2586 © 1994 The Chemical Society of Japan NOTES *Bull. Chem. Soc. Jpn.*, **67**, 2586—2589(1994) [Vol. 67, No. 9

Synthesis and Properties of Dinuclear Copper(II) Complexes Containing Dinucleating Ligands with Imidazole Nitrogen and Two Exogenous Bridging Ligands

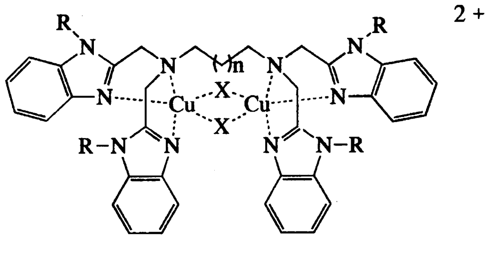
Yasuo Nakao,* Makoto Oonishi, Tomoko Uzu, Hiroko Kashihara, Shinnichiro Suzuki,†
Masahiro Sakai,†† and Yutaka Fukuda††
Chemical Laboratory, Faculty of Education, Okayama University, Okayama 700
† College of General Education, Osaka University, Osaka 560
†† Institute for Molecular Science, Myodaiji, Okazaki 444

(Received April 20, 1994)

Synopsis. Dinuclear copper(II) complexes, $[Cu_2(nR)X_2](ClO_4)_2$ ($X=N_3^-$, NCS^-, and OAc^-) have been synthesized and characterized, where nR=*N*,*N*,*N′*,*N′*-tetrakis[(1-methyl-2-benzimidazolyl)methyl]-1,3-diaminopropane (3Me), *N*,*N*,*N′*,*N′*-tetrakis[(1-ethyl-2-benzimidazolyl)methyl]-1,3-diaminopropane (3Et), *N*,*N*,*N′*,*N′*-tetrakis[(1-methyl-2-benzimidazolyl)methyl]-1,4-diaminobutane (4Me), and *N*,*N*,*N′*,*N′*-tetrakis[(1-ethyl-2-benzimidazolyl)methyl]-1,4-diaminobutane (4Et). Although a weak antiferromagnetic interactions were found for $[Cu_2(3Me)(NCS)_2](ClO_4)_2\cdot 3H_2O$ (coupling constant $J=-2.1$ cm^{-1}, $H=-2JS_1\cdot S_2$) and $[Cu_2(3Me)(OAc)_2](ClO_4)_2\cdot H_2O$ ($J=-2.0$ cm^{-1}), no exchange interaction has been observed to 4.2 K for $[Cu_2(3Me)(N_3)_2](ClO_4)_2\cdot H_2O$. The Electrochemistry of these complexes in *N*,*N*-dimethylformamide showed two electron reductions at +210—−30 mV vs. Ag–AgCl (Cu^{2+}–$Cu^{2+}\rightarrow Cu^+$–Cu^+).

The histidine imidazole group is one of the most important binding sites for many copper-containing proteins. For example, the copper ions in hemocyanin and ascorbate oxidase are coordinated to two or three histidyl-imidazole moieties. A large number of dinuclear copper(I) and copper(II) complexes with chelating ligands containing imidazole groups have been reported so far as models for these copper proteins.[1—6] Among others, the sexadentate benzimidazole-containing ligands (L), such as *N*,*N*,*N′*,*N′*-tetrakis[(2-benzimidazolyl)methyl]-1,2-diaminoethane, give dinuclear copper(II) complexes having the general formula $Cu_2(L)(anion)_4$.[2,3] Some dinuclear copper(I) complexes of the ligands (L) react semireversively with oxygen in solution to give copper(II)-peroxide species.[1]

