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CORRELATION BETWEEN REDUCTION POTENTIAL AND CHARGE-TRANSFER FREQUENCY OF ALKOXO-BRIDGED BINUCLEAR COPPER(II) COMPLEXES OF VARIOUS TRIDENTATE LIGANDS(1)

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Spectral and electrochemical properties of alkoxo-bridged binuclear copper(II) complexes of various tridentate ligands with NNO-, NSO-, SNO- and SSO-donor sets were examined. Reductions of the complexes with NNO-, NSO(and SNO)- and SSO-donor sets occurred at -0.2 – -0.5, 0– -0.2 and +0.15 V vs. SCE respectively, while the charge transfer bands characteristic of the complexes were found at $26–28\times10^3$, $24.5–25\times10^3$ and $\sim23.5\times10^3$ cm^{-1} respectively. It was found that a linear correlation exists between the reduction potentials and the CT frequencies of the complexes.

It is known that the alkoxo-bridged binuclear copper(II) complexes show a characteristic absorption in the near ultra-violet or visible region.(2) Nishida and Kida assigned this band to the charge-transfer from the p_π orbital of the bridging oxygen to the vacant d-orbital of copper(II) ion.(3) Previously we have pointed out that in the binuclear copper(II) complexes of the tridentate alcohols (Fig. 1) substitution of thioether sulfur for amino nitrogen brings about a red-shift of the CT band(4-6) and a positive shift of the reduction potential.(6,7) In order to elucidate further the relation between the reduction potential and the CT frequency, in this study we have reexamined the spectral and electrochemical properties of alkoxo-bridged binuclear copper(II) complexes with various NNO-, NSO- and SNO-donor sets so far reported. In addition to these, we have prepared two new binuclear copper(II) complexes with NNO- and SSO-donor sets and measured electronic spectra and polarograms. The ligands and their abbreviations are given in Table 1.

Preparations. Cu(Im-3-3-nno)ClO_4. The ligand Im-3-3-nnoH was prepared by the reaction of histamine and 3-chloropropanol at 200°C for 30 minutes. A mixture of Im-3-3-nnoH and copper(II) perchlorate hexahydrate in methanol was made weakly alkaline by addition of sodium methoxide. The solution was filtered to separate insoluble materials and allowed to stand in a refrigerator to give deep green crystals. Found: C, 27.67; H, 4.40; N, 12.41%. Calcd for Cu(Im-3-3-nno)$ClO_4\cdot H_2O$: C, 27.51; H, 4.62; N, 12.03%. μ_{eff}=0.62 BM at 295.4 K. The exchange integral (-J) evaluated from the best fit of magnetic susceptibility to the

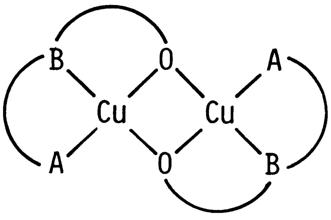
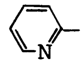
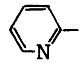
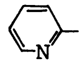


Fig. 1. Skeleton of the binuclear copper(II) complexes (A, B= amino nitrogen or thioether sulfur).

Table 1. Tridentate ligands and their abbreviations.

$R_2N-(CH_2)_3-NH-(CH_2)_2-OH$	R-3-2-nnoH
$R-S-(CH_2)_2-NH-(CH_2)_3-OH$	R-2-3-snoH
 $-(CH_2)_2-NH-(CH_2)_3-OH$	py-3-3-nnoH
 $-(CH_2)_2-S-(CH_2)_3-OH$	py-3-3-nsoH
 $-(CH_2)_2-S-(CH_2)_2-OH$	py-3-2-nsoH
$R-S-(CH_2)_2-S-(CH_2)_2-OH$	R-2-2-ssoH
 $-(CH_2)_2-NH-(CH_2)_3-OH$	Im-3-3-nnoH

Bleaney-Bowers equation in the temperature range 80-300K was 355 cm^{-1}.

Cu(Me-2-2-sso)Cl. This complex was obtained by the reaction of 2-(2-methylthioethylthio)ethanol and anhydrous copper(II) chloride in absolute ethanol in the presence of triethylamine as a green micro crystalline powder. Found: C, 24.06; H, 4.45%. Calcd for Cu(Me-2-2-sso)Cl: C, 24.00; H, 4.43%. μ_{eff}=0.83 BM at 298.5K.

