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Synthesis and Magnetism of $M^{II}Cu^{II}_3$-type Tetranuclear Complexes, the Nickel(II) and the Cobalt(II) Complexes with *N,N'*-Bis(aminoalkyl)oxamidatocopper(II)

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Synopsis. Hetero-metal tetranuclear complexes, tris-[*N,N'*-bis(aminoalkyl)oxamidatocopper(II)]cobalt(II) and tris[*N,N'*-bis(aminoalkyl)oxamidatocopper(II)]nickel(II) perchlorate (or nitrate), were synthesized and characterized. Cryomagnetic investigation demonstrated that a considerably strong antiferromagnetic spin-exchange interaction is operating between copper(II) and cobalt(II) or nickel(II) ions.

Use of metal complexes as a ligand is one of the effective methods for synthesizing hetero-metal polynuclear complexes. *N,N'*-Bis(aminoalkyl)oxamidatocopper(II) acts as a bidentate ligand with its two carbonyl oxygens, and binuclear metal complexes bridged by the oxamide group were first prepared by Ojima and Nonoyama.[1] Subnormal magnetic moments of these complexes are indicative of antiferromagnetic spin-exchange interaction operating between the metal ions.[1] However, cryomagnetic investigation of the oxamide-bridged polynuclear complexes has not yet been reported.

We report here the synthesis and magnetic property of the $M^{II}Cu^{II}_3$-type tetranuclear complexes of *N,N'*-bis(aminoalkyl)oxamides, where copper(II) ions lie at the corners of a triangle with a M(II) ion at the center. *N,N'*-Bis(3-aminopropyl)oxamidatocopper(II) (abbreviated as Cu(apoxa)) and *N,N'*-bis(2-aminoethyl)-oxamidatocopper(II) (Cu(aeoxa)) were used as a ligand in this study.

Experimental

Syntheses. Cu(apoxa) and Cu(aeoxa)·$2H_2O$ were prepared by the method of Ojima and Yamada.[2] Syntheses of the tetranuclear complexes are exemplified by $Co[Cu(apoxa)]_3(ClO_4)_2 \cdot 4H_2O$. Cu(aeoxa) (790 mg) and cobalt(II) perchlorate hexahydrate (366 mg) were dissolved in water (20 ml). The purple solution thus obtained was slowly concentrated at a temperature below 30 °C to give purple crystals. They were collected and dried under reduced pressure.

Elemental analyses of the complexes are given in Table 1.

Measurements. IR spectra were measured with a Hitachi IR spectrophotometer Model 215 on a KBr disk. Electronic spectra were measured with a Shimazu Multipurpose spectrophotometer Model MSP-5000 by a reflection on a powder sample. Magnetic susceptibilities were measured by the Faraday method in the temperature range 80—300 K. The apparatus was calibrated using $HgCo(NCS)_4$.[3] Magnetic moments were determined by the expression, $\mu_{eff} = 2.828\,(\chi_M \times T)^{1/2}$.

IR spectra of the tetranuclear complexes exhibit the C=O stretching band at 1590 cm^{-1}, which is practically the same in frequency as that of Cu(apoxa) and Cu(aeoxa)·$2H_2O$. On the other hand, the C=O deformation at 720 cm^{-1} of the ligand complexes[2] disappeared in the spectra of the tetranuclear complexes. This fact may be attributed to the coordination of the carbonyl oxygens to the nickel(II) and the cobalt(II) ions. The bands due to free perchlorate and nitrate ions were found around 1110 and 1380 cm^{-1} respectively.

Visible spectra of the tetranuclear complexes are characterized by a band at 18000 cm^{-1}, which is assigned to a d-d band of the copper(II) ion. The corresponding band of the mononuclear complexes is found near 20000 cm^{-1}. The shift of this band indicates that the ligand field of the $[CuN_4]$-chromophore is weakened when the carbonyl oxygens coordinate to the M(II) ion. The bands at 9000 and 13000 cm^{-1} for $Co[Cu(apoxa)]_3(ClO_4)_2 \cdot 4H_2O$ are assigned to the ${}^4T_{2g} \leftarrow {}^4T_{1g}$ and the ${}^4A_{2g} \leftarrow {}^4T_{1g}$ transitions, respectively, of a cobalt(II) ion under O_h symmetry. The bands at 8500 and 13500 cm^{-1} for the $Ni^{II}Cu^{II}_3$-complexes are assigned to the ${}^3T_{2g} \leftarrow {}^3A_{2g}$ and the ${}^3T_{1g} \leftarrow {}^3A_{2g}$ transitions, respectively, of an octahedral nickel(II) ion. Based on the IR and visible spectral data, we assumed that the complexes possess the structure shown in Fig. 1.

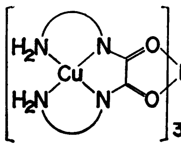

Fig. 1. Structure of complexes.

Magnetic moments of the complexes at room temperature are given in Table 1. Each moment is lower than the value expected for a magnetically non-interacting $Co^{II}Cu^{II}_3$-system (5.85 BM) and $Ni^{II}Cu^{II}_3$-system (4.53 BM), assuming the moments for copper(II), cobalt(II), and nickel(II) ions at 1.85, 4.90, and 3.20 BM, respectively. Furthermore, the moments decrease with lowering of temperature. These

Table 1. Elemental analyses and magnetic moments of complexes

	Found(%)					Calcd(%)					μ_{eff}[a]
	C	H	N	Cu	M	C	H	N	Cu	M	BM
$Co[Cu(apoxa)]_3(ClO_4)_2 \cdot 4H_2O$	25.77	4.69	14.51	17.23	5.40	25.71	5.03	14.99	17.00	5.26	5.11
$Ni[Cu(apoxa)]_3(ClO_4)_2 \cdot 5H_2O$	25.27	5.46	14.68	17.21	5.54	25.31	5.13	14.76	16.74	5.15	4.11
$Ni[Cu(apoxa)]_3(NO_3)_2 \cdot 4H_2O$	27.73	5.01	18.40	18.70	5.54	27.56	5.40	18.74	18.22	5.61	4.21
$Ni[Cu(aeoxa)]_3(ClO_4)_2 \cdot 6H_2O$	20.69	4.29	15.48	17.79	5.63	20.15	4.51	15.67	17.77	5.47	3.49

a) Moment per molecule at room temperature.

facts imply that an antiferromagnetic spin-exchange interaction is operating in the molecules.

