The Mono- and Dinuclear Copper(II) Complexes Containing Tripodal Ligand and Pyridine, Imidazole or Pyrazole

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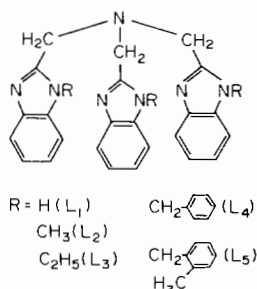*Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558 (Japan)*

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Abstract

Monomeric and dimeric copper(II) complexes containing tris(2-benzimidazylmethyl)amine (L_1) or its derivatives (L_2, L_3, L_4 and L_5) and pyridine (Py), imidazole (ImH) or pyrazole (Pz) have been prepared and characterized by their magnetic susceptibilities, electric conductivities, cyclic voltammetric half-wave potentials, and visible absorption and ESR spectra. The compounds made of L_2, L_3 or L_4 and imidazole are dinuclear copper(II) complexes bridged by imidazolate, while other complexes are mononuclear ones. The susceptibility of $[Cu_2(L_2)_2(Im)](ClO_4)_3 \cdot 3H_2O$ shows an antiferromagnetic interaction ($J = -30$ cm^{-1}) and the X-band ESR spectrum for the powdered sample of this complex exhibits the triplet state of such a dimer in the $\Delta M_s = 2$ region. Likewise, the signals due to the $\Delta M_s = 2$ transition were also observed for the complexes $[Cu_2(L_3)_2(Im)](ClO_4)_3 \cdot 2H_2O$ and $[Cu_2(L_4)_2(Im)](ClO_4)_3 \cdot 2H_2O$. From the comparison of half-wave potentials ($E_{1/2}$) in a series of monomeric copper(II) complexes, the $E_{1/2}$ values for the reduction of Cu(II) to Cu(I) decrease in the order Py > Pz > ImH in DMF and CH$_3$CN solutions.

Introduction

The histidine imidazole group is one of the most important binding sites for metals in biological systems. For example, the copper(II) atoms in plastocyanin [1] and azurin [2] are in a distorted tetrahedral geometry with a 'N$_2$S$_2$' donor set containing two imidazole nitrogen atoms. Interest in these copper proteins possessing unusual environments has prompted us to study copper(II) complexes with tripodal imidazole-containing ligands,

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R = H (L_1)
CH$_3$ (L_2)
C$_2$H$_5$ (L_3)
CH$_2$-phenyl (L_4)
CH$_2$-(methylphenyl) (L_5)

as indicated in the structural formulae L_1–L_5 [3]. In a previous paper [3], we described the relationship between the electrochemical redox behavior and the stereochemical difference in the complexes with tripodal ligands L_1–L_5. As an extension of these investigations dealing with the structure–electrochemistry relationship in copper(II) complexes, the preparation of Cu(L_n)X ($n = 1$–5, X = Py, ImH or Pz) has been performed. We also obtained three dimeric copper(II) complexes Cu$_2$(L_n)$_2$·(Im)$^{3+}$ ($n = 2$, 3, and 4) bridged by imidazolate (Im$^-$), and characterized by magnetic susceptibilities and ESR spectra.

Experimental

Preparation of Tripodal Ligands L_1–L_5

These ligands were prepared by the method reported in the previous papers [3–5].

Preparation of Copper(II) Complexes

To the methanol solution (50 cm^3) of each tripodal ligand (1 mmol) were added pyridine, imidazole or pyrazole (1 mmol) and the methanol solution (50 cm^3) of Cu(ClO$_4$)$_2$·6H$_2$O (0.037 g, 1 mmol). After being stirred at 50 °C for 0.5 h, the reaction mixture was cooled. The green crystalline products obtained were washed with methanol. The analytical data for these compounds are tabulated in Table 1.

