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Synthesis and Characterization of Imidazolate-Bridged Binuclear Copper(II) Complexes

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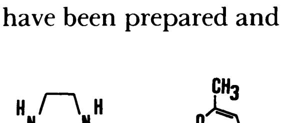
Synopsis. An unsymmetrical quadridentate copper(II) complex containing an imidazole moiety ([CuHL](ClO_4)) reacts with [1,4,7,10-tetraazacyclododecane]copper(II) perchlorate and [2-[2-(2-pyridyl)ethyliminomethyl]pyridine]-copper(II) perchlorate in the presence of one equivalent of triethylamine to give two discrete imidazolate-bridged binuclear copper(II) complexes, **1** and **2** respectively, where [H_2L] denotes the 1:1:1 condensation product of acetylacetone, ethylenediamine, and 4-formylimidazole. The analysis of the cryomagnetic data(ca. 80—300 K) on the basis of the Heisenberg model of a binuclear structure gave the antiferromagnetic interaction parameter($2J$) of -107.7 cm^{-1} for **2**.

Discrete imidazolate-bridged metal complexes are of current interest, since an imidazolate-bridged copper(II)-zinc(II) center has been discovered in bovine erythrocyte superoxide dismutase (BESOD).[1] An X-ray crystallographic study of BESOD has indicated that the copper(II) and zinc(II) ions exist in distorted square planar and tetrahedral coordination environment respectively.[2] A number of imidazolate-bridged binuclear copper(II) complexes have been synthesized and characterized.[3] However, in most cases the two coordination spheres for the complexes are identical.

In this study, two imidazolate-bridged binuclear copper(II) complexes, **1** and **2**, in which the two coordination spheres of copper(II) ions are not identical, as is shown by the schemetic structures, have been prepared and characterized.



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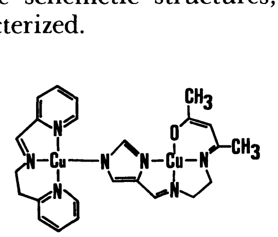

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Experimental

Physical Measurements. The elemental analyses were performed by Mr. Shinichi Miyazaki at the Technical Service Center of Kumamoto University. The melting points were measured on a Yanagimoto micromelting points apparatus and were uncorrected. The electrical conductivity measurements were carried out on a Denki Kagaku AOC-10 conductometer on ca. 10^{-3} mol dm^{-3} solutions in methanol. The thermogravimetric analyses (TGA) were carried out on a Shimadzu TGC 20-type microthermobalance at the heating rate of 5 °C min^{-1}, using a ca. 10 mg sample for each run. The magnetic susceptibilities were obtained by the Faraday method from the temperature of liquid nitrogen to the ambient temperature, according to the procedure reported previously.[4] The susceptibilities were corrected for the diamagnetism of the component atoms by the use of Pascal's constants.

Syntheses. The copper(II) complex containing an imidazole moiety ([CuHL](ClO_4)) was prepared according to the method reported previously,[5] where [H_2L] denotes the unsymmetrical quadridentate Schiff-base ligand derived from acetylacetone, ethylenediamine, and 4-formylimidazole with a mole ratio of 1:1:1. [1,4,7,10-Tetraazacyclododecane]copper(II) perchlorate and [2-[2-(2-pyridyl)ethyliminomethyl]pyridine]copper(II) perchlorate hydrate were prepared by the method of the literature,[6,7] where the complexes are abbreviated as Cu[12]aneN$_4$(ClO_4)$_2$ and Cu(pip)(ClO_4)$_2\cdot H_2O$ respectively.

[CuLCu[12]aneN$_4$](ClO_4)$_2\cdot$2.5H_2O 1. To a solution of [CuHL](ClO_4) (0.764 g, 2 mmol) in 30 cm^3 of 99% methanol was added a solution of triethylamine (0.202 g, 2 mmol) in 20 cm^3 of methanol. To the solution was added dropwise a solution of Cu[12]aneN$_4$(ClO_4)$_2$ (0.868 g, 2 mmol) in 20 cm^3 of methanol. The mixture was warmed at 50 °C for 30 min, after which the solution volume was reduced to one half. The solution was then kept for several days in a refrigerator. During that time, black prisms precipitated. They were collected by suction filtration, washed with methanol, and dried in vacuo. Attempts at recrystallization were unsuccessful. Found: C, 29.75; H, 5.24; N, 14.48%. Calcd for $Cu_2Cl_2O_9N_8C_{19}H_{34}\cdot 2.5H_2O$: C, 29.97; H, 5.16; N, 14.71%. Mp 225 °C(decomp), Λ_M 166.0 S mol^{-1} cm^2(MeOH), TGA, mass loss: 5.85 wt%; Calcd for 2.5H_2O: 5.91 wt%.

[CuLCu(pip)](ClO_4)$_2\cdot$0.5H_2O 2. This complex was prepared by a similar method except that Cu(pip)(ClO_4)$_2\cdot H_2O$ instead of Cu[12]aneN$_4$(ClO_4)$_2$ was used. Blue-green microcrystalline material. Attempts at recrystallization were unsuccessful. Found: C, 37.60; H, 3.63; N, 12.78%. Calcd for $Cu_2Cl_2O_9N_7C_{24}H_{27}\cdot 0.5H_2O$: C, 37.71; H, 3.69; N, 12.84%. Mp 260 °C(decomp), Λ_M 174.1 S mol^{-1} cm^2(MeOH), TGA: mass loss, 1.15 wt%; Calcd for 0.5H_2O: 1.18 wt%.