Electrochemical Measurements. Polarogram of Cu(Im-3-3-nno)ClO_4 was recorded on a Yanagimoto P-1000 Voltammetric Analyzer in N,N-dimethylformamide (DMF) containing 0.1 M tetraethylammonium perchlorate as a supporting electrolyte. The working electrode was a dropping mercury electrode, the auxiliary electrode a platinum coil, and the reference electrode the saturated calomel electrode. Polarogram of Cu(Me-2-2-sso)Cl was measured in dichloromethane because it is unstable in DMF. Its reduction potential was nomalized with the potentials of other complexes determined in DMF, by the use of ferrocene[8)] as an internal standard.

Reduction potentials and CT frequencies of Cu(Im-3-3-nno)ClO_4 and Cu(Me-2-2-sso)Cl are given in Table 2, together with those of the complexes previously reported. All the complexes showed substantially one reduction wave in DMF. In some of these complexes the reduction process was shown to involve a two-electron transfer by controlled potential electrolysis.[7,9)] Based on cyclic voltammetry, the processes were found to be quasi-reversible or irreversible. Thus, the formal reduction potentials were determined by differential pulse polarography. The potentials of the complexes of the ligands with NNO-donor set fall in the range -0.2 — -0.5 V vs. SCE. Potentials of the complexes with NSO- or SNO-donor sets are in the range 0 — -0.2 V. The reduction of Cu(Me-2-2-sso)Cl, which is the first example with SSO-donor set, occurred at +0.15 V.

Absorption spectra of the binuclear copper(II) complexes so far reported were measured in methanol. Thus, we have measured the spectra of the complexes in DMF in this study, and found that the CT frequency is practically invariant in

Table 2. Reduction Potentials and CT Frequencies of Binuclear Copper(II) Complexes.

Complexes	R	X	$E'_{1/2}$ (V vs. SCE)	Ref.	CT ($\tilde{\nu}/10^3 cm^{-1}$)	Ref.
Cu(R-3-2-nno)X	H	BPh_4	-0.50	9	28.0	10
	Me	ClO_4	-0.33		27.0	
	Et	ClO_4	-0.21		26.5	
Cu(py-3-3-nno)X		ClO_4	-0.43	6	26.7	6
		BF_4	-0.39, -0.42		26.5	
		PF_6	-0.40, -0.42		26.7	
Cu(Im-3-3-nno)X		ClO_4	-0.30	This work	26.7	This work
Cu(R-2-3-sno)X	Me	ClO_4	-0.19	7	24.8	4
	Et	ClO_4	-0.17		24.8	
	n-Pr	ClO_4	-0.14		24.8	
	i-Pr	ClO_4	-0.20		24.6	
	n-Bu	ClO_4	-0.16		24.8	
Cu(py-3-3-nso)X		ClO_4	-0.09	6	25.0	6
		PF_6	-0.09		24.8	
Cu(py-3-2-nso)X		ClO_4	-0.06	6	24.6	6
		NO_3	-0.09		24.7	
		BF_4	-0.08		24.5	
		PF_6	-0.09		24.4	
Cu(R-2-2-sso)X	Me	Cl	+0.15[a)]	This work	23.6[a)]	This work

a) Measured in dichloromethane.

DMF and in methanol. The complexes with NNO-donor set show the CT band in the region 26×10^3–28×10^3 cm^{-1}, while the complexes with NSO- and SNO-donor sets show the CT band in the region 24×10^3–25×10^3 cm^{-1}. The frequency of Cu(R-2-2-sso)Cl (with SSO-donor set) is the lowest (23.6×10^3 cm^{-1}) among the complexes studied here.