TABLE 1. Analytical data for the complexes

Complex	H (%)		C (%)		N (%)	
	Found	Calculated	Found	Calculated	Found	Calculated
1 $[Cu(L_1)(Py)](ClO_4)_2 \cdot 2H_2O$	3.69	3.86	44.13	44.36	14.12	14.28
2 $[Cu(L_2)(Py)](ClO_4)_2 \cdot H_2O$	4.05	4.24	47.63	47.49	13.91	13.85
3 $[Cu(L_3)(Py)](ClO_4)_2 \cdot 3.5H_2O$	4.62	5.07	46.75	46.90	12.40	12.50
4 $[Cu(L_4)(Py)](ClO_4)_2 \cdot 0.5H_2O$	4.36	4.42	58.58	58.39	10.86	10.90
5 $[Cu(L_5)(Py)](ClO_4)_2 \cdot 2H_2O$	4.79	4.97	58.13	57.99	10.06	10.21
6 $[Cu(L_1)(Pz)](ClO_4)_2 \cdot 2H_2O$	3.76	3.78	41.72	41.89	16.22	16.29
7 $[Cu(L_2)(Pz)](ClO_4)_2 \cdot H_2O$	3.95	4.18	45.28	45.14	15.86	15.80
8 $[Cu(L_3)(Pz)](ClO_4)_2 \cdot H_2O$	4.13	3.88	47.46	47.57	14.87	15.13
9 $[Cu(L_1)(ImH)](ClO_4)_2 \cdot 2H_2O$	3.66	3.78	42.26	41.89	16.35	16.29
10 $[Cu(L_2)_2(Im)](ClO_4)_3 \cdot 3H_2O$	4.14	4.40	47.04	47.35	15.65	15.50
11 $[Cu_2(L_3)_2(Im)](ClO_4)_3 \cdot 2H_2O$	4.78	4.89	50.19	50.04	14.87	14.83
12 $[Cu_2(L_4)_2(Im)](ClO_4)_3 \cdot 2H_2O$	4.44	4.56	59.34	59.27	11.86	11.90
13 $[Cu(L_5)(ImH)](ClO_4)_2 \cdot H_2O$	4.74	4.82	57.30	57.32	11.38	11.80

Measurements

Visible absorption spectra in DMF solutions were recorded on a Hitachi U-3410 spectrophotometer. Magnetic susceptibility at room temperature was determined using a Gouy magnetic apparatus. The Faraday method was applied for the measurement of magnetic susceptibility over the range from liquid helium temperature to room temperature. The X-band ESR spectra of powdered samples at room temperature were recorded at 9.3 GHz and 100 kHz modulation frequency with a JEOL JES-FE-1X instrument. A Toa Denpa Conduct meter CM-7B was used for conductivity measurements in 10^{-3} mol dm^{-3} DMF solution.

Cyclic voltammetric and controlled-potential coulometric measurements were performed according to the method described previously [3]. The steady-state voltammetric measurements were carried out with a Huso HECS 972 microelectrode potentiostat,

a Huso HECS 321 B potential sweep unit, and a Graphtech WX2400 x-y recorder. The working electrode was a platinum microdisk of 30 μm diameter. All the electrochemical measurements were carried out at 25 °C under an atmosphere of argon, and tetrabutylammonium hexafluorophosphate (0.1 mol dm^{-3}) was used as the supporting electrolyte.

Results and Discussion

We prepared the monomeric and dimeric copper(II) complexes 1−13 containing the tripodal ligands L_1−L_5 and pyridine, imidazole or pyrazole. The color of the crystals, magnetic moments at room temperature, visible absorption spectral and electric conductance data for the complexes 1−13 are indicated in Table 2. Ten compounds 1−9 and

TABLE 2. Physical properties of the complexes

Complex no.	Color	μ_{eff} (K) (BM)	λ_{max} (log ϵ) (nm)	Λ (S cm^2 mol^{-1})
1	yellow−green	1.86(304)	992(2.06), 731(2.00)	139
2	green	1.83(300)	995(2.01), 736(1.95)	142
3	green	1.85(297)	998(2.09), 755(1.94)[a]	168
4	blue−green	1.81(299)	983(2.00), 741(1.96)	138
5	green	1.85(291)	976(1.98), 728(1.98)	146
6	green	1.84(299)	986(2.01), 745(1.93)	140
7	yellow−green	1.87(299)	982(2.03), 741(1.96)	143
8	yellow−green	1.82(300)	991(2.08), 755(1.95)[a]	137
9	green	1.82(303)	862(2.11), 680(1.97)[a]	140
10	yellow−green	1.75(297)	879(2.24)	205
11	yellow−green	1.74(296)	883(2.27)	213
12	yellow−green	1.77(296)	873(2.19)	211
13	blue−green	1.82(298)	840(2.07), 700(2.00)[a]	144

[a]Shoulder.

