Aqueous Copper(III) and Nickel(III) Tetra-aza-macrocyclic Complexes

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Summary. The copper(III) and nickel(III) complexes with the novel tetra-aza-macrocycle 1,4,8,11-tetra-azacyclotetradecane-5,7-dionato(2−) $(L^2)^{2-}$, which contains two deprotonated amido groups, can be generated in aqueous solution by chemical or anodic oxidation of the corresponding Cu^{II} and Ni^{II} species and the authenticity of the oxidation states is demonstrated by voltammetric and e.s.r. investigations.

Encircling of nickel by the 14-membered tetra-amine macrocycle L^1 makes the trivalent state easily accessible,[1] as indicated by the moderately positive $E_{\frac{1}{2}}$ value for the $+2/+3$ redox couple [$E_{\frac{1}{2}}$ $(NiL^1)^{2+/3+}$ 0·97 V *vs.* standard calomel electrode (SCE), in MeCN–0·1 M Et_4NBF_4].[2] Essentially owing to the larger value of the third ionization energy, the attainment of the trivalent state for the copper analogue is much more difficult [$E_{\frac{1}{2}}$ $(CuL^1)^{2+/3+}$ 1·37 V *vs.* SCE, in MeCN–0·1 M Et_4NBF_4]. Furthermore, copper(III) complexes with tetra-amine macrocycles are also unstable in anhydrous acetonitrile[3] and cannot be obtained at all in water.

The copper(II) complex with the tetra-aza-macrocycle $(L^2)^{2-}$, which contains two deprotonated amido groups and two amine nitrogen atoms, dissolves in water as a non-electrolyte† and is insoluble in the most common organic solvents. The complex $[Cu^{II}L^2]$ in aqueous solution undergoes both chemical (using $K_2S_2O_8$) and anodic (at a platinum gauze electrode, at about 0·8 V *vs.* SCE) one-electron oxida-

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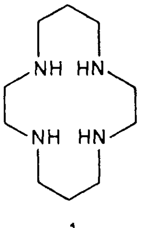
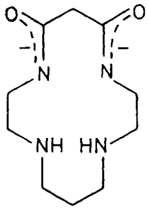
† Complexation of H_2L^2 with Cu_2^+ in aqueous solution, which involves the simultaneous deprotonation of the two amido groups, has been recently investigated through pH-metric titrations (see M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1979, 325).

tion, to produce a yellow-brown solution. This process involves the disappearance of the Cu^{II} four-line e.s.r. signal: this is consistent with the formation of a d^8 complex cation and shows that the oxidation produces an authentic copper-(III) species. Furthermore, addition of a reducing agent (*e.g.* Na$_2$SO$_3$) or imposition of a less positive potential to the platinum gauze electrode, dipped in the yellow solution of the Cu^{III} complex, restores the pink-violet Cu^{II} species. The aqueous $[\mathrm{Cu^{III}L^2}]^+$ complex is not indefinitely stable, but decomposes after a few hours at room temperature. Cyclic voltammetry studies at a carbon paste electrode in 0·1—3·0 M KCl solution showed reversible profiles, in which the ratio of the anodic and cathodic peaks was unity in the explored range of potential scan rate (5—500 mV s^{-1}), and the peak separation was close to 60 mV, as expected for a reversible one-electron process.[4] The $E_{\frac{1}{2}}$ value is moderately positive (0·65 V *vs.* SCE, in 1 M KCl, at 25 °C).



L^1



(L^2)$^{2-}$

Analogous behaviour is observed with nickel; oxidation of the yellow diamagnetic non-electrolyte [Ni^{II}L^2] produces a brown aqueous solution of the Ni^{III} macrocyclic complex. The e.s.r. spectrum of a (5:1) water–methanol solution of the Ni^{III} species, frozen at liquid nitrogen temperature, shows axial symmetry, with $g_\perp$ (2·23) higher than $g_\parallel$ (2·02): this is consistent with the formation of a low-spin d^7 chromophore in an octahedral environment, $[\mathrm{Ni^{III}(L^2)(H_2O)_2}]^+$, and establishes unambiguously the authenticity of the Ni^{III} state. The $E_{\frac{1}{2}}$ value for the Ni^{II}/Ni^{III} redox change, determined from cyclic voltammetry experiments‡ (0·56 V *vs.* SCE, in 1 M KCl, at 25 °C), is somewhat less positive than that of the copper analogue, indicating a slightly easier attainment of the trivalent state. However, the difference between the redox potential values of the copper and nickel complexes with (L^2)$^{2-}$ ($<$0·1 V) appears to be considerably reduced in comparison with that found for the complexes of the 14-membered tetra-amine macrocycle L^1 in acetonitrile solution (0·4 V).

This behaviour may reflect the greater gain in crystal field stabilisation energy in a tetragonal environment for the Cu^{II}(d^9)/Cu^{III}(d^8) redox change, with respect to the Ni^{II}(d^8)/Ni^{III}(d^7) process,[5] as one moves from the tetra-amine macrocycle L^1 to a ligand of enhanced electron donor properties, such as the two-fold negatively charged tetra-aza ligand (L^2)$^{2-}$. The selective stabilisation of Cu^{III} with respect to Ni^{III} by deprotonated amido groups has been observed for polypeptide complexes.[6]

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‡ Unlike the copper analogue, the nickel complex attains a quasi-reversible behaviour at the carbon paste electrode only at an electrolyte concentration ⩾ 1 M.

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