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Copper(II) Complexes with Tripodal Imidazole-containing Ligands. Structure–Electrochemistry Relationship

YASUO NAKAO*, MAKOTO ONODA

Chemical Laboratory, Faculty of Education, Okayama University, Okayama 700, Japan

TAKESHI SAKURAI, AKITSUGU NAKAHARA

Institute of Chemistry, College of General Education, Osaka University, Osaka 560, Japan

ISAMU KINOSHITA and SHUN'ICHIRO OOI

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

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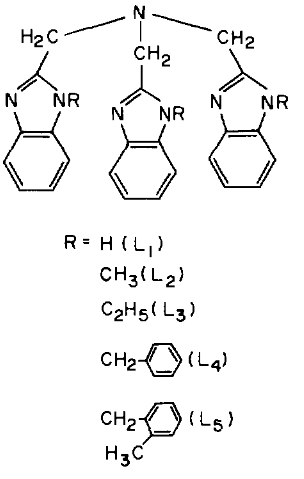
Abstract

Mono- and dimeric copper(II) complexes of tris(benzimidazol-2-ylmethyl)amine (L_1) and of its derivatives with the imidazole N–H protons substituted by a methyl (L_2), ethyl (L_3), benzyl (L_4) or *o*-methylbenzyl (L_5) group were prepared and characterized based on magnetic susceptibility, conductivity, cyclic voltammetric half-wave potential ($E_{1/2}$), infrared, electronic and ESR spectra. The complexes containing H_2O, NO_3^-, Cl^-, Br^-, N_3^-, and *N*-methylimidazole with L_1–L_5 were mononuclear copper(II) complexes, while the complexes with NCS^- or NCO^- and L_1–L_3 [except $[Cu(L_1)NCS](NO_3)$] were dinuclear ones, which dissociate to monomeric complexes in DMF solution. The $E_{1/2}$ values of copper(II) in a series of complexes containing H_2O or NO_3^- decrease in the order $L_5 > L_1 > L_2 > L_3 > L_4$, whereas those in complexes with Br^- and *N*-methylimidazole decrease in the orders $L_4 \gtrsim L_5 > L_1 > L_2 > L_3$ and $L_5 > L_1 > L_4 \gtrsim L_2 > L_3$, respectively. The relationship between the structure of the complexes and the $E_{1/2}$ values are discussed in some detail.

Introduction

The imidazole group of histidine plays key roles in the coordination of copper at the active sites of numerous copper proteins. For example, the molecular structure of *Populus nigra italica* plastocyanin [1] and *Pseudomonas aeruginosa* azurin [2] reveals that copper(II) ion in oxidized proteins is in a highly distorted tetrahedral environment with two sulfur donor atoms and two imidazole nitrogen donor atoms. These facts have prompted us to study copper(II) complexes with unusual environments for the copper(II) ion. A number of copper(II) complexes of tripodal ligands have already been reported [3–8]. In connection with these investigations we report the preparation and characterization of monomeric and dimeric copper(II) complexes containing tripod-like ligands, as exhibited in structural formulae L_1–L_5, which differ from each other in the groups substituted on the imidazole nitrogen. Moreover, the relationship between the redox behavior and the stereochemical differences in tripodal ligands is discussed on the basis of cyclic voltammetric and ESR spectral data.



Experimental

Preparation of Tripodal Ligands

Tris(2-benzimidazylmethyl)amine (L_1) was prepared according to the literature [9]. Ligand L_2 was obtained by the reaction of L_1 with methyl iodide [5]. Ligands L_3, L_4 and L_5 were also prepared by a method similar to that for L_2, using ethyl

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*Author to whom correspondence should be addressed.