13 show normal magnetic moments as monomeric copper(II) complexes. The magnetic moments of the complexes 10–12 at room temperature were lower than those of the complexes 1–9 and 13, suggesting that the complexes 10–12 are dimer. In order to obtain detailed information on the structures of 10–12, the magnetic susceptibility of 10 was measured over the temperature range 4.2–300 K. Figure 1 gives the temperature-dependence of the magnetic susceptibility of 10. The magnetic data show a peak near 50 K and a rapid decrease at lower temperatures, exhibiting an anti-ferromagnetic interaction within the dimeric copper(II) complex. The magnetic parameters are estimated as $g = 2.02$, $N\alpha = 60 \times 10^{-6}$ cgs emu mol^{-1}, and $J = -30$ cm^{-1} from the best fit of the χ_a values to the Bleaney–Bowers equation [6]. Although the antiferromagnetic coupling constants (J) of the other complexes 11 and 12 have not been determined, it is supposed that the antiferromagnetic interactions similar to 10 are present in these complexes from the comparison of room temperature magnetic moments (Table 2) of 10–12 and J value of 10. The half-field $\Delta M_s = 2$ signal at $c.$ 1500 G was clearly seen for 10–12 in the powdered X-band ESR spectra. Figure 2 indicates the ESR spectra of 10, 12 and the monomeric complex 9. From the results of magnetic susceptibilities and ESR spectra described above, it is considered that the compounds 10–12 are dimeric complexes bridged by imidazolate having the structure represented as I. Haddad and Hendrickson have already reported
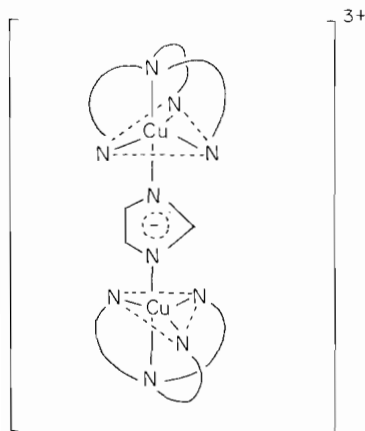
the same type of complexes [Cu$_2$(tren)$_2$(Im)]-(ClO$_4$)$_3$ in which the J value is -38 cm^{-1} [7].

The molar conductances (Table 2) of the compounds 1–9 and 13 show that these monomeric complexes are 1:2 electrolytes in DMF solution [8]. The mononuclear copper(II) complexes exhibit two major absorption bands in the range of 1000–680 nm (Table 2), and in addition a lower energy band for 1–9 and 13 is in higher intensity. This fact indicates that the stereochemistry around cop-
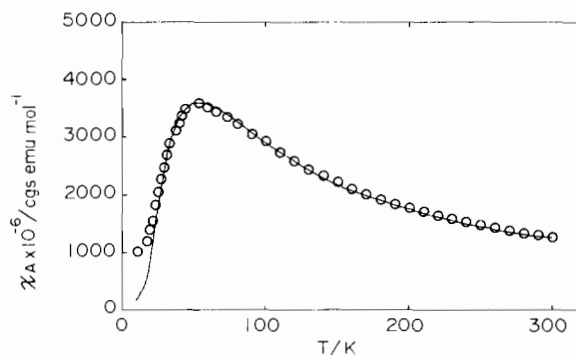

Fig. 1. Temperature-dependence of the magnetic susceptibility of 10.

per(II) is a trigonal-bipyramid in the mononuclear complexes. The d–d absorption bands of these complexes were observed at a longer wavelength in [Cu(L$_n$)Py]$^{2+}$ or [Cu(L$_n$)Pz]$^{2+}$ than in [Cu(L$_n$)ImH]$^{2+}$ (Table 2), suggesting that the copper(II) complexes with pyridine or pyrazole are less stable than the corresponding imidazole containing complexes.

The half-wave potentials ($E_{1/2}$) determined by averaging the anodic and cathodic peak potentials in cyclic voltammetry are represented in Table 3 together with the peak separation (ΔE_p). Curve (a) in Fig. 3 is the cyclic voltammogram of 3 as a
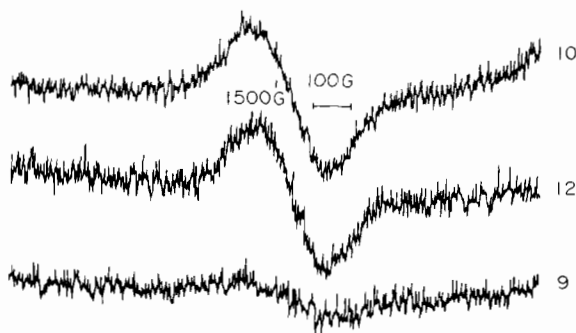

Fig. 2. ESR spectra ($\Delta M_s = 2$ region) for the dinuclear complexes 10 (power 5 mW, amplitude 2500), 12 (power 5 mW, amplitude 3200) and the mononuclear complex 9 (power 5 mW, amplitude 4000).

