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Preparation and Properties of *N*,*N*-Dialkylethylenediamine *N*-Oxide Complexes of Nickel(II), Copper(II), and Cobalt(III)

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The complexes of Ni(II), Cu(II), and Co(III) with *N*,*N*-Dialkylethylenediamine (alkyl=CH_3, C_2H_5, and C_3H_7) have been prepared. It was revealed that these ligands coordinate to metal ions as bidentate ligands with amino and tertiary amine oxide groups. Two forms have been obtained for the 1 : 2 nickel(II) complexes, the hydrated green form with $\mu_{eff}=3.3$ and the anhydrous red or reddish brown form with zero or very low magnetic moment. They are easily convertible into each other. Formation of square planar diamagnetic Ni(II) complexes with ionic-type ligand was interpreted in terms of the steric effect of the alkyl groups.

Only a few studies have been made on the metal complexes of tertiary amine oxide[1,2] compared with those of complexes of pyridine *N*-oxide and its derivatives.[3,4] It was reported that trimethylamine oxide forms tetrahedral complexes with cobalt(II), zinc(II), and cadmium(II) in alcoholic solution,[2] but octahedral or square planar complexes were not known.

We have attempted to prepare stable metal chelates involving a tertiary amine oxide as a coordinating group, using *N*,*N*-dialkylethylenediamine *N*-oxide as a neutral ligand. We succeeded in the preparation of new complexes of Cu(II), Ni(II), and Co(III) of tertiary amine oxide. It is to be noted that diamagnetic square planar nickel(II) complexes were readily obtained by using a ligand of the 2N2O-type which may be expected to form rather ionic bond with a metal ion.

Experimental

Preparation. N,N-*Dimethylethylenediamine* N-*Oxide (abbreviated as dimen-O)*: To 15 g of *N*,*N*-dimethylethylenediamine diluted with the same amount of water was added dropwise 220 m*l* of 3% hydrogen peroxide. After standing for 24 hours at room temperature, the solution was evaporated at 65°C under reduced pressure and a sirup of *N*-oxide was obtained. This was used for the preparation of complexes without further purification.

N,N-*Diethylethylenediamine* N-*Oxide (abbreviated as dieen-O)* and N,N-*Dipropylethylenediamine* N-*Oxide (abbreviated as dipen-O)*: The above two compounds were prepared by a method similar to that for dimen-O.

Bis-N,N-*(dimethylethylenediamine* N-*oxide)*nickel(II) *Perchlorate 1.5 hydrate (=[Ni(dimen-O)$_2$](ClO$_4$)$_2$·1.5H$_2$O)*: To a solution of 1.2 g of the ligand in 50 m*l* of 95% ethanol was added 2.0 g of nickel(II) perchlorate hexahydrate dissolved in 50 m*l* of 95% ethanol. Green crystals were immediately formed. They were collected on a glass filter and washed with ethanol.

Found: C, 19.61; H, 5.51; N, 11.52%. Calcd for [Ni(dimen-O$_2$)](ClO$_4$)$_2$·1.5H$_2$O : C, 19.49; H, 5.51; N, 11.36%. $\mu_{eff}=3.3$ B.M.

*Bis-(*N,N-*dimethylethylenediamine* N-*oxide)nickel(II) Perchlorate (=[Ni(dimen-O)$_2$](ClO$_4$)$_2$)*: The compound was prepared by recrystallization of the green hydrated form from ethanol as red crystals. It is also obtained by heating the hydrated complex over phosphoric anhydride at 80°C.

Found: C, 20.50; H, 5.24; N, 11.83. Calcd for [Ni(dimen-O)$_2$](ClO$_4$)$_2$: C, 20.62; H, 5.19; N, 12.02%. $\mu_{eff}=0.6$ B.M.

Bis-(N,N-diethylethylenediamine N-*oxide)nickel(II) Perchlorate (=[Ni(dieen-O)$_2$](ClO$_4$)$_2$*: To a solution of 1.5 g of the ligand in 40 m*l* of 99% ethanol was added 2.0 g of nickel(II) perchlorate hexahydrate dissolved in 40 m*l* of 99% ethanol. The resulting deep green solution was cooled in a refrigerator for 24 hr. Reddish brown crystals were formed. Recrystallization was carried out from ethanol.

Found: C, 27.50; H, 6.35; N, 10.51. Calcd for [Ni(dieen-O)$_2$](ClO$_4$)$_2$: C, 27.61; H, 6.18; N, 10.73%. Diamagnetic.

When the reddish brown crystals are kept in the humid atmosphere for one day, they gradually change into pale blue powder containing 2 mol of water for one nickel atom. This is readily reconverted into the reddish brown anhydride by heating at 100°C or keeping it in a desiccator over phosphoric anhydride.

