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Preparation and Properties of the Dinuclear Copper(II) Complexes Containing the Derivatives of *N*,*N*,*N'*,*N'*-Tetrakis(2-benzimidazolyl))-2-hydroxy-1,3-diaminopropane and an Exogenous Bridging Ligand

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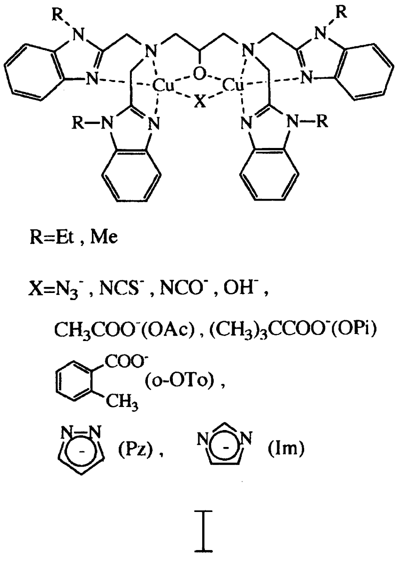
Synopsis. The dinuclear copper(II) complexes of HL-Et or HL-Me and a bridging ligand (X (X=N_3^-, NCS^-, NCO^-, OH^-, OAc^-, $(CH_3)_3CCOO^-$ (OPi^-), *o*-$C_6H_4(CH_3)COO^-$ (OTo^-), pyrazolate (Pz^-), and imidazolate (Im^-))) have been prepared and characterized, where HL-Et=*N*,*N*,*N'*,*N'*-tetrakis[(1-ethyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane and HL-Me=*N*,*N*,*N'*,*N'*-tetrakis[(1-methyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane. The magnetic moments of these complexes differ depending upon their bridging groups. The electrochemistry in *N*,*N*-dimethylformamide showed that only one-electron reduction (Cu^{2+}–Cu^{2+}→Cu^{+}–Cu^{2+}) can occur for the dinuclear complexes bridged by X=N_3^-, OAc^-, OPi^-, OTo^-, Pz^-, whilst the other complexes showed irreversible processes.

The synthesis of dinuclear copper complexes with ligands containing imidazole groups is of current interest as models of the ligating sites of type III-copper proteins, hemocyanin and tyrosinase.[1,2] A large number of synthetic models which mimic the dinuclear copper center have been reported.[1—3] In connection with these studies, we describe here the preparation and characterization of the dimeric copper(II) complexes, **1**—**15** (structural formula **I** Chart 1), containing *N*,*N*,*N'*,*N'*-tetrakis[(1-ethyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane (HL-Et) or *N*,*N*,*N'*,*N'*-tetrakis[(1-methyl-2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane (HL-Me) and an exogenous small ligand. The bridging ligands, such as N_3^-, NCS^-, and NCO^-, have greatly contributed to giving a perturbation to the ESR silent dinuclear site of type III-copper proteins.



I

Chart 1.

Experimental

Synthesis of the Ligands HL-Et and HL-Me. HL-Et was prepared according to a method described in the literature.[4] HL-Me was also prepared by a similar method to that for HL-Et using methyl iodide instead of ethyl bromide. HL-Me: mp 105—106.5 °C (uncorrected); ^1H NMR ($CDCl_3$) δ=2.63 (4H, d), 3.40 (12H, s), 3.85—4.05 (10H, m), 7.1—7.7 (16H, m). Found: C, 67.34; H, 6.33; N, 19.99%. Calcd for $C_{39}H_{42}N_{10}O\cdot1.5H_2O$: C, 67.50; H, 6.55; N, 20.20%.

