2]$ (M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II); X = Cl, I); $[M(DMEO)_2](ClO_4)_2$ (M = Cu(II), Zn(II)); and $[M^n(DMEO)_3](ClO_4)_n$ (M = Ni(II), Fe(III), Co(III)). Their structures were investigated by thermogravimetric analysis, conductivity, magnetism, and visible and infrared spectral measurements and were found to be in agreement with those expected for a chelating ligand with one oxygen and one nitrogen donor atom. The ligand dihydrochloride, DMEO·2HCl, also formed compounds with metal halides, formulated as $[H_2DMEO]^{2+}[MCl_4]^{2-}$ (M = Mn(II), Cd(II), Pd(II)). The pK_a values of the ligand dihydrochloride were also determined.

Introduction

A number of stable coordination compounds of transition metal ions with aromatic N-oxides, such as pyridine N-oxides,[1-3] 2,2′-bipyridine N,N′-dioxide,[4,5] and pyridine N-oxide α-carboxylic acid,[6] have been prepared recently and studied in some detail. Among the aliphatic N-oxides, only trimethylamine N-oxide[7,8] has so far been investigated in regard to its donor properties, and its metal complexes seem to be much more difficult to form and less stable than those of the aromatic N-oxides. Different coordinating ability can be expected for aromatic and aliphatic N-oxides simply on the basis of their electronic structures, and we thought it worthwhile, in connection with previous work on aromatic N-oxide complexes, to collect more experimental evidence on the donor properties of aliphatic N-oxides. For this purpose we chose the ligand N,N-dimethylethylenediamine N-oxide, $(CH_3)_2N(O)CH_2CH_2NH_2$ (DMEO), which in addition to the amine N-oxide functional group has a primary amino group capable of coordination and can form a six-membered chelate ring with metal ions. Because of chelation, the metal complexes of this ligand would be expected to be reasonably stable even if the oxygen atom of the amine oxide group forms relatively weak coordinate bonds.

Experimental

Conductivity measurements at 25° were made on freshly prepared solutions as soon as thermal equilibrium had been reached (about 25 min.). In a few cases more time was required to dis-

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TABLE I

FORMULAS AND SOME PROPERTIES OF N,N-DIMETHYLETHYLENEDIAMINE N-OXIDE–METAL COMPLEXES ($L = (CH_3)_2N(O)CH_2CH_2NH_2$)

Compound	Color	M.p.	ν(N–O), cm.$^{-1}$ [b]	μ_{eff}, B.M.	Conductivity mmole l.$^{-1}$	Λ_M [d]
$[FeL_3](ClO_4)_3$	Brown	212° exp.[a]	916 s	5.80	1.088	208
$[CoL_3](ClO_4)_3$	Violet	176° dec.	909 s	0	1.115	189
$[NiL_3](ClO_4)_2$	Blue	~171° dec.	910 s	3.15	1.016	154
$[CuL_2](ClO_4)_2$	Purple	~161° dec.	904 s	1.83	1.063	155
$[ZnL_2](ClO_4)_2$	White	162°	919 s	0	1.143	155
$[CoLCl_2]$	Violet	199° dec.[a]	907 s	4.55	1.263	6.48[e]
$NiLCl_2 \cdot 2H_2O$	Green	216° dec.[a]	912 s	3.25	1.184	72.3[f]
$[CuLCl_2]$	Blue	129°	902 s	1.75	1.017	72.3[f,g]
$[ZnLCl_2]$	White	172° dec.	907 s	0	1.494	5.21[f]
$ZnLI_2$	Cream	158°[a]	911 s	0	1.340	78.3
$[MnLCl_2]$	Tan	~123° dec.	915 s	5.86	4.507	10.6
$MnCl_2 \cdot L \cdot 2HCl$	Pink	117–119° dec.	919 m, 924 sh, 943 m(?)	5.89	1.174	67.2[f]
$PdCl_2 \cdot L \cdot 2HCl$	Pink	>152° dec.	921 m, 944 m(?)	0	1.217	46.7[e]
$CdCl_2 \cdot L \cdot 2HCl$	White	204° dec.[a]	918 m, 941 m(?)	0	0.952	73.1
$L \cdot 2HCl$	White	165° dec.	930 s			
L	White	. . .	948 b[c]			

[a] Darkens above 150°. [b] In KBr; s, strong; m, medium; b, broad; sh, shoulder. [c] Shows a marked solvent effect. [d] Ohm^{-1} cm.^{2} mole^{-1}, in DMF. [e] Changes with time. [f] Dissolves very slowly. [g] Λ_M in water at ~10^{-3} M concentration is 228, corresponding to a 2:1 electrolyte.

solve the sample. The solvent was freshly distilled[9] N,N-dimethylformamide (DMF), with a specific conductivity of 6.93×10^{-7} ohm^{-1} cm.$^{-1}$ at 25°. The values of the molar conductivities are listed in Table I.

