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Electrochemical Studies of Binuclear Copper(II) Complexes

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Two symmetrical binuclear complexes of copper(II) with Schiff base ligands have been studied by cyclic voltammetry. There is no evidence of difference between the $Cu^{II}Cu^{II}/Cu^{II}Cu^{I}$ and $Cu^{II}Cu^{I}/Cu^{I}Cu^{I}$ reduction potentials, nor of any $Cu^{I} \rightarrow Cu^{II}$ intervalence charge transfer. The mixed-valence $Cu^{II}Cu^{I}$ complexes are considered to be of the Robin and Day Class I.

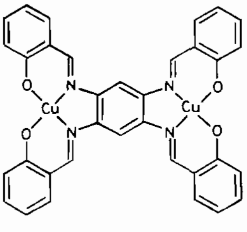
Introduction

The complexes $Cu_2^{II}(TSAB)$ (I) and $Cu_2^{II}(TSAMM)$ (II)** were prepared and reduction at the platinum electrode was studied by cyclic voltammetry. In principle, two one-electron processes are possible,

$$LCu^{II}Cu^{II} + \bar{e} \rightleftharpoons LCu^{II}Cu^{I}, E_1^{\ominus} \tag{1}$$

$$LCu^{II}Cu^{I} + \bar{e} \rightleftharpoons LCu^{I}Cu^{I}, E_2^{\ominus} \tag{2}$$

(where L denotes the macrocyclic ligand) and if the mixed-valence species is appreciably stabilised by resonance this is expected to be shown by the difference ($E_1^{\ominus} - E_2^{\ominus}$) [1]. Moreover, a stronger interaction might be expected in complex I where the metal sites are coplanar than in II where they are orthogonal. In fact, we find no appreciable interaction: the two copper sites in each complex appear to react independently and the spectra are similar to those of the mononuclear analogues Cu(SAB) (III) and Cu(SAP) (IV)**.



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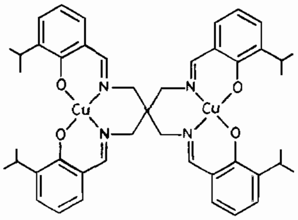

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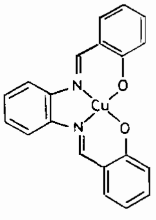

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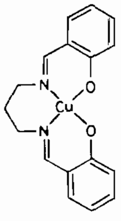

IV

Experimental

Preparation of the Complexes

$Cu_2(TSAB)2H_2O$

The di-salicylaldehyde complex of copper(II) [2], 0.61 g, was slowly added, under nitrogen, and with heating and stirring to a solution of 1, 2, 4, 5-tetraminobenzene tetrahydrochloride (ICN Pharmaceuticals Inc) 0.28 g, in methanol (3 ml) containing the appropriate concentration of sodium methoxide. The red-brown product was recrystallised from diphenyl ether to remove the insoluble polymer $Cu_4(TSAB)$ [3].

$Cu_2(TSAMM)$

o-isopropylsalicylaldehyde was prepared [4] from *o*-iso-propylphenol (Aldrich), and the copper(II) complex was obtained in the usual way [2]. Tetrakis(aminomethyl)methane was prepared by the

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**TSAB = 1,2,4,5-tetrakis(salicylaldimino)benzene, TSAMM = tetrakis(salicylaldiminomethyl)methane, SAB = 1,2-bis(salicylaldimino)benzene, SAP = 1,3-bis(salicylaldimino)propane.

TABLE I. Standard Electrode Potentials ($Cu^{II/I}$) from Cyclic Voltammetry.[a]

Complex	$E_1^{\ominus}/V^b$	$\Delta V_{pp}/V$
I	−1.28	0.100
II	−1.08	0.180
III	−1.01	0.300
IV	−1.11[c]	0.100

[a] T = 20 °C, DMF, 0.1 *M* $NaClO_4$. [b] ±0.01 V. [c] Gagné *et al.* reported $E_{1/2}$ = −1.099 V in DMF, 0.1 *M* (t-$Bu_4N[ClO_4]$) [9].

