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Synthesis and Magnetisms of Oxamido- and Oxamato-Bridged Binuclear Nickel(II)-Copper(II) Complexes

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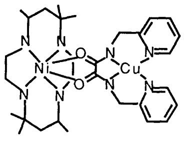
Synopsis. Oxamido- and oxamato-bridged binuclear nickel(II)–copper(II) complexes $[\mathrm{CuL^1Ni(Me_6[14]aneN_4)}](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$ (**1**), $[\mathrm{CuL^2Ni(Me_6[14]aneN_4)}]\mathrm{ClO_4}$ (**2**), and $[\mathrm{CuL^3Ni(Me_6[14]aneN_4)}]\mathrm{ClO_4}$ (**3**) have been synthesized and characterized, where $\mathrm{Me_6[14]aneN_4}$=*rac*-(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, $\mathrm{H_2L^1}$=*N,N'*-bis(2-pyridylmethyl)oxamide, $\mathrm{H_3L^2}$=*N*-methyl-*N'*-(4-methyl-6-oxo-3-azahept-4-enyl)oxamide, $\mathrm{H_3L^3}$=*N*-(4-methyl-6-oxo-3-azahept-4-enyl)oxamic acid. The cryomagnetic susceptibilities (4.2—300 K) were well reproduced by the equation derived from $H=-2JS_{\mathrm{Ni}}\cdot S_{\mathrm{Cu}}$ ($S_{\mathrm{Ni}}=1$, $S_{\mathrm{Cu}}=1/2$) with the J values $-78.2\ \mathrm{cm^{-1}}$, $-64.5\ \mathrm{cm^{-1}}$, and $-72.8\ \mathrm{cm^{-1}}$ for (**1**), (**2**), and (**3**), respectively.

Hetero-metal polynuclear complexes are of current interest to see the magnetic spin-exchange mechanism between metal ions[1] and to gain an insight into the active sites of some multimetalloenzymes.[2] Two synthetic strategies for hetero-metal polynuclear complexes have been developed; (1) the use of a "binucleating ligand" exhibiting inequivalent coordination sites with respect to the ligand field or the stereochemistry[3] and (2) the use of a "ligand complex" involving coordination ability to other metal ions.[4] The latter method has advantage toward synthesis of hetero-metal complexes with systematic combination of metal ions. In this study we used three copper(II) complexes capable of acting as bidentate chelating ligand $[\mathrm{CuL^1}]$,[5] $\mathrm{Na[CuL^2]}$,[6] and $\mathrm{Na[CuL^3(H_2O)]}$[6] to synthesize three binuclear nickel(II)–copper(II) complexes $[\mathrm{CuL^1Ni(Me_6[14]aneN_4)}](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$ (**1**), $[\mathrm{CuL^2Ni(Me_6[14]aneN_4)}]\mathrm{ClO_4}$ (**2**), and $[\mathrm{CuL^3Ni(Me_6[14]aneN_4)}]\mathrm{ClO_4}$ (**3**), respectively, where $\mathrm{Me_6[14]aneN_4}$=*rac*-(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, $\mathrm{H_2L^1}$=*N,N'*-bis(2-pyridylmethyl)oxamide, $\mathrm{H_3L^2}$=*N*-methyl-*N'*-(4-methyl-6-oxo-3-azahept-4-enyl)oxamide, $\mathrm{H_3L^3}$=*N*-(4-methyl-6-oxo-3-azahept-4-enyl)oxamic acid. This paper deals with the synthesis and magnetic property of the nickel(II)–copper(II) complexes.



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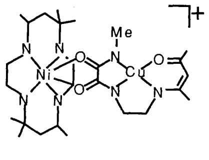

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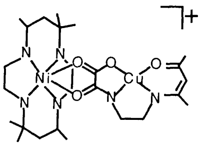


3

Experimental

Synthesis. The component complexes $[\mathrm{Ni(Me_6[14]aneN_4)}](\mathrm{ClO_4})_2$,[7] $[\mathrm{CuL^1}]$,[5] $\mathrm{Na[CuL^2]}$,[6] and $\mathrm{Na[CuL^3(H_2O)]}$[6] were prepared according to the methods of literatures.

$[\mathrm{CuL^1Ni(Me_6[14]aneN_4)}](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$ (1). To a solution of $[\mathrm{CuL^1}]$ (0.4 mmol) in 15 $\mathrm{cm^3}$ of acetonitrile was added an aqueous solution (10 $\mathrm{cm^3}$) of $[\mathrm{Ni(Me_6[14]aneN_4)}](\mathrm{ClO_4})_2$ (0.4 mmol). The resulting solution was gently warmed for 10 min on a water bath and filtered. The filtrate was cooled to room temperature and kept for several hours to form reddish brown precipitates, which were collected by suction filtration, washed successively with water and diethyl ether, and dried in vacuo. Found: C, 40.05; H, 5.63; N, 12.39; Ni, 6.50; Cu, 7.06 %. Calcd for $\mathrm{C_{30}H_{52}N_8O_{11}Cl_2NiCu}$: C, 40.31; H, 5.86; N, 12.54; Ni, 6.57; Cu, 7.11 %. Λ_{M} 252 S $\mathrm{mol^{-1}\ cm^2}$ in $\mathrm{CH_3CN}$.