Preparation of Copper(II) Complexes. $[Cu_2(HL\text{-}Et)(H_2O)_4](ClO_4)_4\cdot H_2O$[4] and $[Cu_2(HL\text{-}Me)(H_2O)_4](ClO_4)_4\cdot H_2O$. These complexes were prepared by mixing $Cu(ClO_4)_2\cdot6H_2O$ and HL-Et or HL-Me in a ratio of 2:1 in ethanol at room temperature. The complexes obtained after cooling in a refrigerator were washed with ethanol. $[Cu_2(HL\text{-}Me)(H_2O)_4](ClO_4)_4\cdot H_2O$: Found: C, 36.36; H, 4.05; N, 10.96%. Calcd for $C_{39}H_{50}N_{10}O_{21}Cl_4Cu_2\cdot H_2O$: C, 36.53; H, 3.93; N, 10.92%.

$[Cu_2(L\text{-}Et)(X)](ClO_4)_2\cdot nH_2O$ (X=N_3^-,[4] NCS^-, NCO^-, OH^-, and OAc^-[4]) (1, 2, 3, 4, and 5). To $[Cu_2(HL\text{-}Et)(H_2O)_4](ClO_4)_4\cdot H_2O$ (0.40 g, 0.30 mmol) in ethanol (20 cm^3) was added NaN_3 (0.020 g, 0.30 mmol), NaNCS (0.024 g, 0.30 mmol), NaNCO (0.020 g, 0.30 mmol), NaOH (0.024 g, 0.60 mmol), or $CH_3COONa\cdot3H_2O$ (0.041 g, 0.30 mmol). The reaction mixture was stirred at room temperature for 1 d, and then allowed to stand for several hours in a refrigerator. Crude complexes containing N_3^- and NCS^- were recrystallized from acetonitrile–ether by vapor diffusion. On the other hand, the NCO^-, OH^-, and OAc^- containing complexes were washed with ethanol or ethanol containing a small volume of acetonitrile. $[Cu_2(L\text{-}Et)(NCS)](ClO_4)_2$ (**2**): Found: C, 47.82; H, 4.75; N, 13.98%. Calcd for $C_{44}H_{49}N_{11}O_9Cl_2SCu_2$: C, 47.78; H, 4.47; N, 13.93%. $[Cu_2(L\text{-}Et)(NCO)](ClO_4)_2\cdot8H_2O$ (**3**): Found: C, 42.82; H, 5.32; N, 12.04%. Calcd for $C_{44}H_{49}N_{11}O_{10}Cl_2Cu_2\cdot8H_2O$: C, 42.97; H, 4.76; N, 12.49%. $[Cu_2(L\text{-}Et)(OH)](ClO_4)_2\cdot2H_2O$ (**4**): Found: C, 46.63; H, 4.67; N, 12.38%. Calcd for $C_{43}H_{50}N_{10}O_{10}Cl_2Cu_2\cdot2H_2O$: C, 46.90; H, 4.95; N, 12.72%.

[Cu$_2$(L-Et)(X)](ClO$_4$)$_2$·nH$_2$O (X=OPi$^-$, *o*-OTo$^-$, Pz$^-$,[4] Im$^-$) (6, 7, 8, and 9). To [Cu$_2$(HL-Et)(H$_2$O)$_4$](ClO$_4$)$_4$·H$_2$O (0.40 g, 0.30 mmol) in ethanol (20 cm^3) was added pivalic acid (0.031 g, 0.30 mmol), *o*-toluic acid (0.041 g, 0.30 mmol), pyrazole (0.020 g, 0.30 mmol), or imidazole (0.020 g, 0.30 mmol) and succeedingly sodium hydroxide (0.024 g, 0.60 mmol) was added. After being stirred at room temperature for 1 d, the reaction mixture was cooled in a refrigerator. The resulting precipitate was collected by filtration, and washed with ethanol or ethanol containing a small volume of acetonitrile. [Cu$_2$(L-Et)(OPi)](ClO$_4$)$_2$·1.5H$_2$O (**6**): Found: C, 48.52; H, 4.88; N, 11.92%. Calcd for C$_{48}$H$_{58}$N$_{10}$O$_{11}$Cl$_2$Cu$_2$·1.5H$_2$O: C, 49.01; H, 5.24; N, 11.91%. [Cu$_2$(L-Et)(*o*-OTo)](ClO$_4$)$_2$·1/2H$_2$O (**7**): Found: C, 51.31; H, 4.76; N, 11.75%. Calcd for C$_{51}$H$_{56}$N$_{10}$O$_{11}$Cl$_2$Cu$_2$·1/2H$_2$O: C, 51.38; H, 4.83; N, 11.75%. [Cu$_2$(L-Et)(Im)](ClO$_4$)$_2$·3H$_2$O (**9**): Found: C, 46.76; H, 4.62; N, 14.13%. Calcd for C$_{46}$H$_{52}$N$_{12}$O$_9$Cl$_2$Cu$_2$·3H$_2$O: C, 47.25; H, 5.01; N, 14.38%.