method of Litherland and Mann [5] and recrystallised from water as $[C(CH_2NH_3)_4][HSO_4]_4$. The copper complex (0.6 g) and amine bisulphate (0.25 g) were mixed with 4 ml water, then 4 ml ethanol and 6.1 ml 0.5 *M* NaOH, and refluxed for a minimum of 2 hours. The dark grey product, soluble in CH_2Cl_2, $CHCl_3$, acetone and methanol, had λ_{max} 630 nm, λ_{min} 552 nm. Cu(SAB) and Cu(SAP) were prepared by published methods [6] and recrystallised from chloroform. Solutions of these complexes in DMF were dried over molecular sieve prior to electrochemical measurements. Sodium perchlorate was recrystallised from water and dried in an oven at 120 °C. DMF was dried over anhydrous $CuSO_4$ or $MgSO_4$, redistilled twice, and stored over 4A molecular sieves [7].

Cobalt sepulchrate solutions were prepared by reducing cobalt(III) sepulchrate chloride [8] in DMF, with amalgamated zinc.

Measurements

For cyclic voltammetry the PAR 175 Universal Programmer and 174A Polarographic Analyzer were used. CV and potentiometric titrations were carried out in a double-walled glass cell, with water circulated for temperature control. Working electrodes were platinum wires, cleaned between each run by alternate heating and quenching in 1 *M* HNO_3. All measurements were carried out under nitrogen, scrubbed with $Cr^{2+}\cdot aq$ and dried by passing through conc. H_2SO_4. Reference electrodes were $Ag/AgNO_3$ in CH_3CN with 0.1 *M* $NaClO_4$ connected through a salt bridge containing DMF saturated with $NaClO_4$. Potentials reported here are *versus* n.h.e., standardised by running the ferrocene couple in the same medium, and taking $E^{\ominus}$ (Fe^+/Fc) = +0.400 V [9].

Results

Cyclic voltammograms for the mononuclear complexes showed only one wave in the range −1.0 to −2.0 V (*vs.* Ag^+/Ag). The peak-to-peak separations imply quasi-reversibility for the propylenediamine-based complex (IV) but irreversibility for the phenylenediamine complex (III). Both oxidation and reduction waves can be seen in both complexes, though, again in the complex III, the oxidation wave is less pronounced than the reduction wave. Values of $E^{\ominus}$ estimated as the mean of the peak values are listed in Table I. For complex IV, this agrees satisfactorily with a previous report [9].

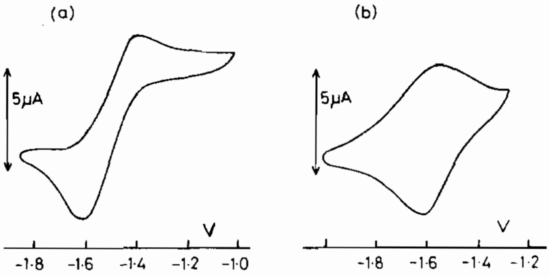

Fig. 1. Cyclic voltammograms of (a) Cu_2^{II} (TSAMM) and (b) Cu_2^{II} (TSABB), in DMF, 0.1 *M* $NaClO_4$, complex concentrations 1.0 × 10^{-4} *M*; reference electrode Ag/Ag^+ in CH_3CN with 0.1 *M* $NaClO_4$.

The binuclear complexes likewise exhibited only one wave, quasi-reversible, in the range −0.5 to −1.8 V (Fig. 1) in contrast to the complex studied by Gagné, which gave two reversible waves, separated by 0.39 V [9]. The observed potentials (Table I), compared with those of the mononuclear complexes, are consistent with the $Cu^{II/I}$ couple, eqn. 1. In an effort to detect the second reduction (2), solutions of $Cu^{II}Cu^{II}$ (TSAB) and $Cu^{II}Cu^{II}$ (TSAMM) were partially reduced, and the cyclic voltammetry was repeated with the semi-reduced solutions which corresponded stoichiometrically to $Cu^{II}Cu^{I}$. The reduction was carried out by titration with cobalt(II) sepulchrate [8]. The $Cu^{II/I}$ wave remained at the same potentials within experimental error (−1.08 ± 0.01 V, −1.28 ± 0.01 V).