Infrared absorption spectra were obtained using a Perkin-Elmer Model 221 recording spectrophotometer with a grating (4000–1400 cm.$^{-1}$) and a sodium chloride prism (1400–650 cm.$^{-1}$). Samples were examined in KBr disks, and a check was made in Nujol mulls, particularly for the hygroscopic complexes. The values assigned to the N–O stretching frequency are listed in Table I.

Magnetic susceptibility measurements were made by the Gouy method on finely powdered samples at room temperature.[10,11] The values of the magnetic moments, μ_{eff}, calculated from the magnetic susceptibilities, are listed in Table I.

Thermogravimetric studies were carried out with an automatic recording thermobalance,[12] using very finely powdered samples of about 50 mg.

Melting points were determined on a Fisher-Johns melting point apparatus and are listed in Table I.

pH titrations employed a Beckman Model G pH meter and a silver–silver chloride electrode *vs.* a glass electrode with a recommended pH range of 0–11. Commercial buffers (Beckman Instruments, Inc.), as well as buffers prepared in this laboratory,[13] were used as a check.

Near-infrared, visible, and ultraviolet spectra were taken on a Cary Model 14 spectrophotometer. The solvent for solution spectra was DMF; solid spectra were taken in Nujol mulls and KBr pellets. The absorption frequencies and extinction coefficients of the Co(II), Co(III), Ni(II), and Cu(II) complexes are listed in Table II.

Preparation of the Ligand: N,N-Dimethylethylenediamine N-Oxide, $(CH_3)_2N(O)CH_2CH_2NH_2$.—N,N-Dimethylethylenediamine (Aldrich Chemical Co.) was distilled under reduced pressure. Fifteen grams of the central fraction was cooled at 0° and treated with 300 ml. of 3% H_2O_2. The reaction mixture was allowed to stand at room temperature until no KI–starch paper test for hydrogen peroxide resulted and then was reduced to a viscous sirup by evaporating at about 45° under reduced pressure. The residue was diluted with 25 ml. of water and evaporated again as above, to remove the last traces of hydrogen peroxide. The residue was evacuated over phosphoric anhydride and after several days a white, crystalline product formed. The product was recrystallized from absolute ethanol by repeated treatment with anhydrous ethyl ether and prolonged cooling at 0°. Chromatographic fractionation on neutral alumina, using absolute ethanol as solvent, gave a single sharp peak, thus indicating the product to be relatively pure in spite of a faint yellow color. The compound was extremely hygroscopic and further characterization and analysis were carried out on its dihydrochloride.

TABLE II

ELECTRONIC SPECTRA OF SOME COMPLEXES[a] ($L = (CH_3)_2N(O)CH_2CH_2NH_2$)

Compound	λ_{max}, mμ	ν, cm.$^{-1}$	ε[c]
$[CoLCl_2]$	668	15,000	250
	611	16,400	205
$[CoL_3](ClO_4)_3$	568	17,600	167
	400	25,000	190
$NiLCl_2 \cdot 2H_2O$	1130	8,850	7
	630	15,900	11
	415	24,100	19
$[NiL_3](ClO_4)_2$	1020	9,800	10
	610	16,400	7
	370	27,000	20
$[CuLCl_2]$	795	12,600	84
	440[b]	22,700	155
$[CuL_2](ClO_4)_2$	588	17,000	66

[a] About 10^{-3} M solutions in DMF. [b] Not observed in the solid (in Nujol) spectrum. [c] Molar extinction coefficient.

Preparation of N,N-Dimethylethylenediamine N-Oxide Dihydrochloride, $[(CH_3)_2N^+(OH)CH_2CH_2N^+H_3]Cl_2$.—The amine oxide was dissolved in 100 ml. of methanol and treated slowly at 0° with 50 ml. of concentrated HCl, with stirring. The solution was then concentrated on a steam bath until a crust formed, cooled at 0° for several hours, and diluted with an equal volume of absolute ethanol. The precipitate thus formed was filtered off, washed twice with absolute ethanol, and dried over phosphoric anhydride *in vacuo*. Dilution of the mother liquor with several volumes of absolute ethanol gave a second crop of crystals which

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was collected, washed, and dried as above. The product was recrystallized by dissolving in a small amount of boiling methanol, filtering hot, cooling, and then adding excess acetone. The white plates thus formed, after drying over silica gel at reduced pressure, had m.p. 165° with decomposition. The compound is soluble in water and methanol, very slightly soluble in ethanol, and insoluble in acetone, ether, and low polarity solvents.

