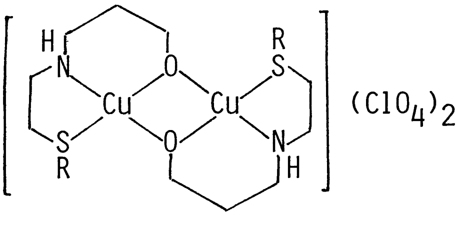
CHEMISTRY LETTERS, pp. 795-798, 1980.

ELECTROCHEMICAL PROPERTIES OF SOME ALKOXO-BRIDGED BINUCLEAR COPPER(II) COMPLEXES WITH SULFUR-CONTAINING LIGANDS[1)]

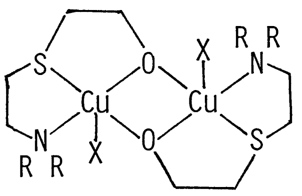
Masahiro MIKURIYA, Makoto AIHARA*, Yumiko NISHI*,
Hisashi OKAWA, and Sigeo KIDA
Department of Chemistry, Faculty of Science, Kyushu University 33,
Hakozaki, Higashiku, Fukuoka 812
*Fukuoka Women's University, Kasumigaoka, Higashiku, Fukuoka 813

Electrochemical properties of alkoxo-bridged binuclear copper(II) complexes with sulfur-containing tridentate ligands, $Cu\{RS(CH_2)_2NH(CH_2)_3O\}ClO_4$ and $Cu\{R_2N(CH_2)_2S(CH_2)_2O\}X$ (R=alkyl; X=Cl, Br), were investigated. The former showed a two-electron reduction, Cu(II)-Cu(II)⟶Cu(I)-Cu(I), near -0.2 V (vs. SCE), while the latter showed two one-electron reductions at ~0.2 and -0.3~-0.6 V (vs. SCE): Cu(II)-Cu(II)⟶Cu(II)-Cu(I)⟶Cu(I)-Cu(I).

Recently much attention has been denoted to electrochemical properties of binuclear copper(II) complexes in connection with redox-property of type III copper. Type III copper is believed to be magnetically coupled copper(II) ions which undergo a reversible two-electron reduction to Cu(I)-Cu(I).[2)] The reduction potentials of type III coppers are more than 0.24 V vs. SCE.[2)] On the other hand, all binuclear copper(II) complexes so far studied have negative reduction potentials.[3-10)] This might be attributed to the fact that these complexes contain only oxygen and/or nitrogen donor atoms favolable for copper(II) ion. Because of a high-affinity of sulfur donor atom to copper(I) ion, binuclear copper(II) complexes of sulfur-containing ligands seem more mimic to type III coppers. Thus, we investigated electrochemical properties of two series of alkoxo-bridged binuclear copper(II) complexes with sulfur-containing tridentate ligands, $Cu\{RS(CH_2)_2NH(CH_2)_3O\}ClO_4$ (abbreviated as $Cu(R\text{-}sno)ClO_4$, where R=CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, t-C_4H_9) and $Cu\{R_2N(CH_2)_2S(CH_2)_2O\}X$ (Cu(R-nso)X, where R=CH_3, C_2H_5, n-C_3H_7, n-C_4H_9; X=Cl, Br). The synthesis, structure, and



$Cu(R\text{-}sno)ClO_4$



Cu(R-nso)X (X=Cl, Br)

spectral and magnetic properties of these complexes have already been reported.[11-13] The Cu(R-sno)ClO_4 complexes possess an alkoxo-bridged binuclear structure with an essentially square-planar coordination geometry around the metal ion.[11] On the other hand, Cu(R-nso)X can not take a planar structure because of its strained fused-ring system. An X-ray crystallographic study of Cu(CH_3-nso)Br demonstrated a distorted square-pyramidal configuration around the metal.[13] Therefore, the present complexes enable us to investigate the sulfur donation effect and the structural effect on the electrochemical property of binuclear copper(II) complexes.

All electrochemical measurements were carried out in N,N-dimethylformamide (DMF) containing 0.1 M tetraethylammonium perchlorate at 25°C using a three-electrode cell. The saturated calomel electrode (SCE) was used as a reference, which was connected to a sample solution through a salt bridge. A Fuso Polarographic Analyzer Model 312 was used for measuring dc polarography, differential pulse polarography (D.P.P) and cyclic voltammetry (C.V.). A dropping mercury electrode or a hanging mercury drop electrode was used as a working electrode. The counter electrode was platinum.

