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Electrochemical Behavior of Alkoxo-bridged Binuclear Copper(II) Complexes with *N*,*N*-Dialkyl-*N*′-(hydroxyalkyl)alkanediamine

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Synopsis. The alkoxo-bridged binuclear copper(II) complexes with *N*,*N*-dialkyl-*N*′-(hydroxyalkyl)alkanediamine were investigated by electrochemical methods. The binuclear complexes exhibited two non-separable sequential, one-electron steps, the half-wave potentials of which were almost identical, in *N*,*N*-dimethylformamide. On the other hand, the complexes gave two distinctive one-electron reduction waves in acetonitrile.

Recently electrochemical investigations of binuclear copper(II) compounds have continued to increase. One of the interests in this field is the properties of the particular proteins in which a pair of copper(II) ions is strongly anti-ferromagnetically coupled.[1)] The copper atoms bound in such proteins are referred to as type III coppers. Binuclear metal nuclei in proteins usually undergo two-electron reduction in one step. A tentative series of intermediates during the reduction has been proposed.[2)] Synthetic binuclear copper(II) complexes exhibit either a one-electron reduction step[3–5)] or a two-electron reduction step.[6–8)]

The present report deals with the electrochemical behavior of the alkoxo-bridged binuclear copper(II) complexes with *N*,*N*-dialkyl-*N*′-(hydroxyalkyl)alkanediamine, $[Cu(R_2N(CH_2)_3NH(CH_2)_2O)]X$ (abbreviated hereafter as [Cu(R-3-2)]X, R=H, CH_3, C_2H_5 and $X=ClO_4^-$ or $B(C_6H_5)_4^-$) in non-aqueous solvents. A schematic structure of the complexes studied is illustrated in Fig. 1.

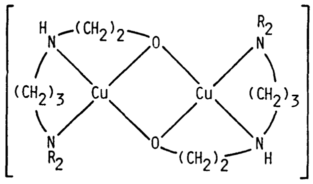

Fig. 1. Structure of the complexes of the [Cu(R-3-2)]X type.

Experimental

Synthesis of the Complexes: The complexes were prepared according to the method reported previously.[9)]

Electrochemical Measurements: All measurements were carried out in an 0.1 M tetraethylammonium perchlorate (TEAP) solution of *N*,*N*-dimethylformamide (DMF) or acetonitrile (AN) at 25±0.1 °C. A Fuso model 312 polarograph and a DME (or HMDE) were employed for polarographic and cyclic voltammetric measurements. The reference electrode was SCE with a salt bridge.[10)] Controlled-potential electrolysis was performed at a mercury pool under stirring. ESR controlled-potential electrolysis experiments were carried out under an atmosphere of nitrogen gas. The other apparatus was the same as described previously.[10)]

Results and Discussion

The typical current-sampled dc polarogram for the binuclear copper(II) complex with the $[Cu(C_2H_5\text{-}3\text{-}2)]$X formula in DMF is shown in Fig. 2. The second wave for the binuclear complex with the [Cu(H-3-2)]X type formula was observed at more negative regions (*ca.* −1.0 V *vs.* SCE) of potential, while the maxima were observed on the shoulder of the second waves for the binuclear complexes with $[Cu(C_2H_5\text{-}3\text{-}2)]$X or $[Cu(CH_3\text{-}3\text{-}2)]$X type formula. A detailed discussion of these waves, however, is omitted here.

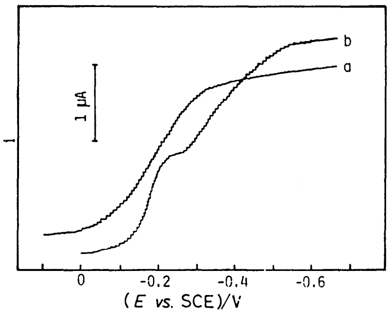

Fig. 2. Current-sampled d.c. polarograms of 0.5 mM $[Cu(C_2H_5\text{-}3\text{-}2)]$X in DMF (curve a) and AN (curve b).

TABLE 1. POLAROGRAPHIC DATA FOR [Cu(R-3-2)]X IN 0.1 M TEAP-SOLVENT AT 25 °C

	$E_{1/2}$ *vs.* SCE / V	I_d / μA	Slope / mV	n[a)]
In DMF				
[Cu(H-3-2)]X	−0.498	1.20	62	2.0
$[Cu(CH_3\text{-}3\text{-}2)]$X	−0.327	1.70	79	2.0
$[Cu(C_2H_5\text{-}3\text{-}2)]$X	−0.212	1.50	110	1.9
In AN				
[Cu(H-3-2)]X	−0.560	2.04	116	2.1
$[Cu(CH_3\text{-}3\text{-}2\text{-})]$X	−0.237[b)]	0.73	*ca.* 50	
	−0.452[c)]	1.05	117	2.1
$[Cu(C_2H_5\text{-}3\text{-}2)]$X	−0.166[b)]	0.96	*ca.* 50	
	−0.364[c)]	1.23	116	2.0

a) These values for *n* were determined by controlledpotential electrolysis at −0.7 V *vs.* SCE. b) First wave. c) Second wave.

The limiting current of each of the first steps was found to be diffusion-controlled. Table 1 gives the results obtained.