Anal. Calcd. for $(CH_3)_2N(O)CH_2CH_2NH_2 \cdot 2HCl$: C, 27.13; H, 7.97; Cl, 40.04. Found: C, 27.00; H, 7.96; Cl, 40.18.

Preparation of the Complexes. Bis(N,N-dimethylethylenediamine N-oxide)copper(II) Perchlorate, $[Cu\{(CH_3)_2N(O)CH_2CH_2NH_2\}_2](ClO_4)_2$.—$Cu(ClO_4)_2 \cdot 6H_2O$ (1 g., 2.7 mmoles) in 25 ml. of methanol was added to a solution (0.7 g., 6.7 mmoles) of the ligand in methanol (10 ml.). Fine violet crystals formed soon after mixing and were filtered off, washed with methanol, and dried over phosphoric anhydride *in vacuo*. The compound is soluble in water and DMF, slightly soluble in methanol, and insoluble in ethanol and acetone.

Anal. Calcd. for $[Cu\{(CH_3)_2N(O)CH_2CH_2NH_2\}_2](ClO_4)_2$: C, 20.41; H, 5.14; Cu, 13.50. Found: C, 20.65; H, 5.15; Cu, 13.39.

Bis(N,N-dimethylethylenediamine N-oxide)zinc(II) Perchlorate, $[Zn\{(CH_3)_2N(O)CH_2CH_2NH_2\}_2](ClO_4)_2$.—This compound was prepared as described for the copper(II) complex and has a similar solubility.

Anal. Calcd. for $[Zn\{(CH_3)_2N(O)CH_2CH_2NH_2\}_2](ClO_4)_2$: C, 20.33; H, 5.12; Zn, 13.83. Found: C, 20.40; H, 5.10; Zn, 13.53.

Tris(N,N-dimethylethylenediamine N-oxide)nickel(II) Perchlorate, $[Ni\{(CH_3)_2N(O)CH_2CH_2NH_2\}_3](ClO_4)_2$.—This compound was prepared as described for the copper(II) complex, using a 1:3 nickel:ligand ratio. Precipitation of the product was favored by dilution of the reaction mixture with absolute ethanol. The solubility is similar to that of the copper(II) complex.

Anal. Calcd. for $[Ni\{(CH_3)_2N(O)CH_2CH_2NH_2\}_3](ClO_4)_2$: C, 25.28; H, 6.37; Ni, 10.30. Found: C, 25.23; H, 6.38; Ni, 10.45.

Tris(N,N-dimethylethylenediamine N-oxide)iron (III) Perchlorate, $[Fe\{(CH_3)_2N(O)CH_2CH_2NH_2\}_3](ClO_4)_3$.—This complex was prepared similarly to the Zn(II) complex. The product darkens in contact with moist air and when finely divided explodes on heating. Its solubility is appreciable in DMF but low in alcohols.

Anal. Calcd. for $[Fe\{(CH_3)_2N(O)CH_2CH_2NH_2\}_3](ClO_4)_3$: C, 21.62; H, 5.44; Fe, 8.38. Found: C, 21.20; H, 5.31; Fe, 8.36.

Tris(N,N-dimethylethylenediamine N-oxide)cobalt(III) Perchlorate, $[Co\{(CH_3)_2N(O)CH_2CH_2NH_2\}_3](ClO_4)_3$.—The ligand (1.0 g., 9.6 mmoles) and $[Co(NH_3)_5Cl]Cl_2$ (0.5 g., 2.0 mmoles) were dissolved in 50 ml. of water and the mixture was heated on a water bath at 50–60° for 40 min. The color of the solution turned from pink to dark violet. After cooling, a large volume of acetone (200 ml.) was added and a dark violet, sirupy product separated. This was removed by decantation, washed with acetone, and dissolved in 100 ml. of methanol to give a violet solution. After filtering, the solution was treated with 2 g. of $NaClO_4$ (16.4 mmoles) dissolved in a very small volume of methanol. A violet powder precipitated, which was collected, recrystallized from a 1:1 methanol–water mixture, and dried over H_2SO_4 *in vacuo*. The crystals (rhombs) thus obtained are soluble in water and DMF, very slightly soluble in alcohols, and insoluble in nonpolar solvents.

Anal. Calcd. for $[Co\{(CH_3)_2N(O)CH_2CH_2NH_2\}_3](ClO_4)_3$: C, 21.52; H, 5.42; Co, 8.80. Found: C, 21.61; H, 5.52; Co, 8.69.