In this study we synthesized a series of copper(II) complexes **1**—**12** (structural formula **I** in Chart 1) containing *N*,*N*,*N′*,*N′*-tetrakis[(1-methyl-2-benzimidazolyl)methyl]-1,3-diaminopropane (3Me), *N*,*N*,*N′*,*N′*-tetrakis[(1-ethyl-2-benzimidazolyl)methyl]-1,3-diaminopropane (3Et), *N*,*N*,*N′*,*N′*-tetrakis[(1-methyl-2-benzimidazolyl)methyl]-1,4-diaminobutane (4Me), or *N*,*N*,*N′*,*N′*-tetrakis[(1-ethyl-2-benzimidazolyl)methyl]-1,4-diaminobutane (4Et) and two exogenous bridging ligands. The magnetic, infrared and visible absorption spectral, and electrochemical properties of these copper(II) complexes are described and compared with those of the dinuclear copper(II) mixed ligand complexes composed of *N*,*N*,*N′*,*N′*-tetrakis[(1-methyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane (HL-Me) or *N*,*N*,*N′*,*N′*-tetrakis[(1-ethyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane (HL-Et) and a small ligand, such as azide ion.[4,5)]



n = 1 , 2

R = Me , Et

X = N_3^- , NCS^- , OAc^-

Chart 1. Structural formula **I**.

Experimental

Synthesis of Ligands. *N*,*N*,*N′*,*N′*-Tetrakis[(2-benzimidazolyl)methyl]-1,3-diaminopropane and *N*,*N*,*N′*,*N′*-Tetrakis[(2-benzimidazolyl)methyl]-1,4-diaminobutane. These compounds were prepared from 1,2-diaminobenzene and 1,3-diaminopropanetetraacetic acid or 1,4-diaminobutanetetraacetic acid by the reported procedure.[1,3]

***N*,*N*,*N′*,*N′*-Tetrakis[(1-methyl-2-benzimidazolyl)methyl]-1,3-diaminopropane (3Me) and *N*,*N*,*N′*,*N′*-Tetrakis[(1-methyl-2-benzimidazolyl)methyl]-1,4-diaminobutane (4Me).** Ten mmoles of *N*,*N*,*N′*,*N′*-tetrakis[(2-benzimidazolyl)methyl]-1,3-diaminopropane or *N*,*N*,*N′*,*N′*-tetrakis[(2-benzimidazolyl)methyl]-1,4-diaminobutane were suspended in dry tetrahydrofuran (150 cm^3) under an argon atmosphere. To this solution was added sodium (0.92 g, 40 mmol) and stirred for about 3 h at 60 °C. Methyl iodide (9.9 g, 70 mmol) was added, and the reaction mixture was left stirring for 1 d at 40 °C. After removal of the solvent to dryness under reduced pressure, the resulting powder was washed with water. Recrystallization from methanol containing charcoal gave 3Me and 4Me. Yield 76% for 3Me and 89% for 4Me.

3Me: ^{1}H NMR (100 MHz, $CDCl_3$) $\delta=1.3$—1.7 (2H, m), 2.60 (4H, t), 3.20 (12H, s), 3.78 (8H, s), 7.0—7.6 (16H, m). Found: C, 71.32; H, 6.49; N, 21.37%. Calcd for $C_{39}H_{42}N_{10}\cdot 0.5H_2O$: C, 70.99; H, 6.57; N, 21.23%.

4Me: Found: C, 67.41; H, 6.77; N, 19.99%. Calcd for $C_{40}H_{44}N_{10}\cdot 2.5H_2O$: C, 67.63; H, 6.96; N, 19.93%.

***N,N,N′,N′*-Tetrakis[(1-ethyl-2-benzimidazolyl)methyl]-1,3-diaminopropane (3Et) and *N,N,N′,N′*-Tetrakis[(1-ethyl-2-benzimidazolyl)methyl]-1,4-diaminobutane (4Et).** These compounds were also synthesized using the same method as that for 3Me and 4Me using ethyl iodide. Yield 90% for 3Et and 81% for 4Et.

3Et: ^{1}H NMR (100 MHz, $CDCl_3$) δ=1.04 (12H, t), 1.64 (2H, m), 2.66 (4H, t), 3.6—4.0 (8H, q and 8H, s), 7.0—7.7 (16H, m). Found: C, 72.12; H, 7.25; N, 19.49%. Calcd for $C_{43}H_{50}N_{10}\cdot 0.5H_2O$: C, 72.12; H, 7.19; N, 19.57%.

4Et: ^{1}H NMR (200 MHz, $CDCl_3$–CD_3OD) δ=0.80 (12H, t), 1.15—1.35 (4H, m), 2.28—2.49 (4H, m), 3.5—3.7 (8H, q and 8H, s), 7.0—7.5 (16H, m). Found: C, 71.34; H, 7.40; N, 19.17%. Calcd for $C_{44}H_{52}N_{10}\cdot H_2O$: C, 71.50; H, 7.38; N, 18.96%.

