

Dicopper(II) and Dicopper(III) complexes with a Double-ring Octa-aza Macrocycle

Armando Buttafava, Luigi Fabbrizzi,* Angelo Perotti, and Barbara Seghi

Istituto di Chimica Generale ed Inorganica, Università di Pavia, Viale Taramelli, 12, 27100 Pavia, Italy

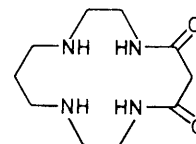
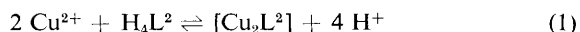
The novel double-ring octa-aza molecule (**2**) incorporates two copper(II) ions in aqueous solution, with simultaneous release of four protons; the resulting dicopper(II) complex shows a weak metal-metal interaction and is easily oxidized to the trivalent state by two consecutive one-electron steps separated by 110 mV.

Dinuclear metal complexes stable in solution are quite scarce.¹ This low thermodynamic stability prevents investigation of the solution properties (*e.g.* redox reactivity) of bi-metallic systems which are currently proposed as models for metalloproteins containing two or more proximate metal centres and which are also involved in electron transfer processes.² Previous experience of the co-ordinating properties in solution of the cyclic molecule (**1**) (H_2L^1) prompted us to develop dinucleating ligands in which two subunits of type (**1**) were linked through carbon atoms.† Macrocycle (**1**) incorporates a copper(II) ion with simultaneous deprotonation of two amido-groups to form a very stable complex³ and permits the oxidation of the encircled cation to the trivalent state at a relatively low potential, 0.65 V *vs.* standard calomel electrode (S.C.E.), at 25 °C in 1M KCl.⁴

Previous synthetic routes to analogous double-ring molecules have involved linking through the nitrogen atoms of pre-cyclized subunits.⁵ However, the present approach is more

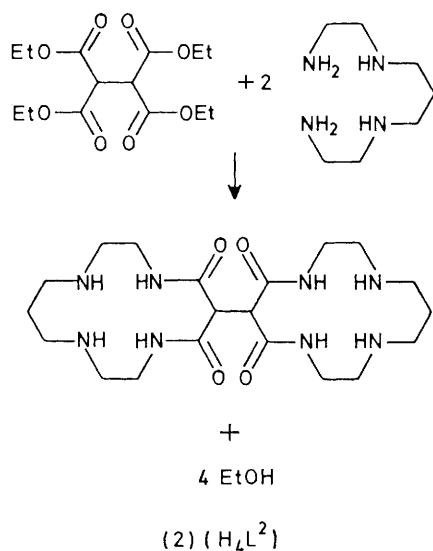
simple and direct and involves the one-step aminolytic condensation of tetraethyl 1,1,2,2-ethanetetra-carboxylate with 2 equiv. of 1,4,8,11-tetra-aza-undecane (5×10^{-2} mol dm⁻³, refluxing ethanol, 3 days).

The double-ring octa-aza macrocycle (**2**) (H_4L^2) separated as microcrystals on concentration of the ethanolic solution (yield 30%). Titration with standard base of an aqueous solution containing (**2**) and Cu^{2+} in a 1:2 molar ratio showed that, in the pH range 4–5.5, two copper(II) ions are incorporated by the ligand and four protons are released.



(1) (H_2L^1)

† Substitution on nitrogen atoms may drastically reduce the co-ordinating ability of the ligand towards transition metal ions.



The constant for equilibrium (1) was calculated through computer analysis of the titration data⁶ ($\log K = -1.343 \pm 0.005$, at 25 °C, in 0.1 mol dm⁻³ aqueous NaClO₄).[‡]

The X-band e.s.r. spectrum§ of a frozen aqueous solution of [Cu₂L²], Figure 1(B), was compared with that of the mononuclear reference species [CuL¹] [Figure 1(A)]. Figure 1(B) is typical of a triplet state in which the metal-metal interaction is much greater than the hyperfine interaction, the value of A_{\parallel} (100 gauss) (1 gauss = 10⁻⁴ T) being very close to a half of that found for the monomeric species [Figure 1 (A), 210 gauss].

In the spectrum (B) two septuplets can be identified and their barycentres are separated by a value of $2D_{\parallel} = ca. 136$ gauss = 0.0126 cm⁻¹.¶ Assuming that the zero-field splitting is purely dipolar⁷ and using the equation⁸ $D_{\parallel} = 0.65 g_{\parallel}^2/R^3$, a value of R , the Cu-Cu distance, of 7.8 Å can be calculated.