Dichloro(N,N-dimethylethylenediamine N-oxide)copper(II), $[Cu\{(CH_3)_2N(O)CH_2CH_2NH_2\}Cl_2]$.—One gram (9.6 mmoles) of the ligand, dissolved in 50 ml. of ethanol, was slowly added to a solution of $CuCl_2 \cdot 2H_2O$ (2.0 g., 11.7 mmoles) in ethanol (10 ml.). A blue-green precipitate formed immediately; this was filtered off and washed with acetone, then extracted with 60 ml. of methanol. Upon standing the methanol solution yielded deep blue prisms. The product was filtered off, washed with methanol, and dried at reduced pressure over phosphoric anhydride. Its solubility in DMF is lower than that of the copper(II) perchlorate complex.

Anal. Calcd. for $[Cu\{(CH_3)_2N(O)CH_2CH_2NH_2\}Cl_2]$: C, 20.13; H, 5.07; Cu, 26.63. Found: C, 19.94; H, 4.89; Cu, 26.62.

Dichloro(N,N-dimethylethylenediamine N-oxide)zinc(II), $[Zn\{(CH_3)_2N(O)CH_2CH_2NH_2\}Cl_2]$.—The amine oxide (0.6 g., 5.6 mmoles) was dissolved in 50 ml. of ethanol and added slowly to 2.0 g. of $ZnCl_2$ (14.7 mmoles) dissolved in 10 ml. of ethanol. Immediately a flocculent white precipitate formed, which was filtered off, washed with ethanol, and dried over phosphoric anhydride at reduced pressure. The product is less soluble than the perchlorate complex in water and DMF and more soluble in solvents of lower polarity.

Anal. Calcd. for $[Zn\{(CH_3)_2N(O)CH_2CH_2NH\}_2Cl_2]$: C, 19.98; H, 5.03; Zn, 27.19. Found: C, 19.60; H, 5.07; Zn, 27.67.

Diiodo(N,N-dimethylethylenediamine N-oxide)zinc(II), $Zn\{(CH_3)_2N(O)CH_2CH_2NH_2\}I_2$.—This iodo complex was prepared similarly to the chloro complex.

Anal. Calcd. for $Zn\{(CH_3)_2N(O)CH_2CH_2NH_2\}I_2$: C, 11.35; H, 2.86; Zn, 15.44. Found: C, 11.57; H, 3.08; Zn, 15.37.

Dichloro(N,N-dimethylethylenediamine N-oxide)cobalt(II), $[Co\{(CH_3)_2N(O)CH_2CH_2NH_2\}Cl_2]$.—The complex was prepared similarly to the $ZnCl_2$ complex.

Anal. Calcd. for $[Co\{(CH_3)_2N(O)CH_2CH_2NH_2\}Cl_2]$: C, 20.53; H, 5.17; Co, 25.19. Found C, 20.37; H, 5.06; Co, 24.97.

Dichloro(N,N-dimethylethylenediamine N-oxide)manganese(II), $[Mn\{(CH_3)_2N(O)CH_2CH_2NH_2\}Cl_2]$.—One gram of $MnCl_2 \cdot 4H_2O$ (5.0 mmoles), dissolved in 20 ml. of ethanol, was treated with 1.0 g. of the ligand (9.6 mmoles) dissolved in ethanol (10 ml.). A light brown precipitate formed immediately. Dilution with a small volume of ethyl ether gave further precipitation. The product was filtered off, dissolved in methanol, and reprecipitated by dilution with ethyl ether. It was then washed with ether and dried at reduced pressure over phosphoric anhydride.

Anal. Calcd. for $[Mn\{(CH_3)_2N(O)CH_2CH_2NH_2\}Cl_2]$: C, 20.88; H, 5.26; Mn, 23.88. Found: C, 21.06; H, 5.52; Mn, 23.67.

Diaquodichloro(N,N-dimethylethylenediamine N-oxide)nickel(II), $Ni\{(CH_3)_2N(O)CH_2CH_2NH_2\}Cl_2 \cdot 2H_2O$.—A solution of the ligand (0.6 g., 5.6 mmoles) in 40 ml. of ethanol was added to a solution of $NiCl_2 \cdot 6H_2O$ (2 g., 8.4 mmoles) in 50 ml. of ethanol. There was no immediate precipitate but the green solution became darker. On standing, a light blue-green precipitate formed and was filtered off and discarded. On addition of 250 ml. of tetrahydrofuran a light green precipitate was obtained. The product was filtered off, washed with a small amount of ethanol, and dried at reduced pressure over phosphoric anhydride. It is appreciably soluble in ethanol, methanol, and water but only slightly soluble in DMF.