An example of a cyclic voltammogram of Cu(R-sno)ClO_4 is shown in Fig. 1. All complexes of this series, Cu(R-sno)ClO_4, exhibit essentially identical electrochemical behavior irrespective of substituent groups. The reduction peak at -0.237 V vs. SCE seems to correspond to reduction of copper(II) to copper(I). No other reduction occurs until about -1.4 V vs. SCE, at which an irreversible reduction takes place. The anodic wave appears at 0.200 V vs. SCE. Although the anodic and cathodic peaks are almost symmetric, the separation between these peak potentials is much larger than 58 mV expected for a reversible one-electron process.[14] Controlled-potential electrolysis at a stirred mercury pool electrode was carried out in order to determine the number of electrons transferred. Since controlled-potential electrolysis at -0.6 V vs. SCE gave n value of 2.0 ± 0.1, it was confirmed that this reduction involves a two-electron process: Cu(II)-Cu(II) $\longrightarrow$Cu(I)-Cu(I). The results of cyclic voltammetry for Cu(R-sno)ClO_4 are listed

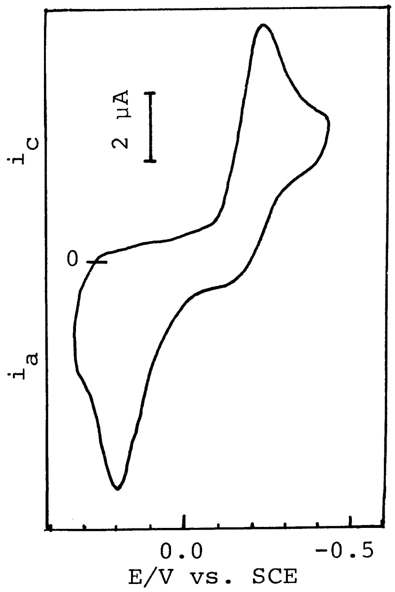


Fig. 1. Cyclic Voltammogram of Cu(C_2H_5-sno)ClO_4 in DMF.

Table 1. Cyclic Voltammetric and Differential Pulse Polarographic Data of Cu(R-sno)ClO_4.[a)]

Complex	C.V.		D.P.P.
R	E_{pc} [b)]	E_{pa} [c)]	E_p [d)]
CH_3	-0.248	0.207	-0.191
C_2H_5	-0.237	0.200	-0.171
n-C_3H_7	-0.227	0.182	-0.138
i-C_3H_7	-0.224	0.202	-0.195
n-C_4H_9	-0.217	0.201	-0.162
t-C_4H_9	-0.225	0.224	-0.197

a) DMF solution

b) E_{pc}=cathodic peak potential (V vs. SCE)

c) E_{pa}=anodic peak potential (V vs. SCE)

d) E_p=peak potential (V vs. SCE)

in Table 1. Polarograms measured by the use of dc polarography showed a maximum wave. On the other hand, differential pulse polarography provided a well-resolved polarogram, indicating a two-electron reduction near -0.2 V vs. SCE. The peak potentials E_p are given in Table 1. Previously, Aihara and Kubo showed that reductions of $Cu\{R_2N(CH_2)_2NH(CH_2)_3O\}X$ (R=CH_3, C_2H_5; X=ClO_4, $B(C_6H_5)_4$) occur at -0.4 $\sim$ -0.5 V vs. SCE in DMF.[10] Therefore, the substitution of the thioether group for the amino group raises the reduction potential of Cu(II)-Cu(II) → Cu(I)-Cu(I) by 0.2 $\sim$ 0.3 V. Positive shift of the Cu(II) → Cu(I) reduction potential by substituting sulfur donor atom for nitrogen or oxygen donor atom was also shown for mononuclear copper(II) complexes.[15,16]

A typical cyclic voltammogram of Cu(R-nso)X is shown in Fig. 2. An anodic and two cathodic peaks are observed for these complexes. The first step is quasi-reversible with a potential separation of 93 mV between the cathodic and the anodic peaks. The second step is irreversible showing only cathodic peak at -0.609 V. The results obtained for Cu(R-nso)X from cyclic voltammetry are summarized in Table 2. Dc polarograms for these complexes gave two cathodic waves. The differential pulse polarograms showed two symmetric peaks at 0.1 $\sim$ 0.2 and -0.3 $\sim$ -0.6 V vs. SCE, which are also given in Table 2. Based on controlled-potential electrolyses at -0.1 and -0.6 V vs. SCE, the number of electrons transferred at these potentials were determined to be one and two, respectively. Thus, it is clear that Cu(R-nso)X undergoes two one-electron reductions as follows: $Cu(II)\text{-}Cu(II) \longrightarrow Cu(II)\text{-}Cu(I) \longrightarrow Cu(I)\text{-}Cu(I)$. It is to be noted that the first reduction potential is the highest among binuclear copper(II) complexes so far reported and is close to those of type III coppers. High reduction potentials of these complexes may be interpreted in terms of the sulfur donation and the structural distortion from a square-plane.