Preparation of Copper(II) Complexes. $[Cu_2(3\text{-}Me)(N_3)_2](ClO_4)_2\cdot H_2O$ (1). To a methanol solution (30 cm^3) of 3Me (0.651 g, 1.0 mmol) were successively added each methanol solution (5 cm^3) of copper(II) perchlorate hexahydrate (0.741 g, 2.0 mmol) and sodium azide (0.130 g, 2.0 mmol). After it had been stirred at room temperature for 1 d, green-brown products were collected by filtration and washed with methanol. This was recrystallized from acetone. Found: C, 43.83; H, 4.00; N, 20.17%. Calcd for $[Cu_2(C_{39}H_{42}N_{10})(N_3)_2](ClO_4)_2\cdot H_2O$: C, 43.41; H, 4.12; N, 20.78%.

$[Cu_2(3Et)(N_3)_2](ClO_4)_2\cdot 2H_2O$ (2), $[Cu_2(4Me)(N_3)_2](ClO_4)_2\cdot 2H_2O$ (3), and $[Cu_2(4\text{-}Et)(N_3)_2](ClO_4)_2\cdot 3H_2O$ (4). These complexes were also prepared in the same way as that for $[Cu_2(3Me)(N_3)_2](ClO_4)_2\cdot H_2O$ (1).

2: Found: C, 44.84; H, 4.46; N, 19.44%. Calcd for $[Cu_2(C_{43}H_{50}N_{10})(N_3)_2](ClO_4)_2\cdot 2H_2O$: C, 44.78; H, 4.72; N, 19.43%.

3: Found: C, 43.40; H, 4.14; N, 20.34%. Calcd for $[Cu_2(C_{40}H_{44}N_{10})(N_3)_2](ClO_4)_2\cdot 2H_2O$: C, 43.24; H, 4.36; N, 20.18%.

4: Found: C, 44.32; H, 4.59; N,18.73%. Calcd for $[Cu_2(C_{44}H_{52}N_{10})(N_3)_2](ClO_4)_2\cdot 3H_2O$: C, 44.59; H, 4.94; N, 18.91%.

$[Cu_2(3Me)(NCS)_2](ClO_4)_2\cdot 3H_2O$ (5), $[Cu_2(3Et)(NCS)_2](ClO_4)_2\cdot 2.5H_2O$ (6), $[Cu_2(4\text{-}Me)(NCS)_2](ClO_4)_2\cdot H_2O$ (7), and $[Cu_2(4Et)(NCS)_2](ClO_4)_2\cdot 2H_2O$ (8). These were prepared in the same method to the corresponding complex with N_3^- using sodium thiocyanate (0.161 g, 2.0 mmol).

5: Found: C, 43.39; H, 4.27; N, 14.01%. Calcd for $[Cu_2(C_{39}H_{42}N_{10})(NCS)_2](ClO_4)_2\cdot 3H_2O$: C, 42.93; H, 4.23; N, 14.66%.

6: Found: C, 45.18; H, 4.48; N, 14.22%. Calcd for $[Cu_2(C_{43}H_{50}N_{10})(NCS)_2](ClO_4)_2\cdot 2.5H_2O$: C, 45.25; H, 4.65; N, 14.08%.

7: C, 45.59; H, 4.08; N, 15.40%. Calcd for $[Cu_2(C_{40}H_{44}N_{10})(NCS)_2](ClO_4)_2\cdot H_2O$: C, 45.56; H, 4.01; N, 15.19%.

8: C, 45.98; H, 4.57; N, 13.80%. Calcd for $[Cu_2(C_{44}H_{52}N_{10})(NCS)_2](ClO_4)_2\cdot 2H_2O$: C, 46.07; H, 4.72; N, 14.02%.

$[Cu_2(3Me)(OAc)_2](ClO_4)_2\cdot H_2O$ (9), $[Cu_2(3Et)(OAc)_2](ClO_4)_2\cdot 2H_2O$ (10), $[Cu_2(4Me)(OAc)_2](ClO_4)_2$ (11), and $[Cu_2(4Et)(OAc)_2](ClO_4)_2$ (12). These complexes were also prepared in the same way as complex **1** using sodium acetate trihydrate (0.272 g, 2.0 mmol).