Anal. Calcd. for $Ni\{(CH_3)_2N(O)CH_2CH_2NH_2\}Cl_2 \cdot 2H_2O$: C, 17.81; H, 5.98; Ni, 21.76. Found: C, 17.89; H, 5.62; Ni, 21.35.

Manganese(II) and Cobalt(II) Perchlorate Complexes of N,N-Dimethylethylenediamine N-Oxide.—Reaction of Co(II) and Mn(II) perchlorates (hydrated) in ethanol with an ethanol solution of the ligand gave products which appeared to be sensitive to moisture and/or air and were contaminated with oxides or basic salts of the metals. Extensive characterization of these products was not carried out, as they could not be obtained of analytical purity.

Manganese(II) Chloride Complex of N,N-Dimethylethylenediamine N-Oxide Dihydrochloride, $MnCl_2 \cdot (CH_3)_2N(O)CH_2CH_2NH_2 \cdot 2HCl$.—One gram of DMEO·2HCl (5.7 mmoles) was dissolved in excess methanol and treated with a methanol solution of $MnCl_2 \cdot 4H_2O$ (2.0 g., 10.0 mmoles). The resulting solution was filtered and evaporated under reduced pressure. A crystalline precipitate formed which was broken up mechanically and washed several times with ethanol. The light pink, crystalline product thus obtained was dried over silica gel at reduced pressure. It is soluble in water, slightly soluble in methanol, and very slightly soluble in ethanol.

Anal. Calcd. for $MnCl_2 \cdot (CH_3)_2N(O)CH_2CH_2NH_2 \cdot 2HCl$: C, 15.86; H, 4.66; Cl, 46.82; Mn, 18.13. Found: C, 16.23; H, 4.81; Cl, 47.23; Mn, 17.97.

Cadmium(II) Chloride Complex of N,N-Dimethylethylenediamine N-Oxide Dihydrochloride, $CdCl_2 \cdot (CH_3)_2N(O)CH_2CH_2NH_2 \cdot 2HCl$.—One gram of $CdCl_2 \cdot 2.5H_2O$ (4.4 mmoles), dissolved in 100 ml. of methanol, was treated with DMEO·2HCl (1.5 g., 8.5 mmoles), which had been dissolved in 25 ml. of methanol by warming. A white precipitate soon appeared and became extensive on cooling. The product was filtered off, washed with methanol, and dried over $CaCl_2$. Its solubility is similar to that of the corresponding Mn(II) compound, but is lower in methanol.

Anal. Calcd. for $CdCl_2 \cdot (CH_3)_2N(O)CH_2CH_2NH_2 \cdot 2HCl$: C, 13.33; H, 3.92; Cd, 31.19; Cl, 39.35. Found: C, 13.65; H, 3.86; Cd, 31.22; Cl, 39.48.

Palladium(II) Chloride Complex of N,N-Dimethylethylenediamine N-Oxide Dihydrochloride, $PdCl_2 \cdot (CH_3)_2N(O)CH_2CH_2NH_2 \cdot 2HCl$.—DMEO·2HCl (0.5 g., 2.8 mmoles) was dissolved in 15 ml. of methanol and added slowly to 0.07 g. of $PdCl_2$ dissolved in 15 ml. of methanol containing excess LiCl. Salmon-pink plates soon began to form. The product was filtered off, washed with methanol, and dried over $CaCl_2$. Its solubility is similar to that of the manganese(II) analog; the solutions are yellow.

Anal. Calcd. for $PdCl_2 \cdot (CH_3)_2N(O)CH_2CH_2NH_2 \cdot 2HCl$: C, 13.56; H, 3.98; Pd. 30.02. Found: C, 14.08; H, 4.01; Pd, 30.04.