Examination of scale molecular models suggests that this distance could correspond to a stereochemical arrangement in which the double-ring complex is stretched to keep the two subunits as far apart as possible [as in formula (2), but with the two macrocycles lying in different planes owing to the tetrahedral nature of the two linking carbon atoms].

The differential pulse voltammetry profile of an aqueous solution of [Cu₂L²], obtained using a carbon paste electrode, showed two well separated peaks [$E_{p1} = 0.578$ V, $E_{p2} = 0.681$ V; at the pulse amplitude used (10 mV) $E_{1/2}$ values corresponding⁹ to these peaks are $E_{1/2}(1) = 0.58$ and $E_{1/2}(2) =$

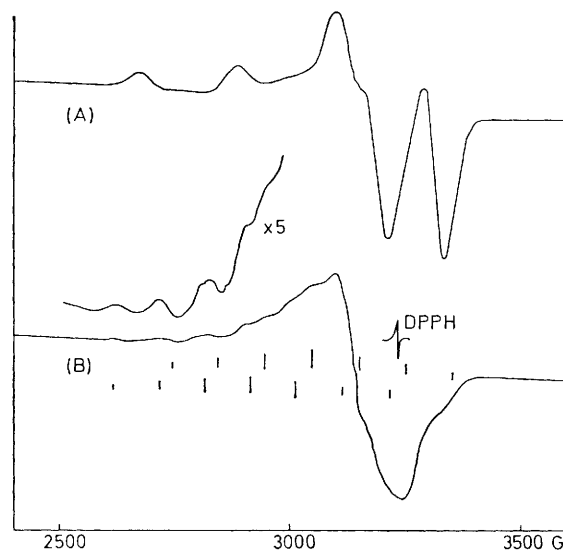


Figure 1. E.s.r. spectra of aqueous frozen solution (77 K, 0.1 M NaClO₄) containing (A) CuL¹ and (B) Cu₂L². DPPH = diphenylpicrylhydrazyl.

0.69 V vs. S.C.E.]. The intensity of each individual peak is very close to that found for a CuL¹ solution with the same concentration of metal complex. The behaviour is consistent with the stepwise one-electron oxidation of each metal centre. The separation of the potentials $\Delta E_{1/2}$ (110 mV) is slightly greater than that expected on a purely statistical basis (35.61 mV) and may reflect the electrostatic repulsion between the copper ions, separated by *ca.* 8 Å. In this connection one should consider that the two cations are partially shielded by the negative charge on the deprotonated amido-groups which interface the metal centres.

Most of the redox processes of general interest, *e.g.* oxidation or reduction of organic and biorganic substrates, involve the release/uptake of a pair of electrons in a single step. Complexes of the type described here, in which the two metal centres are a relatively short distance apart and exhibit quasi-independent redox activity, may be considered as potential redox catalysts for these two-electron processes.

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‡ H₄L², which contains four amine nitrogen atoms, behaves in aqueous solution as a tetraprotic base, with the following stepwise protonation constants:

$H_{4+(n-1)}(L^2)^{(n-1)+} + H^+ \rightleftharpoons H_{4+n}(L^2)^{n+}$ $n = 1-4$;
0.1M NaClO₄ at 25 °C (log units) ($n = 1$) 9.96 ± 0.01; ($n = 2$) 9.45 ± 0.01; ($n = 3$) 5.40 ± 0.02; ($n = 4$) 4.62 ± 0.01.

§ E.s.r. and electrochemical studies refer to solutions containing (2) and Cu²⁺ and adjusted to the minimum pH at which the [Cu₂L²] species is present as 100%.

¶ g_{\perp} (2.03 calc. from $g_{\parallel} + 2g_{\perp} = 3g_{iso}$) and g_{\parallel} (2.17) values for [Cu₂L²] are equal to those found for [CuL¹] (2.03 and 2.17, respectively). Furthermore, the room temperature spectrum of aqueous [Cu₂L²] corresponds to a triplet situation: the signal, centred at a value of $g_{iso} = 2.08$, is split into seven peaks and the corresponding a value (*ca.* 48 gauss) is half of that found for the [CuL¹] complex under the same conditions [$g_{iso} = 2.08$; a (Cu) = 95 gauss].

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