9: Found: C, 46.47; H, 4.34; N, 12.68%. Calcd for $[Cu_2(C_{39}H_{42}N_{10})(CH_3COO)_2](ClO_4)_2\cdot H_2O$: C, 46.40; H, 4.54; N, 12.59%.

10: Found: C, 47.10; H, 4.88; N, 11.62%. Calcd for $[Cu_2(C_{43}H_{50}N_{10})(CH_3COO)_2](ClO_4)_2\cdot 2H_2O$: C, 47.55; H, 5.10; N, 11.80%.

11: Found: C, 47.38; H, 4.52; N, 12.61%. Calcd for $[Cu_2(C_{40}H_{44}N_{10})(CH_3COO)_2](ClO_4)_2$: C, 47.65; H, 4.55; N, 12.63%.

12: Found: C, 49.13; H, 4.96; N, 11.91%. Calcd for $[Cu_2(C_{44}H_{52}N_{10})(CH_3COO)_2](ClO_4)_2$: C, 49.48; H, 5.03; N, 12.02%.

Measurements. Magnetic susceptibilities at room temperature, infrared absorption spectra, and conductivity measurements were carried out as described in a previous paper.$^{7)}$ ^{1}H NMR spectra were recorded with Varian VXR-200 and JNM-MH-100 instruments in $CDCl_3$. Variable-temperature (4.2—270 K) magnetic susceptibilities were measured by a high-sensitivity Faraday balance with superconducting magnet (Oxford Instruments, Inc.). The temperature was measured by a platinum thermometer and by a carbon resistance thermometer, which were calibrated against a magnetic thermometer with the use of a paramagnetic complex, $[Cr(NH_3)_6]Cl_3$.$^{8)}$ Visible absorption spectra were recorded on a Hitachi U-3410 spectrophotometer.

Results and Discussion

We prepared a series of copper(II) complexes **1**—**12** containing a dinucleating ligand with imidazole nitrogens and two exogenous bridging ligands. These complexes gave the characteristic IR bands due to the different bridging anions [$\nu_{as}(N_3^-)$ 2100—2050 cm^{-1}, $\nu_{CN}(NCS^-)$ 2120—2080 cm^{-1}, $\nu_{as}(COO^-)$ 1585—1580 cm^{-1} and $\nu_s(COO^-)$ 1400—1390 cm^{-1}]. These data indicate that two azide ions bridge in a μ-1,1-fashion for complexes **1**—**4**$^{9)}$ and also two acetato ions in **9**—**12** link between two copper(II) ions as Cu–O–C–O–Cu.$^{10)}$

The magnetic moments at room temperature and the absorption spectral data for **1**—**12** are summarized in Table 1. The magnetic moments of these complexes are close to those for mononuclear Cu(II) complexes or dinuclear copper(II) complexes without any intermetallic interaction. In order to obtain detailed information on the magnetic properties of these complexes, the magnetic susceptibilities of **1**, **5**, and **9** were measured over the temperature range 4.2—270 K. There is no evidence for an exchange coupling between the two copper(II) ions of **1** from the temperature-dependence of the magnetic susceptibility (χ_a) and moments (μ_{eff}) for **1**. The magnetism of this complex and similar complexes **2**—**4** are quite different from that (diamagnetism) of $[Cu_2(L\text{-}Et)(N_3)](BF_4)_2$ bridged by an azido and an alkoxo, where HL-Et represents *N,N,N′,N′*-tetrakis[(1-ethyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane.$^{4)}$ Figure 1 gives the temperature-dependence of the magnetic susceptibility for the complex **5** bridged