Results and Discussion

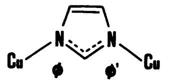
The complex containing an imidazole moiety [CuHL]$^+$ reacts with [1,4,7,10-tetraazacyclododecane]-copper(II) and [2-[2-(2-pyridyl)ethyliminomethyl]pyridine]copper(II) in the presence of one equivalent of triethylamine to give the imidazolate-bridged binuclear copper(II) complexes, **1** and **2** respectively. The complexes crystallize as hydrates. The solvent molecules in the crystals were detected by TGA, where weight losses corresponding to those to be expected from the elemental analyses were observed. The molar electrical conductances of Complexes **1** and **2** are 166.0 and 174.1 S mol^{-1} cm^2 in methanol respectively. These values are in the expected range of the 2:1 electrolyte in methanol (160—220 S mol^{-1} cm^2),[8] indicating that Complexes **1** and **2** have the formulas of $[CuLCu[12]aneN_4]^{2+}(ClO_4^-)_2$ and $[CuLCu(pip)]^{2+}(ClO_4^-)_2$ respectively.

The χ_A vs. T plots for Complexes **1** and **2** are shown in Fig. 1. The maximum in the χ_A vs. T plot of **1** is not observed in the temperature range studied(ca. 80—300 K), indicating that the magnetic interaction parameter ($|2J|$) is less than 89.5 cm^{-1} when obtained by means of the equation $|2J|=1.61\ kT_{\max}$, where $T_{\max}$ is the temperature with the maximum magnetic susceptibility. The maximum at ca. 100 K in the plot of **2** is indicative of antiferromagnetic intramolecular exchange interaction. The magnetic susceptibility data of **2** were analyzed by means of a least-squares method using the SALS program,[9] in which the g and J values were refined as variable parameters on the basis of the Bleaney-Bowers Eq. 1 for isotropic exchange in a copper(II) dimer:

$$\chi_A = \frac{Ng^2\beta^2}{kT}\left[\frac{1}{3+\exp(-2J/kT)}\right] + N\alpha \qquad (1)$$

The temperature-independent paramagnetism($N\alpha$) was taken to be 60×10^{-6}, while the other symbols have their usual meanings. The best-fit values are $g=2.104$ and $2J=-107.7$ cm^{-1}, where the generalized R factor, $R=[\sum[\chi_A(\text{obsd})-\chi_A(\text{calcd})]^2/\sum\chi_A(\text{obsd})^2]^{1/2}$, using as a convenient statistical indicator of the quality of the least-squares fits, was calculated to be 0.005. In Fig. 1, theoretical curve with the parameters of g and J obtained is shown as a solid line.

Lippard and his co-workers pointed out that the magnitude of the exchange interaction parameter($2J$) for the imidazolate-bridged copper(II) complexes depends on the angles, ϕ and ϕ', defined in the drawing: i.e., increasing the ϕ and ϕ' angles leads to an increase in $|J|$.[3a)] The X-ray analysis of



[CuHL](ClO$_4$) revealed the ϕ angle to be 143.1(1)°.[5] For the μ-Im$[Cu(pip)]_2(NO_3)_3\cdot2.5H_2O$ complex, it was reported to have the ϕ angle of 120—128° and $2J=-53.8$ cm^{-1}.[3a)] The larger $2J$ value of $[CuLCu(pip)](ClO_4)_2\cdot0.5H_2O$ **2** than that of μ-Im$[Cu(pip)]_2(NO_3)_3\cdot2.5H_2O$ is reasonable judging from the angles of ϕ and ϕ'.

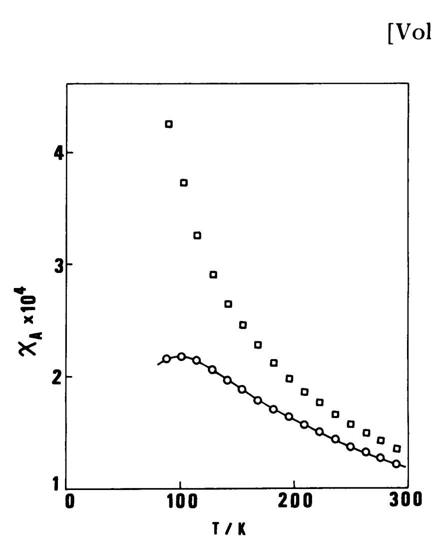


Fig. 1. Plots of χ_A vs. T for the binuclear copper(II) complexes **1** (□) and **2** (○), where the solid line represents the theoretical curve of Eq. 1 with the parameters of $g=2.104$, $2J=-107.7$ cm^{-1} for **2**.

References

1) J. A. Fee, *Biochim. Biophys. Acta*, **295**, 107 (1973).

2) J. S. Richardson, K. A. Thomas, B. H. Rubin, and D. C. Richardson, *Proc. Natl. Acad. Sci. U. S. A.*, **72**, 1349 (1975).

3) a) G. Kolks, S. J. Lippard, J. V. Waszczak, and H. R. Lilienthal, *J. Am. Chem. Soc.*, **104**, 717 (1982) and the references cited therein; b) M. Suzuki, I. Ueda, H. Kanatomi, and I. Murase, *Bull. Chem. Soc. Jpn.*, **56**, 3421 (1983) and the references cited therein.

4) M. Mikuriya, H. Okawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **54**, 2943 (1983).

5) N. Matsumoto, H. Murakami, T. Akui, J. Honbo, H. Okawa, and A. Ohyoshi, to be submitted for publication.

6) E. K. Barefield and F. Wagner, *Inorg. Chem.*, **12**, 2435 (1973).

7) G. Kolks, C. R. Frihart, P. K. Coughlin, and S. J. Lippard, *Inorg. Chem.*, **20**, 2933 (1981).

8) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).

9) T. Nakagawa and Y. Oyanagi, "Saishojijoho Niyoru Jikkendeta Kaiseki," The University of Tokyo Press (1982).