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iodide, benzyl chloride or *o*-methylbenzyl chloride, respectively. After the addition of ethyl iodide, benzyl chloride or *o*-methylbenzyl chloride into the reaction mixture containing L_1, the reactions were carried out for 0.5, 1 and 4 h, respectively. Each reaction mixture was allowed to stand for 1 day and concentrated to *ca.* one-fourth of its original volume. The products were filtered off and washed with ether. L_3: melting point (m.p.) 188–190 °C. *Anal.* Found: C, 73.28; H, 6.70; N, 19.85. Calc. for $C_{30}H_{33}N_7$: C, 73.28; H, 6.78; N, 19.95%. L_4: m.p. 200–201 °C. *Anal.* Found: C, 79.69; H, 5.81; N, 14.40. Calc. for $C_{45}H_{39}N_7$: C, 79.72; H, 5.81; N, 14.47%. L_5: m.p. 203–204.5 °C. *Anal.* Found: C, 79.23; H, 6.31; N, 13.00. Calc. for $C_{48}H_{45}N_7 \cdot 0.5H_2O$: C, 79.08; H, 6.37; N, 13.45%.

Preparation of Metal Complexes

[Cu(L$_n$)(H$_2$O)](ClO$_4$)$_2$ (n = 1–5, 1–5)

These complexes were prepared by mixing $Cu(ClO_4)_2 \cdot 6H_2O$ and the tripodal ligands L_1, L_2, L_3, L_4 or L_5 in a ratio of 1:1 in methanol at 50 °C. The crystals obtained after cooling in a refrigerator were washed with methanol.

[Cu(L$_n$)NO$_3$]NO$_3$ (n = 1–5, 6–10), [Cu(L$_n$)Cl]Cl (n = 1–3, 11–13), and [Cu(L$_n$)Br]Br (n = 1–5, 14–18)

These complexes were prepared by the same procedure as that for $[Cu(L_n)(H_2O)](ClO_4)_2$ using $Cu(NO_3)_2 \cdot 3H_2O$, $CuCl_2 \cdot 2H_2O$ or $CuBr_2$, respectively.

[Cu(L$_n$)N$_3$]NO$_3$ (n = 1–3, 19–21)

To a methanolic solution (50 cm^3) of L_1 (0.82 g, 2.0 mmol) were added an aqueous solution of NaN_3 (0.07 g, 1.0 mmol) and the mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.48 g, 2.0 mmol) and 10 cm^3 of methanol. After being stirred at 50 °C for 1 h, the reaction mixture was cooled. The products obtained were washed with methanol.

The corresponding complexes containing L_2 or L_3 were isolated in the same way as described for $[Cu(L_1)N_3]NO_3$. IR (KBr), ~2050 cm^{-1} (N_3^-).

[Cu(L$_1$)NCS]NO$_3$ (22), [Cu$_2$(L$_n$)$_2$(NCS)](NO$_3$)$_3$ (n = 2, 3, 23–24), and [Cu$_2$(L$_n$)$_2$(NCO)](NO$_3$)$_3$ (n = 1–3, 25–27)

These were also prepared in the same way as for $[Cu(L_1)N_3]NO_3$ using NaNCS or NaNCO. IR (KBr) of 22–24, ~2100 cm^{-1} (NCS^-); and of 25–27, ~2200 cm^{-1} (NCO^-).

[Cu(L$_n$)(N-MeIz)](ClO$_4$)$_2$ (n = 1–5, 28–32)

To 25 cm^3 of methanol were successively added L_1, L_2, L_3, L_4 or L_5 (1.0 mmol), *N*-methylimidazole (*N*-MeIz) (0.08 g, 1.0 mmol), and $Cu(NO_3)_2 \cdot 3H_2O$ (0.24 g, 1.0 mmol). The reaction mixture was then stirred for 1 h at 50 °C. After cooling, the crystalline products were isolated by filtration and washed with methanol.

The analytical data for the compounds described above are tabulated in Table I.