Table 1. Physical Properties of the Complexes

Complex		μ_{eff}[a]	λ_{max} (ε/Cu)[b]	
		BM	nm	
1	$[Cu_2(3Me)(N_3)_2](ClO_4)_2 \cdot H_2O$	1.93	663 (303),	400 (2600)
2	$[Cu_2(3Et)(N_3)_2](ClO_4)_2 \cdot 2H_2O$	1.87	660 (247),	397 (1780)
3	$[Cu_2(4Me)(N_3)_2](ClO_4)_2 \cdot 2H_2O$	1.91	665 (277),	402 (2260)
4	$[Cu_2(4Et)(N_3)_2](ClO_4)_2 \cdot 3H_2O$	1.94	660 (290),	399 (2290)
5	$[Cu_2(3Me)(NCS)_2](ClO_4)_2 \cdot 3H_2O$	1.87	672 (148),	371 (708)
6	$[Cu_2(3Et)(NCS)_2](ClO_4)_2 \cdot 2.5H_2O$	1.88	673 (163),	372 (820)
7	$[Cu_2(4Me)(NCS)_2](ClO_4)_2 \cdot H_2O$	1.92	671 (138),	374 (804)
8	$[Cu_2(4Et)(NCS)_2](ClO_4)_2 \cdot 2H_2O$	1.86	668 (159),	374 (840)
9	$[Cu_2(3Me)(OAc)_2](ClO_4)_2 \cdot H_2O$	1.94	660 (116)	
10	$[Cu_2(3Et)(OAc)_2](ClO_4)_2 \cdot 2H_2O$	1.97	660 (121)	
11	$[Cu_2(4Me)(OAc)_2](ClO_4)_2$	1.90	663 (118)	
12	$[Cu_2(4Et)(OAc)_2](ClO_4)_2$	1.87	662 (117)	

a) Room temperature. b) DMF solutions.

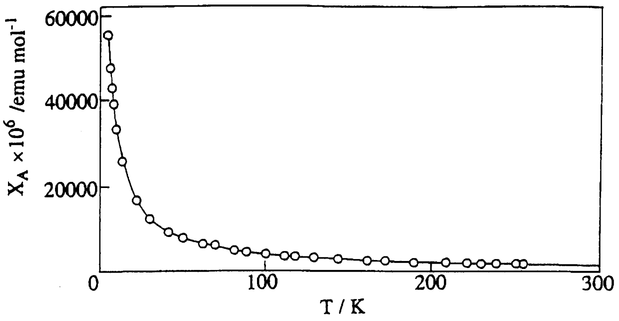


Fig. 1. Temperature dependence of the magnetic susceptibility of **5**. The open circles indicate observed susceptibility. The solid line shows the theoretical susceptibility calculated by the modified Bleaney–Bowers equation.[11)]

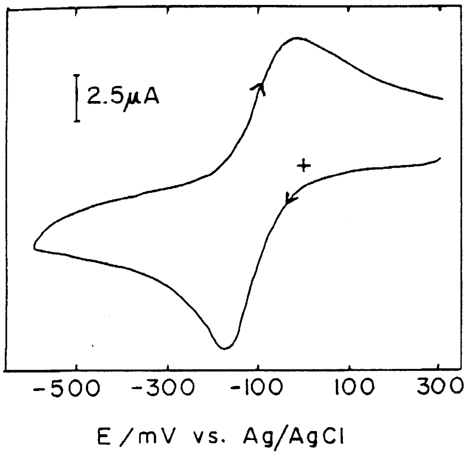


Fig. 2. Cyclic voltammogram of **9** in DMF at the scan rate of 100 mV s^{-1}.

by thiocyanate. Simulation of the data using the following modified Bleaney–Bowers Equation 1[11)] gives a weak antiferromagnetic exchange interaction, in agreement with the slight decrease of μ_{eff}/Cu in the range of about 260 to 50 K (1.87 BM at 256 K and 1.78 BM at 50 K).

$$\chi_A = \frac{Ng^2\beta^2}{kT}\frac{1}{3+\exp(-2J/kT)}(1-p) + \frac{Ng^2\beta^2}{4kT}\cdot p + N\alpha \qquad (1)$$