Results and Discussion

In order to compare the basicity of DMEO with that of the related compounds, in particular the parent amine, $(CH_3)_2NCH_2CH_2NH_2$, the acid dissociation constants pK_{1a} and pK_{2a} of $[DMEO(H)_2]^{+2}$ were determined by titration of the chloride with sodium hydroxide. The method used was similar to that described by Irving and Griffith[14] for the parent amine, except that it was not necessary to use the simultaneous equations suggested by these authors because the pK_a values of $[DMEO(H)_2]^{2+}$ differed by about 5 pK units. Each point of the titrations was evaluated and the agreement between the calculated values was generally within 0.02 pK unit, particularly near the neutralization midpoints. Points above pH 10 were poor because of the interaction of sodium ions with the glass electrode. Values obtained by a graphical method (neutralization midpoints) also agreed within 0.02 pK unit with the average calculated values. The values thus obtained, $pK_{1a} = 3.62$ and $pK_{2a} = 8.36$, are lower than those of the corresponding amine,[14] $pK_{1a} = 6.63$ and $pK_{2a} = 9.53$. The value of pK_{1a} is also lower than the pK_a of many aliphatic amine oxides,[15] which fall in the range 4.0–5.5, very likely because of the acid strengthening effect of the $H_3N^+{-}CH_2CH{-}$ group, as observed for the diacid salts of ethylenediamines.[14] On the other hand, the lowering of the pK_{2a} value with respect to the parent amine may be ascribed to the inductive effect of the polar $-N^+{-}O^-$. As the values of pK_{1a} and pK_{2a} indicate, DMEO is still fairly basic. Difficulties may, therefore, be expected in the preparation of the coordination compounds of some metal ions, especially since water is always present in the reaction mixture (the difficulty in completely dehydrating the ligand may be related to the tendency of the amine oxide to chemically bind water). Also, exposure of the ligand to air may result in the formation of some carbonate or carbamate by reaction with atmospheric carbon dioxide. For these reasons, and because aliphatic amine oxides easily undergo decomposition[16,17] or rearrangements,[15] the preparation of the metal complexes of DMEO presented some experimental difficulties and in a few cases complexes were formed but could not be satisfactorily purified. Such was the case, for example, of the complexes of $Mn(ClO_4)_2 \cdot 6H_2O$ and $Co(ClO_4)_2 \cdot 6H_2O$.

The values of the acid dissociation constants of the diprotonated DMEO indicate that the ligand has less affinity for the proton than the corresponding amine and might, therefore, be expected to have less tendency to coordinate to metal ions. On the other hand, steric factors are much more favorable for DMEO than for the amine. In fact not only does the donor oxygen atom $O{-}N(CH_3)_2{-}$ replace the highly hindered tertiary nitrogen $N(CH_3)_2{-}$, but also a more flexible six-membered chelate ring is formed in place of a five-membered ring. This difference in steric requirements may explain why stable complex cations of the type $[M(chelate)_3]^{2+}$ could be obtained for DMEO but not for the parent amine.

The coordination compounds of DMEO prepared in a pure state and characterized are listed in Table I, together with some of their properties. The structural formulas assigned to the complexes are deduced from their analyses and conductivity, magnetic, and visible spectral data and show that DMEO is not able to replace easily donor anions, such as Cl^- or I^-, within the coordination sphere. Complex cations of the type $[M^n(DMEO)_2]^{n+}$ and $[M^n(DMEO)_3]^{n+}$ could only be prepared from metal salts of poor coordinating anions such as the perchlorate.

Conductivity measurements show that the metal halide complexes, $MX_2 \cdot DMEO$, are nonelectrolytes and should be formulated $[M(DMEO)X_2]$, whereas the metal perchlorate complexes are electrolytes. The values of the molar conductivities of the latter, in 10^{-3} M dimethylformamide solution, are listed in Table II and agree with the values generally expected for complex salts of similar charge.[1]

The magnetic moments of the solid $[M(DMEO)_3](ClO_4)^n$ complexes, together with their electronic spectra in solution, indicate an octahedral configuration.[18] The close similarity between the spectra of $[Ni(DMEO)_3](ClO_4)_2$ and $[Ni(glycinato)_3]$[19] gives an approximate evaluation of the ligand strength of DMEO, in relation to other chelating systems with one oxygen and

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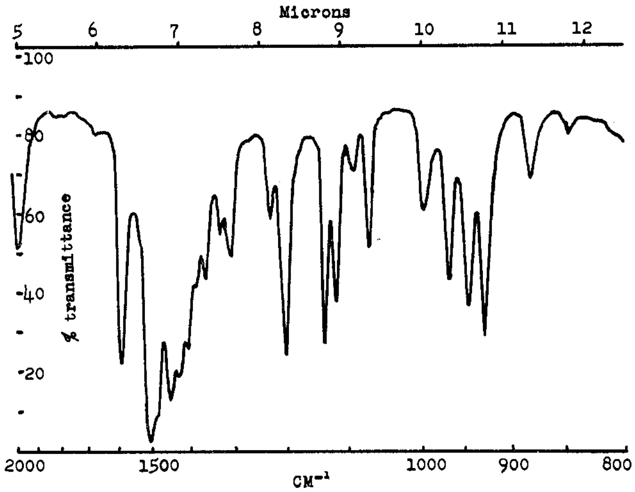

Fig. 1.—Infrared spectrum of N,N-dimethylethylenediamine N-oxide dihydrochloride in a KBr pellet.