The magnetic susceptibility expression for the $M^{II}Cu^{II}{}_3$-system with M(II) ion at the center and copper(II) ions at the corners of a triangle (Fig. 2) was derived by extension of Kambe's approach.[4] The Hamiltonian for this system is given by $\mathscr{H} = -J(S_T{}^2 - S_{123}{}^2)$, where $S_T = S_0 + S_1 + S_2 + S_3$ and $S_{123} = S_1 + S_2 + S_3$. J is the exchange integral between M(II) and copper(II) ions. The states, (S_T, S_{123}; E), formed by the spin-spin coupling for the $Co^{II}Cu^{II}{}_3$-system are as follows: (3, 3/2; $-6J$), 2×(2, 1/2; $-3J$), (2, 3/2; 0), 2×(1, 1/2; J), (1, 3/2; $4J$), and (0, 3/2; $6J$). By applying the Van Vleck equation,[5] the susceptibility expression for this system is given by

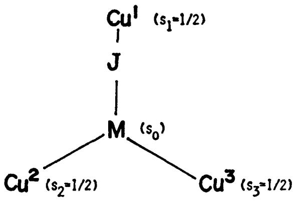

Fig. 2.

$$\chi_M = \frac{2Ng^2\beta^2}{kT} \times \frac{14\exp(6J/kT) + 10\exp(3J/kT) + 5 + 2\exp(-J/kT) + \exp(-4J/kT)}{7\exp(6J/kT) + 10\exp(3J/kT) + 5 + 6\exp(-J/kT) + 3\exp(-4J/kT) + \exp(-6J/kT)} \quad (1)$$

where each symbol has its usual meaning. In the same way the states, (5/2, 3/2; $-5J$), 2×(3/2, 1/2; $-3J$), (3/2, 3/2; 0), 2×(1/2, 1/2; 0), and (1/2, 3/2; $3J$), are formed for the $Ni^{II}Cu^{II}{}_3$-system. The magnetic susceptibility expression for this system is given by

$$\chi_M = \frac{Ng^2\beta^2}{2kT} \times \frac{35\exp(5J/kT) + 20\exp(3J/kT) + 12 + \exp(-3J/kT)}{6\exp(5J/kT) + 8\exp(3J/kT) + 8 + 2\exp(-3J/kT)} + N\alpha. \quad (2)$$

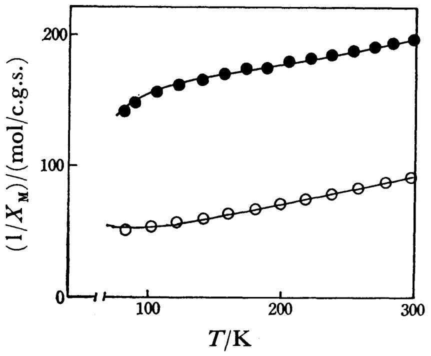

Fig. 3. Temperature variations of inverse magnetic susceptibilities of (○) $Co[Cu(apoxa)]_3(ClO_4)_2 \cdot 4H_2O$ and (●) $Ni[Cu(aeoxa)]_3(ClO_4)_2 \cdot 6H_2O$. Solid lines represent the theoretical values drawn on the basis of the expression (1) with $J = -23$, $g = 2.29$ and $N\alpha = 450 \times 10^{-6}$ (top) and the expression (2) with $J = -75$ cm^{-1}, $g = 2.20$ and $N\alpha = 400 \times 10^{-6}$ c.g.s./mol (bottom).

Magnetic susceptibilities of $Co[Cu(apoxa)]_3(ClO_4)_2 \cdot 4H_2O$ and $Ni[Cu(aeoxa)]_3(ClO_4)_2 \cdot 6H_2O$ were well interpreted in terms of the expressions (1) and (2), respectively. The best fits between the experimental and the theoretical inverse susceptibilities are shown in Fig. 3. Magnetisms of $Ni[Cu(apoxa)]_3(ClO_4)_2 \cdot 5H_2O$ and $Ni[Cu(apoxa)]_3(NO_3)_2 \cdot 4H_2O$ also obeyed the expression (2). The magnetic parameters determined are as follows. $Ni[Cu(apoxa)]_3(ClO_4)_2 \cdot 5H_2O$: $-J = 42$, $g = 2.49$, and $N\alpha = 400 \times 10^{-6}$; $Ni[Cu(apoxa)]_3(NO_3)_2 \cdot 4H_2O$: $-J = 49$ cm^{-1}, $g = 2.40$, and $N\alpha = 400 \times 10^{-6}$ c.g.s./mol. However, the g values of these complexes are large compared with 2.20 of $Ni[Cu(aeoxa)]_3(ClO_4)_2 \cdot 6H_2O$. This would be indicative of the presence of paramagnetic impurity such as hexaaquanickel(II) ion. If this is taken into consideration, the $-J$ values for these complexes might exceed the values obtained above. Thus, we may conclude that a considerably strong antiferromagnetic spin-exchange interaction operates between the copper(II) and M(II) ions through the oxamidebridge.

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