where, g, J, $N\alpha$, and p are, respectively, the g factor, the exchange integral, T.I.P., and the percentage of impure species. The magnetic behavior of the acetato-bridged complex **9** is similar to that of **5**. The magnetic parameters are estimated g=2.09, $N\alpha$=60×10^{-6} cgs emu mol^{-1}, $2J$=−4.2 cm^{-1}, and p=0.01 for **5** and g=2.17, $N\alpha$=60×10^{-6} cgs emu mol^{-1} and $2J$=−4.0 cm^{-1} for **9** from the best fit of the χ_A values to the Bleaney–Bowers equation.[11)] Although the antiferromagnetic coupling constants (J) of the other thiocyanato- and acetato-complexes **6**, **7**, **8**, **10**, **11**, and **12** have not been determined, it is supposed that the antiferromagnetic interactions similar to **5** and **9** are present in these complexes from a comparison of the room-temperature magnetic moments (Table 1) of **5**—**12**. The d–d absorption bands of all twelve complexes show almost symmetric absorptions with their maxima located near 665 nm. Furthermore, all of the azido complexes display an intense band at about 400 nm (Table 1). These bands are assigned to azido to copper(II) CT transitions.[12,13)] The CT bands are also observed for the thiocyanato complexes near 370 nm (Table 1).[13,14)] Further, these λ_{max} values of the d–d absorption bands and the CT-bands in DMF solutions for **1**, **5**, and **9** are similar to those obtained from the electronic spectra of solid states. The molar conductances (Λ values) of **1**, **5**, and **9** in DMF solutions are 146, 155, and 150 S cm^2 mol^{-1}, respectively, showing that these complexes are 1 : 2 electrolytes in DMF solutions.[15)] These results suggest that the structures in the solid states of **1**, **5**, and **9** are maintained in solutions. Probably, complexes **1**—**12** are considered to have the dimeric structure in which the geometries around the two copper(II) ions are square-pyramidal, as elucidated for $[Cu_2(2ME)(NO_3)_3]NO_3 \cdot 4H_2O$.[2,16)]

Table 2. CV Data for the Complexes[a)]

Complex No.	E_{pc}[b)] mV	E_{pa}[b)] mV	$E_{1/2}$[b)] mV
3	0	+100	+50
4	+10	+120	+65
7	+80	+200	+140
8	+90	+210	+150
9	−170	−30	−100
10	−210	+10	−100
11	−190	+200	+5
12	−190	+180	−5

a) DMF solutions. b) Scan rate: 100 mV s^{-1}.

Figure 2 gives the cyclic voltammogram of compound **9** as an example for complexes **3**, **4**, **7**—**12**. The cyclic voltammograms of these complexes are very similar to that of **9**. The number of electrons involved in these redox processes of two compounds **4** and **7** were found to be 2 by constant-potential electrolyses in DMF. The same type two-electron processes (Cu^{2+}–Cu^{2+}→Cu^{+}–Cu^{+}) occur also in other complexes (**3** and **8**—**12**) from the comparison of the steady state voltammetry for these complexes with **4** and **7**. These electrochemical behaviors differ from that of $[Cu_2(L\text{-}Et)(N_3)](ClO_4)_2$, in which a quasi-reversible one-electron process is found (Cu^{2+}–Cu^{2+}→Cu^{2+}–Cu^{+}).[5)] The anodic and cathodic peak potentials and half-wave potentials ($E_{1/2}$) in cyclic voltammetry are given in Table 2. The $E_{1/2}$ values increase in the order $OAc^{-}<N_3^{-}<NCS^{-}$. On the other hand, the $E_{1/2}$ values of the acetato-bridged complexes were observed at a higher potential in **11** and **12** than in **9** and **10**. Therefore, it is estimated that the length of methylene-chain in these compounds influences the stability of copper(II) complexes. The $E_{1/2}$ values of the complexes **3**, **4**, **7**, **8**, **11**, and **12** with 4Me or 4Et are also seen in fairly positive potentials (Table 2). These facts may be correlated to the geometry around the copper(II) ions within the complexes. The determination of molecular structures will be necessary in order to discuss the structure–electrochemistry relationship in more detail.

We thank to Dr. Wasuke Mori of Osaka University for his helpful discussions in magnetic susceptibilities. This work was supported in part by Grant-in-Aid for Scientific Research No. 03453050 and Priority Areas No. 4225102 Bioinorganic Chemistry from the Ministry of Education, Science and Culture, for which we express our thanks.

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16) The abbrebiation 2Me represents *N*,*N*,*N*′,*N*′-tetrakis[(1-methyl-2-benzimidazolyl)methyl]-1,2-diaminoethane.