$[\mathrm{CuL^2Ni(Me_6[14]aneN_4)}]\mathrm{ClO_4}$ (2). To a methanolic solution (20 $\mathrm{cm^3}$) of $\mathrm{Na[CuL^2]}$ (1 mmol) was added an aqueous solution (20 $\mathrm{cm^3}$) of $[\mathrm{Ni(Me_6[14]aneN_4)}](\mathrm{ClO_4})_2$ (1 mmol) to give immediately pink microcrystalline precipitates. They were collected by suction filtration, washed successively with water and diethyl ether, and dried in vacuo. Found: C, 42.63; H, 6.84; N, 13.37; Ni, 7.72; Cu, 8.27 %. Calcd for $\mathrm{C_{26}H_{50}N_7O_7ClNiCu}$: C, 42.76; H, 6.90; N, 13.42; Ni, 8.03; Cu, 8.70%. Λ_{M} 130 S $\mathrm{mol^{-1}\ cm^2}$ in $\mathrm{CH_3CN}$.

$[\mathrm{CuL^3Ni(Me_6[14]aneN_4)}]\mathrm{ClO_4}$ (3). To an aqueous solution (30 $\mathrm{cm^3}$) of $\mathrm{Na[CuL^3(H_2O)]}$ (1 mmol) was added an aqueous solution (20 $\mathrm{cm^3}$) of $[\mathrm{Ni(Me_6[14]aneN_4)}](\mathrm{ClO_4})_2$ (1 mmo) to give purple microcrystalline precipitates. They were collected by suction filtration, washed with water and diethyl ether, and dried in vacuo. Found: C, 41.80; H, 6.54; N, 11.70; Ni, 7.72; Cu, 8.63 %. Calcd for $\mathrm{C_{25}H_{47}N_6O_8ClNiCu}$: C, 41.86; H, 6.60; N, 11.72; Ni, 8.18; Cu, 8.86. Λ_{M} 130 S $\mathrm{mol^{-1}\ cm^2}$ in $\mathrm{CH_3CN}$.

Physical Measurements. Elemental analyses of C, H, and N were obtained at the Elemental Analysis Service Center of Kyushu University. Analyses for Ni and Cu were carried out on a Shimadzu Atomic Absorption/Flame Emission Spectrophotometer Model AA-680. Infrared spectra were recorded on a JASCO IR-810 Spectrophotometer on KBr disks. Electrical conductivity measurements were carried out on a Denki Kagaku Keiki AOL-10 conductivity meter in ca. $1\times10^{-3}\ \mathrm{mol\ dm^{-3}}$ acetonitrile solutions. Magnetic susceptibilities were obtained with a HOXAN HSM-D SQUID magnetometer in the temperature range 4.2—100 K and with a Faraday balance in the temperature range 80—300 K. Data were corrected for magnetization of the sample holder and for the diamagnetism of the component atoms by the use of Pascal's constants. Effective magnetic moment was calculated by the equation $\mu_{\mathrm{eff}}=2.828(\chi_{\mathrm{M}}T)^{1/2}$.

Results and Discussion

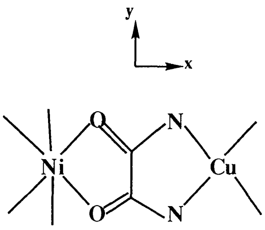
Copper(II) complexes $[\mathrm{CuL^1}]$, $\mathrm{Na[CuL^2]}$, and $\mathrm{Na[CuL^3(H_2O)]}$ acting as bidentate chelating ligands react with $[\mathrm{Ni(Me_6[14]aneN_4)}](\mathrm{ClO_4})_2$ to form binuclear copper(II)–nickel(II) complexes **1**, **2**, and **3**, respectively. The elemental analyses are consistent with the 1 : 1 formulation of Ni and Cu. The molar conductance of **1** falls in the expected range for 1 : 2 electrolytes and those of **2** and **3** in the 1 : 1 electrolytes.[8] The magnetic behavior of **1** is exemplified in detail, since the magnetic behavior of **1**—**3** are similar to each other. The numerical data of the magnetic susceptibility measurements are deposited as Document No. 9013 (Table S1, S2, S3) at the Office of the