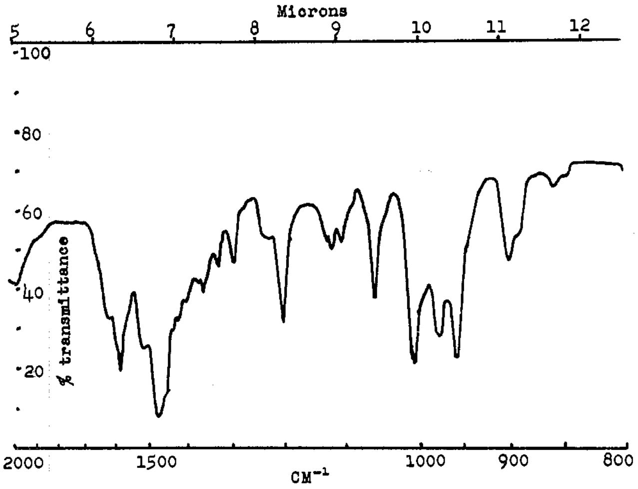

Fig. 2.—Infrared spectrum of N,N-dimethylethylenediamine dihydrochloride in a KBr pellet.

one nitrogen donor. It is to be noted, however, that the spectrum of $[Cu(DMEO)_2](ClO_4)_2$ is closer to that of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ than to that of $[Cu(glycinato)_2]$, though differences are rather small.[20,21] For the compounds of type $[M(DMEO)X_2]$, both magnetism and electronic spectra indicate a tetrahedral configuration. The spectrum of $[Co(DMEO)X_2]$ is typical of the tetrahedral $[CoL_2X_2]$ type of complex.[22] On the other hand, the compound $NiCl_2 \cdot DMEO \cdot 2H_2O$ has a magnetic moment and spectrum[18,19] typical of octahedrally coordinated Ni(II) and should be formulated as $[Ni(DMEO)(H_2O)_2Cl_2]$. This formulation of the Ni(II) chloride complex is also supported by the results of thermogravimetric analysis of the halide complexes. The $[M(DMEO)X_2]$ compounds show a consistently reproducible sharp weight loss at about 160°, leading to a semistable species which in turn begins to lose weight at about 300°. In the case of $[Ni(DMEO)(H_2O)_2Cl_2]$, a gradual decrease in weight occurs at a lower temperature (about 100°) corresponding to the loss of the two water molecules. It is interesting to note that the weight loss at about 160°, while nearly constant for the same compound in repeated experiments, varies appreciably for the different metal complexes.

The infrared spectra of the ligand DMEO and of its metal complexes give additional information about the donor ability of the amine oxide group. Figure 1 shows the infrared spectrum (NaCl region) of $DMEO \cdot 2HCl$. A comparison with the spectra of related compounds such as N-N-dimethylethylenediamine dihydrochloride (Fig. 2), N,N-dimethylethylenediamine,[23] ethylenediamine dihydrochloride,[24] and trimethylamine N-oxide and its hydrochloride[25] indicates that the N–O stretching vibration of $DMEO \cdot 2HCl$ can be assigned to the relatively intense band at 930 cm.$^{-1}$. The less sharp but still fairly intense band observed at 948 cm.$^{-1}$ in the spectrum of DMEO in carbon disulfide also corresponds to this mode and appears to be very sensitive to sample state or solvent or both. Table I shows how the N–O stretching vibration shifts to lower frequencies upon coordination. The shift is analogous to that observed for pyridine N-oxide complexes and can be similarly explained.[26] From the values of the N–O stretching frequencies of the complexes, it appears that the divalent metal perchlorate complexes $[M(DMEO)_x](ClO_4)_2$ follow the Irving–Williams[27] stability series: Mn(II) < Co(II) < Ni(II) < Cu(II) > Zn(II). The values of the N–O frequencies of the halide complexes also follow the Irving–William series, except for the hydrated Ni(II) compound, whicha ctually is a different complex species.

The shifts of the N–O stretching frequencies for the complexes of the tripositive ions, Fe(III) and Co(III), are low in comparison with those observed in similar cases. This somewhat unusual behavior may be plausibly ascribed to the crowding of the DMEO ligands around the smaller, tripositive metal ions.