[Cu$_2$(L-Me)(X)](ClO$_4$)$_2$·nH$_2$O (X=N$_3^-$, NCS$^-$, OH$^-$, OAc$^-$, Pz$^-$, and Im$^-$) (10, 11, 12, 13, 14, and 15). These complexes were also obtained in a similar way to the corresponding complexes with HL-Et using [Cu$_2$(HL-Me)(H$_2$O)$_4$](ClO$_4$)$_4$·H$_2$O. [Cu$_2$(L-Me)(N$_3$)](ClO$_4$)$_2$·5H$_2$O (**10**): Found: C, 41.59; H, 4.36; N, 16.03%. Calcd for C$_{39}$H$_{41}$N$_{13}$O$_9$Cl$_2$Cu$_2$·5H$_2$O: C, 41.67; H, 4.58; N, 16.20%. [Cu$_2$(L-Me)(NCS)](ClO$_4$)$_2$·H$_2$O (**11**): Found: C, 44.60; H, 4.10; N, 14.79%. Calcd for C$_{40}$H$_{41}$N$_{11}$O$_9$Cl$_2$SCu$_2$·H$_2$O: C, 44.98; H, 4.07; N, 14.43%. [Cu$_2$(L-Me)(OH)](ClO$_4$)$_2$ (**12**): Found: C, 46.43; H, 3.99; N, 13.33%. Calcd for C$_{39}$H$_{42}$N$_{10}$O$_{10}$Cl$_2$Cu$_2$: C, 46.43; H, 4.20; N, 13.89%. [Cu$_2$(L-Me)(OAc)](ClO$_4$)$_2$·5H$_2$O (**13**): Found: C, 43.15; H, 4.78; N, 12.25%. Calcd for C$_{41}$H$_{44}$N$_{10}$O$_{11}$Cl$_2$Cu$_2$·5H$_2$O: C, 43.15; H, 4.78; N, 12.28%. [Cu$_2$(L-Me)(Pz)](ClO$_4$)$_2$·2.5H$_2$O (**14**): Found: C, 45.70; H, 4.34; N, 15.24%. Calcd for C$_{42}$H$_{44}$N$_{12}$O$_9$Cl$_2$Cu$_2$·2.5H$_2$O: C, 45.69; H, 4.48; N, 15.23%. [Cu$_2$(L-Me)(Im)](ClO$_4$)$_2$·2H$_2$O (**15**): Found: C, 46.52; H, 4.48; N, 14.84%. Calcd for C$_{42}$H$_{44}$N$_{12}$O$_9$Cl$_2$Cu$_2$·2H$_2$O: C, 46.06; H, 4.43; N, 15.35%.