The reduction potential and the CT frequency of Cu(R-3-2-nno)X considerably depend upon the R group. On the other hand, the reduction potentials and the CT frequencies of Cu(py-3-3-nno)X, Cu(R-2-3-sno)ClO_4, Cu(py-3-3-nso)X and Cu(py-3-2-nso)X are almost independent of the R and X groups. Plots of the CT frequency against the reduction potential for the complexes reveal a nearly linear correlation between them (Fig. 2). The difference in the CT frequency between the complexes with NNO-donor set and with SSO-donor set is about 3×10^3 cm^{-1}, while the difference in the reduction potential is about 0.5 V ($=4\times10^3 cm^{-1}$). Thus, the difference in the CT frequency is somewhat larger than that in the reduction potential. Because of the softness of sulfur donor atom, sulfur-donation results in the stabilization in the copper(I) state.

It should be noted that such a linear correlation is only hold for a series of complexes of similar coordination modes. For example, binuclear copper(II) complex of 1,5-diamino-3-hydroxypentane[11] does not follow the linear correlation of Fig. 2 ($E'_{1/2}$= -0.79 V and $\tilde{\nu}$(CT)=28.3×$10^3$$cm^{-1}$).

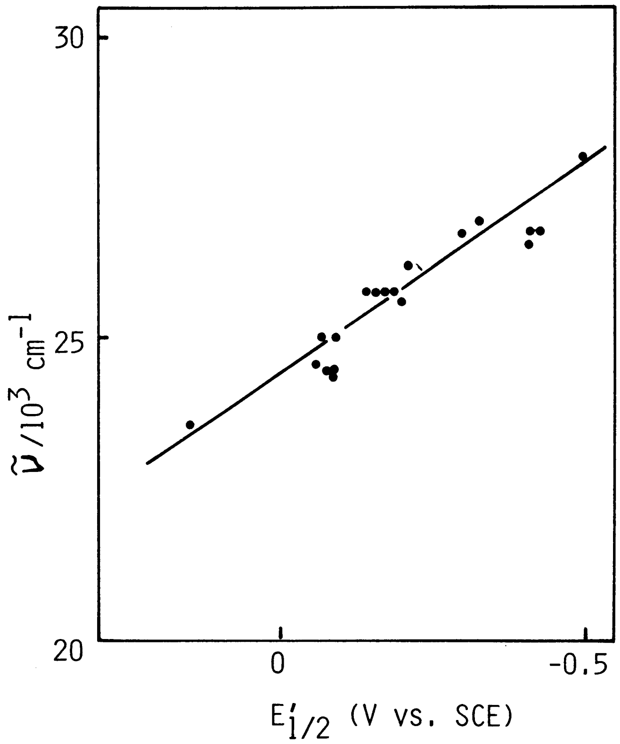


Fig. 2. Correlation between CT frequency and reduction potential for the binuclear copper(II) complexes.

References

1) Binuclear Metal Complexes. Part XLVII. Part XLVI: M. Nakamura, H. Okawa, and S. Kida, Inorg. Chim. Acta, in press.

2) Y. Ishimura, Y. Nonaka, Y. Nishida, and S. Kida, Bull. Chem. Soc. Jpn., 46, 3728 (1973).

3) Y. Nishida and S. Kida, Chem. Lett., 1974, 339.

4) M. Mikuriya, H. Okawa, and S. Kida, Inorg. Chim. Acta, 34, 13 (1974); ibid., 42, 233 (1980).

5) M. Mikuriya, H. Okawa, and S. Kida, Bull. Chem. Soc. Jpn., 53, 2871 (1980).

6) M. Nakamura, M. Mikuriya, H. Okawa, and S. Kida, Bull. Chem. Soc. Jpn., 54, 1825 (1981).

7) M. Mikuriya, M. Aihara, Y. Nishi, H. Okawa, and S. Kida, Chem. Lett., 1980, 795.

8) R. R. Gagne, C. A. Koval, and G. C. Lisensky, Inorg. Chem., 19, 2885 (1980).

9) M. Aihara, Y. Kubo, Y. Nishida, and S. Kida, Bull. Chem. Soc. Jpn., 54, 3207 (1981).

10) Y. Nishida, F. Numata, and S. Kida, Inorg. Chim. Acta, 11, 189 (1974).

11) I. Murase, M. Hatano, M. Tanaka, S. Ueno, H. Okawa, and S. Kida, Submitted to Bull. Chem. Soc. Jpn. for publication.

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