TABLE 3. CV data for the complexes[a]

Complex	$E_{1/2}$[b] (mV)	ΔE[b] (mV)	$E_{1/2}$[c] (mV)	ΔE[c] (mV)
1	−85	210	+75	110
2	−90	140	+50	110
3	−90	180	+40	120
4	−75	270	+85	130
5	−85	310	+95	150
6	−85	170	+75	100
9	−110	180	−35	260

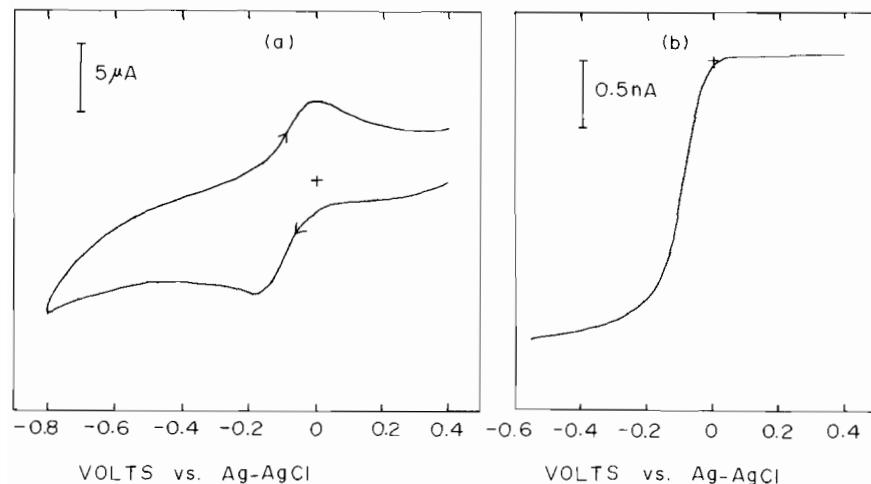[a]Scan rate: 50 mV s^{-1}. [b]DMF solution. [c]CH$_3$CN solution

Fig. 3. Cyclic (a) and steady-state (b) voltammograms of the complex 3 in DMF. (a) Scan rate: 50 mV s^{-1}. (b) Scan rate: 5 mV s^{-1}.

representative example of the complexes 1—6 and 9. In order to establish the number of electrons involved in the redox process of these complexes, the steady-state voltammetry [9] of 3 in DMF was carried out as illustrated in Fig. 3(b) and the ratio of i_1/c^* was determined for this complex together with $[Cu(L_2)NO_3]NO_3$, where i_1 and c^* denote the limiting current and the concentration of a complex, respectively. These values for the complexes 3 and $[Cu(L_2)NO_3]NO_3$ are 2.12 and 2.21 nA mM^{-1}, respectively. The number of electrons involved in the redox process of $[Cu(L_2)NO_3]$-NO$_3$ has already been found to be 1 by controlled-potential coulometry in DMF [3]. Accordingly, the reduction of 3 is a quasi-reversible one-electron process. Moreover, it was identified by the controlled—potential coulometry that the same type of reduction for 3 occurs in 4 and 13. The $E_{1/2}$ values of copper(II) in the complexes 1—5 with pyridine as a unidentate ligand decrease in the order $5 > 4 > 1 > 2 > 3$ in acetonitrile solution, but no difference was observed in DMF solution. The order in acetonitrile is analogous to that obtained for the complexes containing Br$^-$ or N-methylimidazole (N-MeIz), $[Cu(L_n)Br]^+$ and $[Cu(L_n)N$-MeIz$]^{2+}$ ($n = 1—5$) systems [3]. The $E_{1/2}$ values of the complexes with L$_1$ and Py or Pz are more positive than those of the corresponding ImH complexes in DMF and CH$_3$CN solutions. These facts indicate that the reduced copper(I) complexes with pyridine or pyrazole as a unidentate are more stable than that with

imidazole. This is consistent with the results obtained through the comparison of $[Cu(pyep)]^{2+}$ and $[Cu(imep)]^{2+}$ [10]$^{+}$, and $[Cu(2$-Aep=daa=2-Aep$)]^{2+}$ and $[Cu(Hist=daa=Hist)]^{2+}$ [11]$^{+}$, respectively. This conclusion could be useful in the synthesis of model compounds of copper proteins which participate in Cu(II) $\rightleftharpoons$ Cu(I) redox reactions.

Acknowledgement

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†The following abbreviations are used: imep = 2,6-bis[1-[2-(4-imidazolyl)ethylimino]ethyl]pyridine, pyep = 2,6-bis[1-[2-(2-pyridyl)ethylimino]ethyl]pyridine; 2-Aep=daa= 2-Aep and Hist=daa=Hist represent Schiff bases derived from 2-(2-aminoethyl)pyridine and 4-hydroxy-4-methyl-2-pentanone, and histamine and 4-hydroxy-4-methyl-2-pentanone, respectively.