Found: H$_2$O, 6.51. Calcd for [Ni(dieen-O)$_2$](ClO$_4$)$_2$·2H$_2$O: H$_2$O, 6.46%. $\mu_{eff}=3.3$ B.M.

*Bis-(*N,N-*di*-n-*propylethylenediamine* N-*oxide)nickel(II) Perchlorate (=[Ni(dipen-O)$_2$](ClO$_4$)$_2$)*: To a solution of 1.9 g of the *N*-oxide in 20 m*l* of 99% ethanol was added 1.5 g

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[2] S. Kida, This Bulletin, **36**, 712 (1963).

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

[4] S. Kida, J. V. Quagliano, J. A. Walmsley, and S. Y. Tyree, *Spectrochim. Acta*, **19**, 189 (1963).

of nickel(II) perchlorate hexahydrate dissolved in 20 m*l* of 99% ethanol. Twenty m*l* of dioxane was added to this solution which was then cooled for 48 hr in a refrigerator. Reddish brown crystals were formed. Recrystallization was carried out from a mixed solvent of ethanol and dioxane.

Found: C, 33.20; H, 7.02; N, 9.65. Calcd for [Ni(dipen-O)$_2$](ClO$_4$)$_2$: C, 33.23; H, 6.92; N, 9.60%. diamagnetic.

The hydrated form of this compound was obtained as pale blue powder by the same procedure as for the ethyl homologue. However, the content of water was found to be much higher, *i.e.*, 6 mol of water for one nickel atom.

Found: H$_2$O, 15.15. Calcd for [Ni(dipen-O)$_2$(ClO$_4$)$_2$·6H$_2$O: H$_2$O, 15.74%. μ_{eff}=3.3 B.M.

*Bis-(*N,N*-dimethylethylenediamine N-oxide)copper(II) Perchlorate (=[Cu(dimen-O)$_2$](ClO$_4$)$_2$*: The complex was prepared by the same method as that for [Ni(dimen-O)$_2$](ClO$_4$)$_2$· except for using copper(II) perchlorate 1.5H$_2$O, instead of nickel(II) perchlorate.

Found: C, 20.58; H, 5.19; N, 11.91. Calcd for [Cu(dimen-O)$_2$](ClO$_4$)$_2$: C, 20.41; H, 5.14; N, 11.90%. μ_{eff}=1.74 B.M.

*Bis-(*N,N*-diethylethylenediamine* N*-oxide)copper(II) Perchlorate (=[Cu(dieen-O)$_2$](ClO$_4$)$_2$*: The complex was prepared by a similar method to that for the above complex.

Found: C, 27.18; H, 5.94; N, 10.68. Calcd for [Cu(dieen-O)$_2$](ClO$_4$)$_2$: C, 27.36; H, 6.12; N, 10.63%. μ_{eff}=1.78 B.M.

*Tris-(*N,N*-dimethylethylenediamine* N*-oxide)nickel(II) Perchlorate (=[Ni(dimen-O$_3$)](ClO$_4$)$_2$*: To a solution of 2.0 g of the ligand in 50 ml of 95% ethanol was added 2.0 g of nickel(II) perchlorate hexahydrate dissolved in 50 m*l* of 95% ethanol. Light blue crystals were formed. They were collected on a glass filter, washed with ethanol and dried *in vacuo* over phosphoric anhydride.

Found: C, 25.00; H, 6.13; N, 14.67. Calcd for [Ni(dimen-O)$_3$](ClO$_4$)$_2$: C, 25.28; H, 6.37; N, 14.74%. μ_{eff}=3.2 B.M.

*Tris-(*N,N*-diethylethylenediamine* N*-oxide)nickel(II) Perchlorate (=[Ni(dieen-O)$_3$](*ClO$_4$*)$_2$*: Light blue crystals were obtained by a similar method to that for the above complex.

Found: C, 32.38; H, 7.55; N, 12.49. Calcd for [Ni(dieen-O)$_3$](ClO$_4$)$_2$: C, 33.05; H, 7.40; N, 12.84%. μ_{eff}=3.0 B.M.

*Tris-(*N,N*-dimethylethylenediamine N-oxide)cobalt(III) Perchlorate (=[Co(dimen-O)$_3$](ClO$_4$)$_3$*: To an aqueous solution of 3.2 g of the N-oxide in 20 m*l* water were added 2.5 g of [CoCl(NH$_3$)$_5$]Cl$_2$ and 1 g of active carbon. The mixture was heated on a water-bath for 3 hr and filtered. To this filtrate were added 50 m*l* of acetone and 60 m*l* of ethanol saturated with sodium perchlorate. Deep blue violet crystals were immediately formed. Recrystallization was carried out from ethanol.