Editor of Bull. Chem. Soc. Jpn. The temperature dependences of the magnetic susceptibilities per molecule χ_M and the effective magnetic moments μ_{eff} of **1** are shown in Fig. 1. The magnetic moment at room temperature is 2.98 μ_B, which is smaller than the spin-only value (3.31 μ_B) of Ni(II)-Cu(II) system ($S_{Ni}=1$, $S_{Cu}=1/2$) in the absence of magnetic interaction ($\mu_{eff}^2=\mu_{Ni}^2+\mu_{Cu}^2$). Upon lowering the temperature, the magnetic moment decreases gradually from 2.98 μ_B at 290 K and reaches a plateau of 1.78 μ_B at 34—4.3 K. The plateau value agrees with the spin-only value of $S=1/2$ (1.73 μ_B), indicating that the spins on the Ni(II) and Cu(II) ions are antiferromagnetically coupled. The temperature dependence of the magnetic susceptibilities was analyzed on the basis of the isotropic spin-Hamiltonian $H=-2JS_{Ni}\cdot S_{Cu}$ ($S_{Ni}=1$, $S_{Cu}=1/2$). The magnetic susceptibility expression is given in Eq. 1, where temperature-independent paramagnetism $N\alpha$ is fixed at 280×10^{-6} cm^3 mol^{-1}.

$$\chi_M = \frac{Ng^2\beta^2}{4kT}\,\frac{10+\exp(3J/kT)}{2+\exp(3J/kT)} + N\alpha \qquad (1)$$

The magnetic data were well reproduced by the fitting parameters $g=2.06$ and $J=-78.2$ cm^{-1}, in which the disagreement factor defined as $R=[\Sigma[\mu_{eff}(\text{obsd})-\mu_{eff}(\text{calcd})]^2/\Sigma\mu_{eff}(\text{obsd})^2]^{1/2}$ is 8.9×10^{-3}. The theoretical μ_{eff} vs. T curve using the fitting parameters is represented as a solid line in Fig. 1. Similarly, the temperature-dependences of magnetic moments of **2** and **3** were well simulated by the Eq. 1 and the best-fit parameters are $g=2.11$ and $J=-64.5$ cm^{-1}, and $R=1.4\times10^{-2}$ for **2**, and $g=2.11$, $J=-72.8$ cm^{-1}, and $R=1.5\times10^{-2}$ for **3**.

The magnetic exchange integrals for **1**—**3** indicate that an antiferromagnetic interaction operates between the Ni(II) and Cu(II) ions through an oxamato or oximate bridge. Adopting similar discussion by Kahn et. al,[1] the magnetic property can be explained in terms of the nature of the magnetic orbitals.[1,3] If the whole molecule is considered to assume C_{2v} symmetry as the first approximation, the 3d orbitals transform as $a_1(d_z{}^2)$, $a_1(d_{x^2-y^2})$, $a_2(d_{yz})$, $b_1(d_{xy})$, and $b_2(d_{xz})$, where the molecular axes are taken as shown in the figure. One unpaired electron of the Cu(II) ion occupies the $b_1(d_{xy})$ orbital and two unpaired electrons of the Ni(II) ion occupy $a_1(d_{z^2})$ and $b_1(d_{xy})$ orbitals. Because there is no orthogonality of the magnetic orbitals between the Cu(II) and Ni(II) ions, an antiferromagnetic interaction between the two ions should be observed.



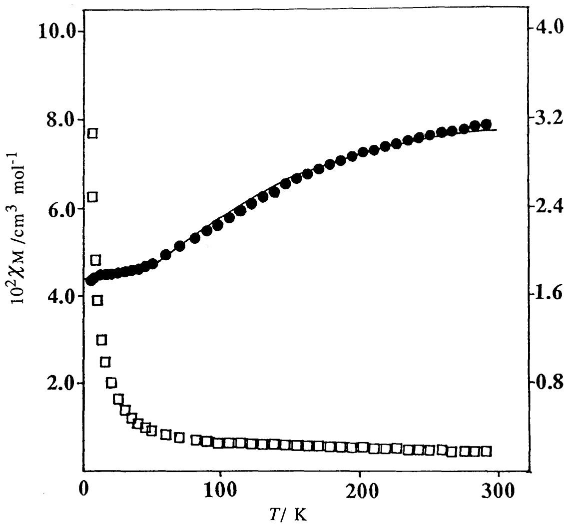


Fig. 1. Plots of the temperature dependence of the molar magnetic susceptibility χ_M (□) and the effective magnetic moment μ_{eff} (●) for [CuL^{1}Ni(Me$_6$[14]aneN$_4$)] (**1**), where the solid line of μ_{eff} vs. T plot represents the theoretical curve of Eq. 1 with the parameters of $g=2.06$ and $J=-78.2$ cm^{-1}.

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