In a further attempt to define the values of $E_1^{\ominus}$, and $E_2^{\ominus}$, solutions of $Cu^{II}Cu^{II}$ (TSAMM) were titrated potentiometrically with cobalt(II) sepulchrate. Typical titration curves are shown in Fig. 2. In all experiments only one end-point could be detected, corresponding to the overall 2:1 reaction

$$Cu^{II}Cu^{II}L + 2Co(sep)^{2+} = Cu^{I}Cu^{I}L + 2Co(sep)^{3+} \qquad (3)$$

Reaction (3) reaches equilibrium quite slowly ($t_{1/2}$ ~ 1 min with $[Cu_2]$ = 1 × 10^{-4} *M* and $[Co^{II}]$ = 1 × 10^{-3} *M*). The corresponding reaction with Cu_2-(TSAB) was much slower and reproducible potentials could not be obtained.

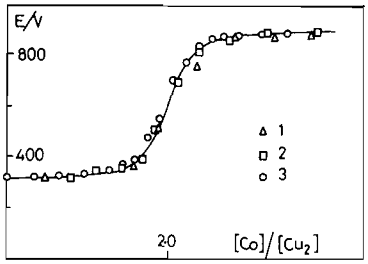

Fig. 2. Potentiometric titrations of Cu_2^{II} (TSAMM) with Co(sepulchrate)$^{2+}$, in DMF, 25 °C. Data points 1, 2, 3, concentrations $[Cu_2]_T$ = 1.0 × 10^{-7} *M*, 2.0 × 10^{-3} *M*, 3.0 × 10^{-7} *M*.

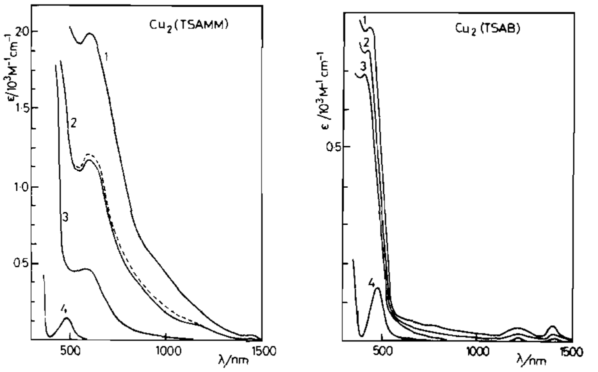

Fig. 3. Absorption spectra of Cu_2 (TSAMM) and Cu_2 (TSAB) and reduction products. DMF, 25 °C. Full-line curves: (1) the Cu_2^{II} complexes; (2) the same solutions after 50% reduction with Co(sep)$^{2+}$; (3) the same after 100% reduction; (4) Co(sep)$^{2+}$. The broken line is the average of spectra (1) and (3).

Absorption spectra of dicopper(II) complexes and of semi- and fully reduced solutions are shown in Fig. 3. For Cu_2(TSAMM), the extinction coefficients are large enough to ensure that interference by Co(sep)$^{3+}$ is negligible. The spectrum of the solution corresponding to $Cu^{II}Cu^{I}$ is indistinguishable from the mean of the $Cu^{II}Cu^{II}$ and $Cu^{I}Cu^{I}$ solution spectra, again in contrast to Gagné's mixed-valence complex [1], which shows bands at λ = 1300 and 1800 nm ($\epsilon \sim$ 400–600 M^{-1} cm^{-1}) assigned to intervalence charge-transfer [9]. For Cu_2(TSAB) there is also no absorption associated with the $Cu^{II}Cu^{I}$ oxidation state.

Conclusions

The similarity of the observed reduction potentials of the complexes to those of mononuclear analogues, the lack of difference between successive $E^{\ominus}$ values (eqn. 1, 2) and the absence of intervalence charge transfer bands, all indicate that in both systems I and II, interaction between the Cu^{II} and Cu^{I} centres is negligible. The mixed-valence species evidently belong to the Robin and Day Class I, as does the cobalt analogue of complex I, previously reported by Espenson and Kirker [10].

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