The present work was partially supported by a Grant-in-Aid for Scientific Research No. 454199 from the Ministry of Education, Science and Culture.

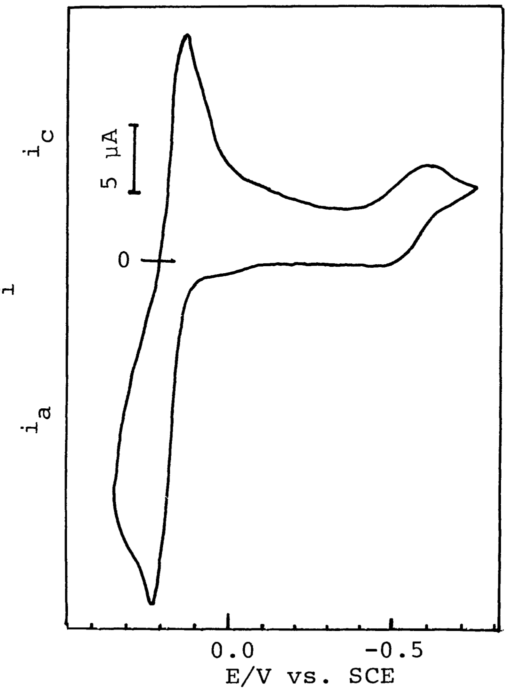


Fig. 2. Cyclic Votammogram of $Cu(n\text{-}C_3H_7\text{-}nso)Cl$ in DMF.

Table 2. Cyclic Voltammetric and Differential Pulse Polarographic Data of Cu(R-nso)X.[a)]

Complex		C.V.				D.P.P.	
		first step			second step	first step	second step
R	X	E_{pc} b)	E_{pa} c)	ΔE_p d)	E_{pc}	E_p e)	E_p
CH_3	Cl	0.107	0.218	0.111	-0.599	0.200	-0.490
C_2H_5	Cl	0.104	0.224	0.120	-0.542	0.128	-0.567
$n-C_3H_7$	Cl	0.118	0.211	0.093	-0.609	0.210	-0.461
$n-C_4H_9$	Cl	0.113	0.213	0.100	-0.585	0.184	-0.459
CH_3	Br	——	0.194	——	-0.420	0.147	-0.384
C_2H_5	Br	0.057	0.187	0.130	-0.443	0.146	-0.372
$n-C_3H_7$	Br	0.064	0.166	0.102	-0.456	0.165	-0.346
$n-C_4H_9$	Br	0.088	0.187	0.099	-0.440	0.163	-0.316

a) DMF solution

b) E_{pc}=cathodic peak potential (V vs. SCE)

c) E_{pa}=anodic peak potential (V vs. SCE)

d) $\Delta E_p = |E_{pc} - E_{pa}|$ (V)

e) E_p=peak potential (V vs. SCE)

References

1) Binuclear Metal Complexes. Part XXXIV. Part XXXIII: Ref. 13.
2) J. A. Fee, Structure and Bonding, 23, 1 (1975).
3) A. W. Addison, Inorg. Nucl. Chem. Lett., 12, 899 (1976).
4) R. R. Gagné, C. A. Koval, and T. J. Smith, J. Am. Chem. Soc., 99, 8367 (1977).
5) J. J. Grzybowski, P. H. Merrell, and F. L. Urbach, Inorg. Chem., 17, 3078 (1978).
6) D. E. Fenton, R. R. Schroeder, and R. L. Lintvedt, J. Am. Chem, Soc., 100, 1931 (1978).
7) D. E. Fenton and R. L. Lintvedt, J. Am. Chem. Soc., 100, 6367 (1978).
8) R. R. Gagné, C. A. Koval, T. J. Smith, and M. C. Cimolino, J. Am. Chem. Soc., 101, 4571 (1979).
9) R. R. Gagné, R. P. Kreh, and J. A. Dodge, J. Am. Chem. Soc., 101, 6917 (1979).
10) M. Aihara and K. Kubo, Rev. Polarogr. (Kyoto), 25, 44 (1979).
11) M. Mikuriya, H. Okawa, and S. Kida, Inorg. Chim. Acta, 34, 13 (1979).
12) M. Mikuriya, H. Okawa, and S. Kida, Inorg. Chim. Acta, submitted for publication.
13) M. Mikuriya, H. Okawa, and S. Kida, Bull. Chem. Soc. Jpn., submitted for publication.
14) R. S. Nicholson and I. Shain, Anal. Chem., 36, 706 (1964).
15) G. S. Patterson and R. H. Holm, Bioinorg. Chem., 4, 257 (1975).
16) D. E. Nikles, M. J. Powers, and F. L. Urbach, Inorg. Chim. Acta, 37, L499 (1979).

(Received April 28, 1980)