Measurements

Melting points were determined on a micro melting point apparatus and are uncorrected. IR spectra were measured with a Jasco A-102 infrared spectrophotometer with KBr disk. Visible absorption spectra of DMF solutions were recorded on a Shimadzu MPS-5000 spectrophotometer. Magnetic susceptibility at room temperature was determined using a Gouy magnetic apparatus. 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. The ESR spectra of DMF solutions were measured at 77 K using the apparatus mentioned above. A Toa Denpa Conduct Meter CM-7B was used for conductivity measurements in 10^{-3} M DMF solutions.

Cyclic voltammetry and constant-potential electrolysis were carried out using a Hokuto Denko potentiostat–galvanostat HA-501, Hokuto Denko function generator HB-104 and Yokogawa Denki Type 3086 X–Y recorder. These measurements were performed at 25 °C in DMF solutions containing 10^{-1} M $(C_2H_5)_4NClO_4$ and 10^{-3} M copper(II) complex deoxygenated by bubbling nitrogen. Cyclic voltammetry was carried out using a glassy carbon disk electrode of 3 mm diameter (Yanaco GC-P2) as a working electrode and an Ag/AgCl electrode as a reference electrode, and a coiled platinum wire was used as an auxiliary electrode. An 'H' cell, a platinum gauze working electrode, a silver wire reference electrode and a coiled platinum wire auxiliary electrode were used for constant-potential electrolysis.

Results and Discussion

A number of copper(II) complexes containing L_1 have already been prepared and characterized by Thompson *et al.* [3, 4]. We synthesized a series of complexes **1**–**32** with the ligand L_1 and its derivatives L_2, L_3, L_4 or L_5. The color of the crystals, magnetic moments at room temperature and electric conductance data for these copper(II) complexes are given in Table II. The magnetic moments of **1**–**32** were close to the values for copper(II) complexes without copper(II)–copper(II) interaction. It is evident that the complexes **1**–**5** and **28**–**32** bearing H_2O or *N*-MeIz are monomeric from the non-bridging character of these ligands. The molar conductances (Table II) of **1**–**5** and **28**–**32** show that these com-