Measurements. ^{1}H NMR spectrum was recorded with a Varian VXR-200 Instrument in CDCl$_3$. Magnetic susceptibility, conductivity, and infrared absorption spectra measurements were carried out as described in a previous paper.[5] Visible and near-infrared absorption spectra were recorded on a Hitachi U-3410 spectrophotometer. Cyclic and steady-state voltammetric measurements were performed according to a previously mentioned method.[6]

Results and Discussion

Copper(II) Complexes with HL-Et. We prepared a series of copper(II) complexes **1**—**9**, of which three (**1**, **5** and **8**) had been synthesized by McKee et al.[4] The azido, thiocyanato, cyanato, and hydroxo complexes **1**—**4** gave the characteristic IR bands due to the different bridging groups [ν_{as}(N$_3^-$) 2020, 2050(sh) cm^{-1}, ν_{CN}(SCN$^-$) 2110 cm^{-1}, ν_{CN}(NCO$^-$) 2200 cm^{-1}, ν_{OH}(OH$^-$) 3450 cm^{-1}]. The acetato complex **5**, showed ν_{as}(COO) and ν_{s}(COO) bands at 1560 and 1420 cm^{-1}, respectively. Likewise, in carboxylato complexes **6** and **7** similar bands are observed at 1550 and 1415 cm^{-1}. The splitting between ν_{as}(COO) and ν_{s}(COO) in these complexes(**5**—**7**) are 135—165 cm^{-1}, suggesting that the carboxylate group bridges between two coppers as has been confirmed by X-ray crystallography for the acetato complex, **5** (Cu–O–C–O–Cu).[4,7,8] It appears that the carboxylate groups give similar dinuclear sites, regardless the structure of the bridging ligands. The magnetic moments at room temperature as well as the absorption spectral and electric conductance data for these complexes are summarized in Table 1. The magnetic moments of these complexes differ depending on the kind of bridging ligand and geometry around the copper ions (mentioned below). These complexes exhibit two major absorption bands in the 1050—690 nm range (Table 1). The lower energy band of these complexes, except for **1**, showed a higher intensity than did the higher energy band, exhibiting that a stereochemistry around each copper(II) is a trigonal-bipyramid,[9] as had been revealed for the acetato complex, **5**.[4] However, the azido complex, **1**, has a square-pyramidal structure.[4] The molar conductances (Table 1) of **1**—**9** show that these complexes are 1 : 2 electrolytes in DMF solutions.

The anodic and cathodic peak potentials and half-wave potentials ($E_{1/2}$) in cyclic voltammetry are given in Table 2. Figure 1 gives the cyclic voltammogram of **1** as an example for the complexes, **1** and **5**—**8**. The cyclic voltammograms of **5**—**8** are very similar to that of **1**. In order to establish the number of electrons involved in the redox processes of these complexes, the steady-state voltammetry[10] of **1** was car-

Table 1. Physical Properties of Copper(II) Complexes

Complex			μ_{eff}[a]	λ_{max}[b]	Λ[b]
No.	R	X	BM	nm(ε)	S cm^2 mol^{-1}
1[c]	Et	N$_3$	diamag.[c]	948(153),704(200)	121
2	Et	NCS	1.54	1001(110),778(92)	140
3	Et	NCO	1.85	1009(106),740(75)	195
4	Et	OH	1.74	1035(99),750(64)[d]	145
5[c]	Et	OAc	1.89[c]	1056(107),770(60)[d]	155
6	Et	OPi	1.90	1045(112),780(68)[d]	155
7	Et	OTo	1.84	1054(101),780(71)[d]	137
8[c]	Et	Pz	1.90[c]	953(177),690(98)[d]	147
9	Et	Im	1.68	920(134),740(88)[d]	148
10	Me	N$_3$	1.05[e]	920(124),692(123)[d]	128
11	Me	NCS	1.79	990(101),760(76)	130
12	Me	OH	1.84	1015(138),800(125)[d]	125
13	Me	OAc	1.97	1042(106),776(61)[d]	150
14	Me	Pz	1.56	952(142),688(69)[d]	140
15	Me	Im	1.63	911(110),700(66)[d]	130

a) Room temperature. b) DMF solutions. c) Ref. 8. d) Shoulder. e) We suppose that the complex has a property near diamagnetism, since the presence of several % of paramagnetic impurities in the sample 10 is confirmed from the experiment on variable-temperature magnetic susceptibility.