The typical cyclic voltammogram for the binuclear complex with the $[Cu(C_2H_5\text{-}3\text{-}2)]$X formula in DMF is shown in Fig. 3. The peak currents on the cathodic and anodic branches are nearly equal to each other, implying a reversible redox process, whereas the value of potential difference between the two redox peaks is larger than that (42 mV)[8)] of the difference theoretically expected for the reversible two-electron redox step, suggesting a quasi-reversible one.

Constant potential electrolysis was performed at a fixed potential regions more negative than those of the first waves. The results of electrolysis showed the consumption of two electrons for each complex molecule, as summarized in Table 1, suggesting that this process is a two-electron reduction. On electrolytic reduction,

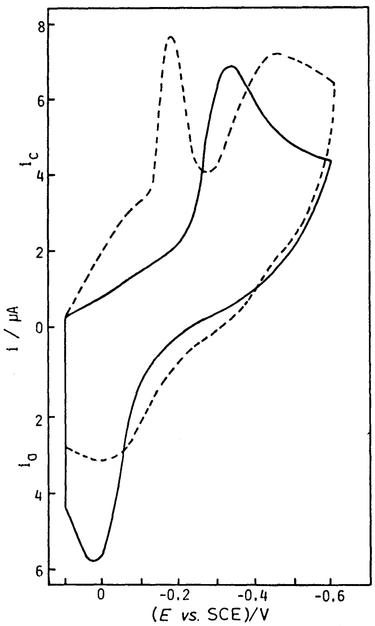

Fig. 3. Cyclic voltammograms of 0.5 mM [Cu(C_2H_5-3-2)]X in DMF (——) and AN (-----) at HMDE, scan rate 200 mV.

the originally green solution became yellow. Exposure to air gradually restored the green color again, suggesting that chemical oxidation can take place reversibly.

The first waves observed in DMF for the binuclear complexes with the [Cu(CH_3-3-2)]X or [Cu(C_2H_5-3-2)]X formula were found to split into two steps in AN as shown in Fig. 2. Differential pulse polarograms also showed two cathodic peak splittings.

The typical cyclic voltammogram of the binuclear complex with the [Cu(C_2H_5-3-2)]X formula in AN is shown in Fig. 3. The two peaks on the cathodic branch were clearly separated from each other, while those on the anodic one were not, suggesting an irreversible anodic process. Therefore, it was concluded that the chemical oxidation takes place reversibly, while the anodic oxidation cannot be followed due to the extremely rapid progress of the former even in a stream of nitrogen. The polarographic data are given in Table 1. Reduction of 1 mM [Cu(R-3-2)]X in AN solution at −0.7 V *vs.* SCE consumes two electrons per a complex molecule. The controlled-potential electrolysis at the potential region of the first wave in AN could not give any data available for the determination of number of electrons transferred because of a non-separable character of the first and the second waves, suggesting that no stable intermediate can exist. That is, the reduction product which had been prepared from the copper(II) complexes through the cathodic reduction did not show any anodic peak on the cyclic voltammogram. On the contrary, the reduced binuclear complexes with [Cu(C_2H_5-3-2)]X formula in AN showed four-line ESR patterns as shown in Fig. 4. These four-line patterns obtained for the frozen solution suggest the location of odd electrons on a single copper nucleus on the ESR time scale.

Voltammetric results in DMF showed that the three complexes undergo two sequential, one-electron reduction steps in which the reduction potentials of both steps are almost identical. The reduction process was quasi-reversible and the replacement of R by ethyl group caused a shift of the reduction potential of the first wave toward a more negative value.

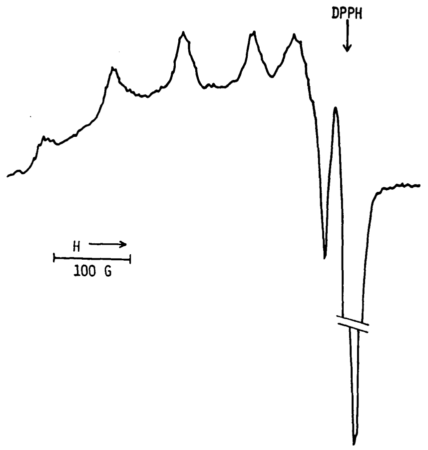

Fig. 4. ESR spectrum obtained for the frozen reduction product of the [Cu(C_2H_5-3-2)]X complex in AN, which was prepared by the controlled-potential electrolysis at −0.25 V *vs.* SCE.

On the other hand, voltammetric results in AN, coupled with those of ESR, showed two one-electron reduction steps occurring at different potentials as follows: Cu(II)–Cu(II)→Cu(II)–Cu(I)→Cu(I)–Cu(I). The solvation of AN may contribute to the formation of a "super complex" with a stable moiety of the Cu(II)–Cu(I) complex. The reduction potential of these complexes shift to a more positive direction of potential in order $H- < CH_3- < C_2H_5-$. The replacement of the *N*-substituent causes the sterical geometry of the complex to alter and simultaneously brings about the changes in properties of releasing electrons.

So far the effect of donor atoms on the standard redox potential of the coplanar Cu(II) complexes has been discussed and the order of positively-increasing redox potential of Cu(II)/Cu(I) couple was found to be $N_4 < N_2O_2 < N_2S_2$ donor sets.[7] The redox potential, E^0, of Cu(II)/Cu(I) couple for the binuclear complex with the [Cu(C_2H_5-3-2)]X formula in DMF was found to be −0.04 V *vs.* NHE, which was more positive than values of the Cu(II)/Cu(I) couple for the other synthetic complexes found in Ref. 7.

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