TABLE I. Analytical Data for the Complexes

Complex	H (%)		C (%)		N (%)	
	Found	Calculated	Found	Calculated	Found	Calculated
1 $[Cu(L_1)(H_2O)](ClO_4)_2 \cdot 2H_2O$[a]	3.59	3.77	39.69	39.81	13.47	13.55
2 $[Cu(L_2)(H_2O)](ClO_4)_2 \cdot 2H_2O$	4.10	4.35	42.21	42.32	12.62	12.80
3 $[Cu(L_3)(H_2O)](ClO_4)_2 \cdot 2H_2O$	4.52	4.87	44.43	44.58	12.09	12.13
4 $[Cu(L_4)(H_2O)](ClO_4)_2 \cdot H_2O$	4.55	4.45	55.16	55.35	9.77	10.04
5 $[Cu(L_5)(H_2O)](ClO_4)_2 \cdot 0.5H_2O$	4.83	4.80	57.15	57.11	9.64	9.71
6 $[Cu(L_1)NO_3]NO_3 \cdot H_2O$[a]	3.70	3.79	47.06	47.01	20.51	20.57
7 $[Cu(L_2)NO_3]NO_3 \cdot 2H_2O$	4.46	4.65	48.01	48.17	18.56	18.73
8 $[Cu(L_3)NO_3]NO_3 \cdot 0.5H_2O$	4.70	5.00	52.35	52.35	18.17	18.32
9 $[Cu(L_4)NO_3]NO_3$	4.56	4.55	62.33	62.45	14.53	14.57
10 $[Cu(L_5)NO_3]NO_3$	5.01	5.01	63.76	63.52	13.66	13.89
11 $[Cu(L_1)Cl]Cl \cdot H_2O$[a]	4.29	4.15	52.19	51.47	17.21	17.51
12 $[Cu(L_2)Cl]Cl$	4.67	4.59	55.52	55.39	16.79	16.63
13 $[Cu(L_3)Cl]Cl$	5.20	5.32	57.20	57.54	15.47	15.66
14 $[Cu(L_1)Br]Br \cdot H_2O$[a]	3.60	3.68	43.62	43.81	14.70	14.91
15 $[Cu(L_2)Br]Br$	4.05	4.02	48.19	48.35	14.57	14.36
16 $[Cu(L_3)Br]Br \cdot H_2O$	4.58	4.82	49.60	49.15	13.51	13.38
17 $[Cu(L_4)Br]Br \cdot H_2O$	4.39	4.50	59.07	58.79	10.66	10.67
18 $[Cu(L_5)Br]Br \cdot 4.5H_2O$	4.94	5.32	56.08	56.27	9.52	9.57
19 $[Cu(L_1)N_3]NO_3 \cdot H_2O$	3.84	3.92	48.75	48.60	25.45	25.98
20 $[Cu(L_2)N_3]NO_3 \cdot 2.5H_2O$	4.41	4.88	48.73	48.96	24.08	23.27
21 $[Cu(L_3)N_3]NO_3 \cdot 3H_2O$	4.95	5.52	50.26	50.51	22.09	21.60
22 $[Cu(L_1)NCS]NO_3 \cdot H_2O$	3.64	3.81	49.22	49.29	20.53	20.70
23 $[Cu_2(L_2)_2NCS](NO_3)_3 \cdot 3H_2O$	4.41	4.63	50.42	50.48	19.21	19.27
24 $[Cu_2(L_3)_2NCS](NO_3)_3$	4.89	4.92	54.14	54.08	18.33	18.62
25 $[Cu_2(L_1)_2NCO](NO_3)_3$	3.85	3.63	50.29	50.29	21.55	21.55
26 $[Cu_2(L_2)_2NCO](NO_3)_3 \cdot 3H_2O$	4.41	4.63	50.42	50.48	19.21	19.27
27 $[Cu_2(L_3)_2NCO](NO_3)_3 \cdot 1.5H_2O$	5.10	5.10	53.88	53.65	17.95	18.47
28 $[Cu(L_1)N\text{-MeIz}](ClO_4)_2 \cdot 1.5H_2O$	3.73	3.89	43.15	43.16	15.90	16.18
29 $[Cu(L_2)N\text{-MeIz}](ClO_4)_2$	4.12	4.20	46.59	46.88	15.72	15.88
30 $[Cu(L_3)N\text{-MeIz}](ClO_4)_2 \cdot 1.5H_2O$	4.89	4.91	47.35	47.30	14.15	14.61
31 $[Cu(L_4)N\text{-MeIz}](ClO_4)_2 \cdot 0.5H_2O$	4.28	4.50	56.94	57.05	12.18	12.22
32 $[Cu(L_5)N\text{-MeIz}](ClO_4)_2 \cdot 0.5H_2O$	4.47	4.89	58.11	58.17	11.52	11.74

[a] These compounds have already been prepared by Thompson *et al.* (ref. 3).

plexes are 1:2 electrolytes in DMF solution. The signal due to the $\Delta M_s = 2$ transition of the powdered ESR spectra was not observed for the complexes **7**, **11**, **14** and **20**, indicating that the Cl^--, Br^-- and N_3^--containing complexes are magnetically monomer.

This conclusion for the chloride and bromide complexes is in accord with that established by Addison *et al.* [4]. On the other hand, different ESR spectra were obtained for the compounds **23**–**27** with NCS^- or NCO^-. Namely, the half-field $\Delta M_s = 2$ signal at *ca.* 1500 G was clearly seen for **23**, **24** and **25** in the powder X-band ESR spectra. Although the $\Delta M_s = 2$ signals were not observed for **26** and **27**, the spectra in the $\Delta M_s = 1$ region exhibited a broader line shape than those of the other monomeric complexes. These facts show that compounds **23**–**27** are probably dimeric complexes bridged by NCS^- or NCO^-. It is considered that complex **22** containing L_1 and NCS^- is a monomer from the absence of a $\Delta M_s = 2$ signal and the narrow line shape of the $\Delta M_s = 1$ signal in the powder ESR spectrum. However, we suppose that complexes **23**–**27** have trigonal-bipyramidal monomeric structures in solution, as mentioned for some L_1-containing complexes [3, 4].