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

Complex No.	E_{pc}[b)] mV	E_{pa}[b)] mV	$E_{1/2}$[b)] mV
1	−290	−190	−240
2	−200	—	—
3	−230	—	—
4	−440	—	—
5	−510	−420	−465
6	−490	−370	−430
7	−440	−340	−390
8	−440	−360	−400
9	−330	—	—
10	−240	−150	−195
11	−160	−90	−125
12	−350	−250	−300
13	−480	−320	−400
14	−440	−350	−395
15	−500	—	—

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

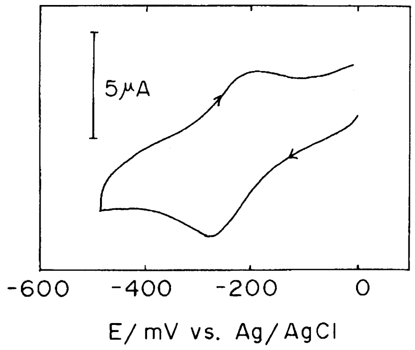
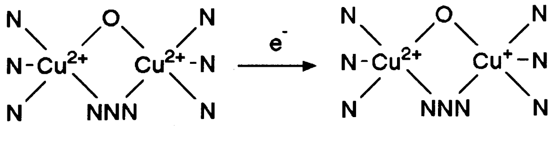


Fig. 1. Cyclic voltammogram of **1** in DMF at the scan rate of 100 mV s^{-1}.

ried out in DMF together with $[Cu(NO_3)(tmbma)]NO_3 \cdot 2H_2O$[9)] (tmbma; tris(*N*-methyl benzimidazole-2-yl-methyl)amine); the ratio of i_l/c^* was determined (i_l and c^* denote the limiting current and the concentration of a complex, respectively). These values for the complexes **1** and $[Cu(NO_3)(tmbma)]NO_3 \cdot 2H_2O$ were 1.98 and 2.33 nA mM^{-1}, respectively. These results are in accordance with the redox process of $[Cu(NO_3)(tmbma)]NO_3 \cdot 2H_2O$, for which we have already shown that the number of electrons involved is 1 in DMF.[9)] Consequently, the reduction of **1** appears to involve the following quasi-reversible one-electron process:



Very similar results were obtained for complexes **5**—**8** by steady-state voltammetry. On the other hand, the reoxidation peak corresponding to the cathodic peak was not observed in each complex (**2**—**4** and **9**), showing that the redox reactions are chemically irreversible. We suppose that these reductions of **2**—**4** and **9** at -200—-440 mV (Table 2) involve a one-electron process. These electrochemical behaviors seem to be distinct from those of the type-III coppers, where the following type two-electron process occurs:[11)]

$$Cu^{2+}\text{-}Cu^{2+} + 2e^- \longrightarrow Cu^{+}\text{-}Cu^{+}.$$

Copper(II) Complexes with HL-Me. Copper(II) complexes **10**—**15** were newly prepared by the same method as that for **1**—**9** using HL-Me. The physical properties of these complexes are given in Tables 1 and 2. The μ_{eff} values of these complexes are greater than those of the corresponding complexes with HL-Et, except for the pyrazolate- and imidazolate-bridged complexes. Detailed structure information, including crystallography, will be required for any further discussion.

The $E_{1/2}$ or E_{pc} values of $[Cu_2(L\text{-}Me)(X)]^{2+}$ are generally higher than those of $[Cu_2(L\text{-}Et)(X)]^{2+}$, and the λ_{max} values are shifted to shorter wavelengths. This tendency in electrochemistry is considered to be due to an increase in the electron density on the benzimidazole nitrogen in the order L-Me<L-Et, being consistent with the results obtained for copper complexes containing tris[(2-benzimidazolylmethyl)]amine derivatives.[9)] This conclusion could be useful in the synthesis of copper(I) complexes as models of copper proteins which participate in Cu(II)$\rightleftharpoons$Cu(I) redox reactions.

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