Found: C, 21.24; H, 5.46; N, 12.34. Calcd for [Co(dimen-O)$_3$](ClO$_4$)$_3$: C, 21.52; H, 5.42; N, 12.55%. diamagnetic.

Optical resolution of the complex was undertaken with the use of optically active trioxalato cobaltate(III) ion, but it was unsuccessful.

Reflectance Spectra. The powder reflectance spectra were measured with a Shimadzu Multipurpose Spectrophotometer Model MPS-50L.

Magnetic susceptibility. Magnetic susceptibilities were measured by Guy's method at room temperature.

Results and Discussion

Cobalt(III) Complexes. An aqueous solution of tris (N,N-dimethylethylenediamine N-oxied)cobalt(III) ion (abbreviated as [Co(dimen-O)$_3$]$^{3+}$) is fairly stable at room temperature, and gives an absorption spectrum similar in contour to those of *fac*-tris-(alaninato) cobalt(III) and of *fac*-tris-(β-alaninato)cobalt(III),[5] but the absorption peaks show a considerable red-shift (~1.7 kK) relative to those of the amino acid complexes as seen in Table 1. This seems to indicate that tertiary amine oxide is located at a lower position in the spectrochemical series than carboxylic acid.

Table 1. Absorption peaks of some Co(III) complexes of 3N-3O coordination in aqueous solution

	I kK(ε)	II kK(ε)
Co(dimen-O)$_3$$^{3+}$	17.62 (120)	24.93 (124)
fac-Co(β-ala)$_3$	19.01 (141)	27.03 (61)
fac-Co(ala)$_3$	19.23 (186)	26.74 (160)
mer-Co(β-ala)$_3$	17.55 (100) 20.49 (64)	27.03 (84)

Copper(II) Complexes. We see from Table 2 that the *d-d* bands of [Cu(dimen-O)$_2$](ClO$_4$)$_2$ and [Cu(dieen-O)$_2$](ClO$_4$)$_2$ (in solid state) are located in a much shorter wave-length region compared with those of the usual Cu-2N-2O type complexes such as [Cugly$_2$]. This is undoubtedly due to the steric effect of alkyl groups attached to nitrogen atoms, which may hinder the coordination to the axial position of the complex.[6]

Table 2. Peaks of reflectance spectra of some copper(II) complexes

complexes	ν_{max} (kK)
Cu(CH$_3$NH$_2$)$_4$(ClO$_4$)$_2$	17.24
Cu(C$_2$H$_5$NH$_2$)$_4$(ClO$_4$)$_2$	16.64
Cu(gly)$_2$	15.97
Cu(dimen)$_2$(ClO$_4$)$_2$	18.02
Cu(dieen)$_2$(ClO$_4$)$_2$	20.37
Cu(dimen-O)$_2$(ClO$_4$)$_2$	17.54
Cu(dieen-O)$_2$(ClO$_4$)$_2$	17.54

gly=NH$_2$CH$_2$COO$^-$, dimen=(CH$_3$)$_2$NCH$_2$CH$_2$NH$_2$
dieen=(C$_2$H$_5$)$_2$NCH$_2$CH$_2$NH$_2$

Nickel Complexes. The 1 : 3 complexes, [Ni(dimen-O)$_3$](ClO$_4$)$_2$ and [Ni(dieen-O)$_3$](ClO$_4$)$_2$, are undoubtedly hexacoordinated species, judging from their reflectance spectra (Table 3) and the bidentate nature of the ligands. Whereas, in the 1 : 2 complexes, however, there are two types, green hydrate ones and red or brown anhydrous ones. The former are readily converted into the latter when they are heated above 80°C or kept in a desiccator over phosphoric anhydride. The anhydrous complexes are

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TABLE 3. PEAKS OF ELECTRONIC SPECTRA AND MAGNETIC MOMENTS OF SOME NICKEL COMPLEXES

Complexes		ν_{max} (kK)				μ_{eff}
Ni(gly)$_2$	(in water)	16.23			27.10	
Ni(β-ala)$_2$	(in water)	16.18			26.67	
Ni(dimen-O)$_3$(ClO$_4$)$_2$	(powder)	16.05			26.74	3.2
Ni(dieen-O)$_3$(ClO$_4$)$_2$		15.92			26.67	3.0
Ni(dimen-O)$_2$(ClO$_4$)$_2$ 1·5H$_2$O		15.27		(24.57)	26.18	3.3
Ni(dimen-O)$_2$(ClO$_4$)$_2$			19.34			0.6
Ni(dieen-O)$_2$(ClO$_4$)$_2$			17.64	21.83		diamag.
Ni(dipen-O)$_2$(ClO$_4$)$_2$			16.95	20.83		diamag.
Ni(dimen)$_2$(ClO$_4$)$_2$				21.60		diamag.
Ni(dipen)$_2$(ClO$_4$)$_2$				20.96		diamag.