The monomeric copper(II) complexes [3] having NO_3^- exhibit one major absorption with a high energy shoulder (Table III). This spectral pattern is typical of five-coordinate trigonal-bipyramidal copper(II). These complexes also give ESR signals characteristic of trigonal-bipyramidal structures ($g_\perp > g_\parallel \sim 2$), as shown in Table III. All the ESR parameters for **6**–**10** show similar values (Table III), suggesting that the stereochemistry around copper(II) in these complexes remains unaltered.

The half-wave potentials determined by cyclic voltammetry are summarized in Table II. Figure 1 shows the cyclic voltammogram of **7** as an example for the complexes **1**–**32**. The numbers of electrons

TABLE II. Physical Properties of the Complexes

Complex	Color	μ_{eff} (K) (BM)	Λ (S cm^2 mol^{-1})	$E_{1/2}$[a] (mV)	ΔE[b] (mV)
1	yellow–green	1.91(297)	151	–53	145
2	green–yellow	1.91(296)	155	–85	170
3	yellow–green	1.92(296.5)	152	–90	150
4	yellow–green	1.84(291)	149	–98	225
5	yellow–green	1.79(290)	142	–24	138
6	green	1.93(296)	100	–65	150
7	green–yellow	1.93(296)	107	–88	145
8	green	1.87(297)	110	–103	175
9	yellow–green	1.82(288)	97	–110	220
10	yellow–green	1.79(288.5)	100	–38	165
11	brown–yellow	1.87(289.5)	44	–118	115
12	yellow–green	1.93(297)	95	–125	110
13	green	1.88(303)	69	–150	180
14	yellow	1.87(292)	67	–80	110
15	yellow–green	1.88(288)	72	–103	85
16	green	1.92(290.5)	73	–125	100
17	yellow	1.8(290.5)	71	–36	105
18	yellow	1.79(291)	73	–42	145
19	green	1.86(298)	75	–220	200
20	yellow	1.92(300)	90	–270	100
21	brown–yellow	1.98(296)		–283	145
22	yellow–green	1.90(299)		–123	155
23	green–yellow	1.91(301)		–143	125
24	yellow–green	1.89(302)		–168	135
25	green	1.79(295)		–155	240
26	green–yellow	1.95(302)		–185	310
27	brown–green	1.91(301)		–198	335
28	yellow–green	1.89(297)	157	–83	195
29	yellow–green	1.90(297)	159	–103	165
30	blue–green	1.86(297)	159	–110	200
31	blue	1.74(289)	148	–100	220
32	blue	1.74(289)	142	–53	185

[a] $E_{1/2} = (E_p^{red} + E_p^{ox})/2$. [b] $\Delta E = E_p^{red} - E_p^{ox}$. Scan rate = 50 mV s^{-1}.

TABLE III. Absorption Spectral Data and ESR Parameters of the Complexes

Complex	λ_{max} (ϵ) (nm)	ESR parameters			
		$g_{\parallel}$	$g_{\perp}$	$A_{\parallel}$ (G)	$A_{\perp}$ (G)
6	1035(96), 750(67)[a]	2.01	2.23	72	98
7	1030(96), 750(69)[a]	2.01	2.24	72	98
8	1035(108), 750(62)[a]	2.01	2.23	74	95
9	1005(107), 735(66)[a]	2.01	2.24	72	95
10	1005(103), 745(70)[a]	2.01	2.24	74	93

[a] Shoulder.