It may be mentioned that the steric requirements of the DMEO ligand, as indicated by scale models, drastically reduce the number of geometrical and conformational isomers possible for the $[M(DMEO)_3]^{n+}$ cations. In fact, the only stable form appears to be the *cis* geometric isomer with the chelate ring in the boat form (somewhat distorted due to the small N–M–O angle) having the oxygen atom and the carbon atom adjacent to the primary amine in the "bow" and "stern" positions. Similar boat conformers are also favored for the chelate rings of complexes of different stereochemistry, such as the tetrahedral $[M(DMEO)_2]^{n+}$. On the other hand, scale models show that for the free DMEO both a *trans* and a staggered conformation are possible, the latter allowing intramolecular hydrogen bonding. Both conformers are probably present in DMEO, as indicated by the broad infrared bands corre-

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sponding to the N–O stretching, CH_2 rocking, and CH_2 wagging vibrations, whereas DMEO·2HCl exists in the *trans* form as shown by the CH_2 rocking vibration at about 740 cm.$^{-1}$ (A_u mode).[28]

The dihydrochloride of the ligand, DMEO·2HCl, reacts with some metal chlorides to give crystalline compounds of the formula MX_2·DMEO·2HCl. We have prepared the Mn(II), Cd(II), and Pd(II) derivatives, but it is to be expected that similar compounds may be formed by other metals. Because of their properties these compounds are formulated as tetrachlorometalates of the diprotonated species $[(CH_3)_2N^+(OH)CH_2CH_2N^+H_3]$ and are similar to the tetrahalogen metalates of other organic cations. It may be noticed that these $[H_2DMEO]$ salts give anomalous conductivity values in DMF solution. This behavior very likely arises from a partial replacement in solution of one chloride of the tetrachlorometalate ion by an amino or aminooxide group. A similar behavior has been reported for the tetrachloropalladate(II) of diprotonated ethylenediamine and of its methylated analogs.[29]

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Infrared Spectra from 80 to 2000 Cm.$^{-1}$ of Some Metal–Ammine Complexes

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The infrared spectra of the complexes $[Co(NH_3)_6]X_3$, $[Co(NH_3)_5X]X_2$, and $[M(NH_3)_6]X_2$, where M = Mn, Fe, Co, Ni, Zn, or Cd and X = Cl, Br, or I, have been measured from 80 to 2000 cm.$^{-1}$. The absorption band corresponding to the N–M^{II}–N bending mode was observed at *ca.* 200 cm.$^{-1}$. The Co(III)–halogen stretching vibration in the halopentaammine complexes was observed below 300 cm.$^{-1}$, but no skeletal vibrations were observed in this region in the spectra of hexaammine–Co(III) complexes. Lattice vibrations have been identified in the region 80–155 cm.$^{-1}$ and a possible explanation of the unusual isotopic shifts of these bands is presented.

Introduction

Although the infrared spectra of numerous metal–ammine complexes have been extensively studied,[2–11] $[Rh(NH_3)_6]Cl_3$ is the only compound for which the far-infrared spectrum (below 300 cm.$^{-1}$) has been reported.[11] The investigation of this region is of particular importance in regard to the long disputed assignment of the skeletal vibrations of these compounds. The lowest frequency band so far observed in the spectra of the hexaammine–metal(II) complexes, at *ca.* 300 cm.$^{-1}$, has been assigned to the M–N stretching mode. On the other hand the band at roughly the same position in the spectra of the complexes of the trivalent metals is now assigned to the N–M–N bending mode[9–11] after being originally assigned to the M–N stretching mode.[5,8] Thus no absorption band is expected below 300 cm.$^{-1}$ in the spectra of the metal(III) complexes, while the N–M–N bending mode of the metal(II) complexes is expected in this region.

We now report the results of a study of the infrared spectra from 80 to 2000 cm.$^{-1}$ of various hexaammine and halopentaammine complexes of cobalt(III) and the series of metal(II) complexes $[M(NH_3)_6]X_2$ where M = Mn, Fe, Co, Ni, Zn, or Cd and X = Cl, Br, or I. The latter three series are particularly well suited to an attempt to correlate the vibration frequencies with some physical property related to the bond strength.

Experimental

All compounds were prepared by standard methods. $[Ni(ND_3)_6]Cl_2$ was prepared by the reaction of gaseous ND_3 with solid $NiCl_2$. $[Co(ND_3)_6]Cl_3$ and $[Co(ND_3)_5Cl]Cl_2$ were prepared by dissolving the corresponding light ammonia complexes in D_2O followed by removal of the water by freeze drying. The process was repeated three times. For the second compound the solid was heated at 80° under vacuum to convert $[Co(ND_3)_5D_2O]Cl_3$ into $[Co(ND_3)_5Cl]Cl_2$. Deuteration was found to be about 90% complete, as judged by the relative intensities of the N–H and N–D stretching bands.

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