β-ala=$NH_2CH_2CH_2COO^-$, dipen=$(C_3H_7)_2NCH_2CH_2NH$

gradually hydrated in the atmosphere to form green complexes. Thus, the conversion of both forms is reversible. The reflectance spectra and the magnetic moments of the former clearly indicate that they are hexa-coordinated ones. Since the latter give the reflectance spectra which show one or two bands in the visible region and no absorption in the near infrared region (800 mμ~1200 mμ), it is evident that they are planar tetra-coordinated complexes. Formation of planar nickel(II) complexes with the ligands expected to form rather ionic bonds with a metal ion should be due to the steric effect of the alkyl groups of the ligand which may hinder coordinating groups from entering the fifth and sixth coordination positions of the tetragonal nickel(II) complex. Measurements of magnetic susceptibility showed that Ni[dimen-O)$_2$](ClO$_4$)$_2$ shows a feeble paramagnetism which could not be eliminated in spite of efforts to purify the complex. Repeated recrystallization and careful dehydration of the sample brought about no magnetic moment smaller than 0.6 B.M. (at room temperature). However, measurements of magnetic susceptibility over the temperature range (300°~77°K) showed that this complex obeys Curie's law.

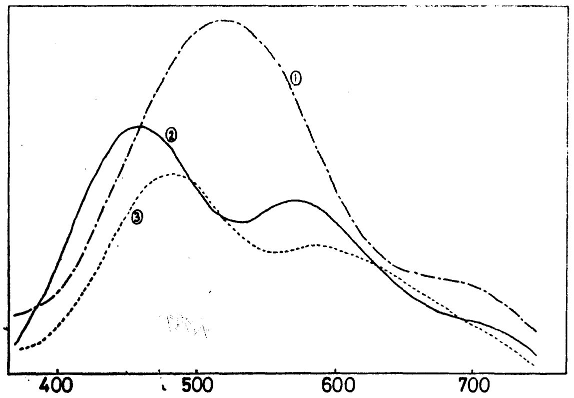

Fig. 1. Refrectance Spectra of ①—— [Ni(dimen-O)$_2$](ClO$_4$)$_2$, ②—— [Ni(dieen-O)$_2$](ClO$_4$)$_2$, and ③---- [Ni(dipen-O)$_2$](ClO$_4$)$_2$.

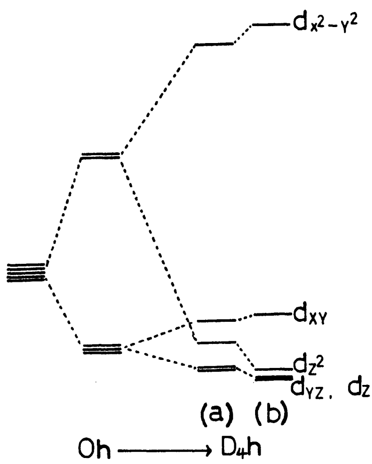

Fig. 2. Assumed energy level splittings of *d*-orbitals for (a) [Ni(dimen-O)$_2$](ClO$_4$)$_2$ and (b) [Ni(dipen-O)$_2$](ClO$_4$)$_2$.

Thus we can conclude that the small paramagnetism is due not to the thermal population of low-lying triplet state as might be anticipated from the energy-level diagram of Maki,[7] but to paramagnetic impurity, probably of the hydrated species. This is consistent with the fact that [Ni(dimen-O)$_2$](ClO$_4$)$_2$ is most easily hydrated among those planar complexes.

It is remarkable that the reflectance spectrum of [Ni(dimen-O)$_2$](ClO$_4$)$_2$ shows one broad band in the visible region, whereas [Ni(dieen-O$_2$](ClO$_4$)$_2$ and [Ni(dipen-O)$_2$](ClO$_4$)$_2$ show two bands in the visible region (Fig. 1). This is explainable in terms of the energy-level diagram[8] given in Fig. 2, granted that the methyl derivatives are less planar than the ethyl and propyl derivatives, i.e., perturbation along the tetragonal axis is somewhat larger in the methyl derivatives.

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[8] Y. Nishida and S. Kida, This Bulletin, **43**, 3814 (1970).