involved in these redox processes of several complexes were found to be 1 by constant-potential electrolyses in DMF. The $E_{1/2}$ values of copper(II) in the complexes with NO_3^- as a counter anion decrease in the order **10** > **6** > **7** > **8** > **9**. The order **6** > **7** > **8** is believed to be due to the increase in the electron density on the imidazole nitrogen in the order $L_1 < L_2 < L_3$. Complex **10** with L_5 exhibited an $E_{1/2}$ value 30–80 mV greater than those with ligands L_1–L_4. From these facts and the similarity of the stereochemistry around copper(II) for **6**–**10**, as described above, it is considered that the reduced copper(I) complex of **10** is more stable than the corresponding complexes containing

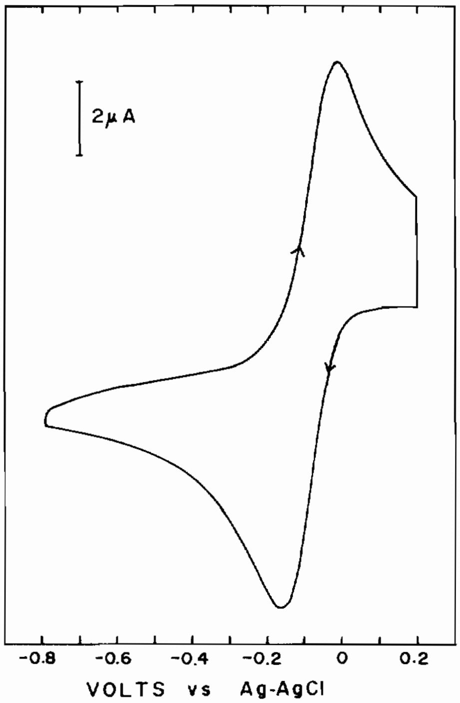

Fig. 1. Cyclic voltammogram of complex 7 in DMF at a scan rate of 50 mV s^{-1}.

L_1–L_4. We imagine that the high stability of the copper(I) complex with L_5 is attributed to favoring a tetrahedrallly distorted structure because of the steric hindrance arising from the *o*-methylbenzyl group. The same result was also seen in complexes **1**–**5** with coordinated water (Table II); that is, the $E_{1/2}$ values decrease in the order **5** > **1** > **2** > **3** > **4**.

Somewhat different results were obtained with the complexes containing Br^- or *N*-MeIz: the $E_{1/2}$ values decrease in the orders **17** $\gtrsim$ **18** > **14** > **15** > **16** and **32** > **28** > **31** $\gtrsim$ **29** > **30** in bromide and *N*-methylimidazole complexes, respectively. In these complexes the copper(I) forms including L_4, as well as L_5, are more stable than those with L_1–L_3 or L_2–L_3. It is assumed that the tetrahedrally distorted structures are more suitable for the complexes **17**, **18**, **31** and **32**, because of steric hindrance between bulky Br^- or *N*-MeIz and L_4 or L_5. The precise structure of these copper(I) complexes is not clear at the present stage. The decrease of $E_{1/2}$ in the order $L_1 > L_2 > L_3$ was also observed for the complexes with Cl^-, N_3^-, NCS^- or NCO^-. On the other hand, the order of $E_{1/2}$ values in all complexes with L_1 follows the sequence $H_2O > NO_3^- > Br^- \gtrsim$ *N*-MeIz $> Cl^- > NCS^- > NCO^- > N_3^-$. Similar results were obtained in the L_2 or L_3 containing complexes.

As is clear from the present data (Tables II and III) and the data for the complexes containing L_1 or its derivatives attained by Addison *et al.* [4] and Sakurai *et al.* [8], the trigonal bipyramidal copper(II) complexes with tripodal ligands L_1–L_5 exhibit low $A_\parallel$ values and high reduction potentials, comparable with those observed for copper proteins [9]. However, the visible absorption spectra and other ESR parameters of the present complexes differ markedly from those for blue copper proteins [9]. These results show that the copper coordination sphere in the complexes **1**–**32** differs from that present in blue coppers such as plastocyanin [1] and azurin [2] which have pseudo-tetrahedral CuN_2S_2 centers.

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