Stabilization by a Strongly Acidic Medium of Trivalent Copper Tetra-aza Macrocyclic Complexes

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The otherwise unstable Cu^{III} complexes with tetra-aza macrocycles (1)—(3) are stabilized in strongly acidic solutions; the Cu^{III} complex with the diene macrocycle (1) shows a greater stability (in 10 M $HClO_4$) than the corresponding Ni^{III} complex, an inversion of the normally observed trend.

Tetra-aza macrocycles stabilize unusually high oxidation states of co-ordinated metal ions (e.g. Ni^{III}, Ag^{II}, Ag^{III}),[1—3] this unique property resulting from combined kinetic and thermodynamic effects.[4]

Copper(III) complexes with both saturated and unsaturated tetra-aza ligands such as (1), (2), and (3) can be generated electrochemically only in anhydrous acetonitrile;[5,6] they tend to decompose with liberation of Cu^{II} cation, fragmentation of the ligand, and simultaneous release of protons.[5,7] A general mechanism for the decomposition of bivalent tetra-aza macrocyclic complexes has been proposed[8] which involves as the first step the formation of a metal radical–ligand species and release of protons: this process is accelerated by bases such as pyridine, triethylamine, and water. In fact, attempts to produce $[Cu^{III}\cdot(3)]^{3+}$ through electrochemical oxidation in water of the corresponding Cu^{II} complex caused instan-taneous decomposition of the complex through a multi-electron process.[9] The above findings suggested that decom-position of the Cu^{III} complex could be quenched or made slower in the presence of acid and prompted us to attempt the preparation of Cu^{III} tetra-aza macrocyclic complexes in strongly acidic solution.
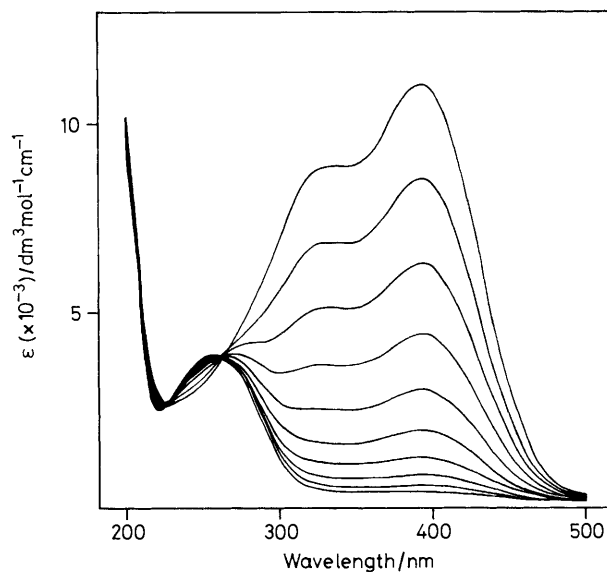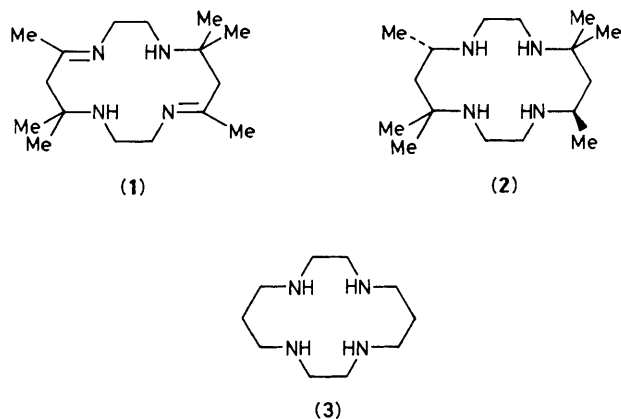
(1)

(2)

(3)

Figure 1. Time-dependent absorption of the $[Cu^{III}\cdot(1)]^{3+}$ complex in 10 M $HClO_4$ solution, generated through controlled potential electrolysis. Spectra were taken every 40 minutes. The intensity of the 400 nm band decreased with time. The calculated half-life time of the trivalent complex is 87 min.
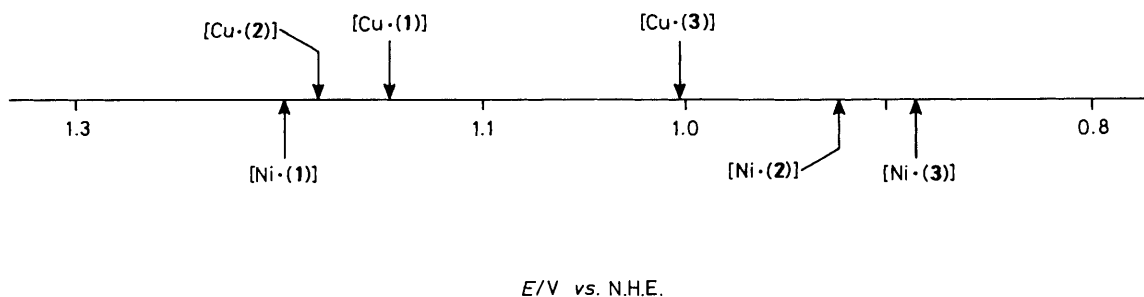
E/V vs. N.H.E.

Figure 2. Half-wave potential values for the M^{III}/M^{II} redox couple (M = Ni, Cu) in tetra-aza macrocyclic complexes, in 10 M $HClO_4$ solution at 25 °C.

We have found that the controlled potential electrolysis (using a platinum gauze as anode) of a solution of $[Cu^{II}\cdot(1)](ClO_4)_2$ in 10 M $HClO_4$† involves the consumption of 1 mol of electrons per mol of the starting complex and generates a bright yellow solution of the Cu^{III} species. The kinetic stability of the trivalent complex was monitored through the decay of the 400 nm band in the u.v. spectrum (see Figure 1). The typical Cu^{III}(tetramine) bands decreased according to a first-order pattern indicating a $t_{1/2}$ value of 87 min.‡§ The authenticity of the oxidation state of the $[Cu\cdot(1)]^{3+}$ complex was demonstrated by e.s.r. experiments performed on frozen solutions (77 K); on completion of the exhaustive electrolysis the 4-line signal of the Cu^{II} complex disappeared, as expected for the formation of a d^8 (low-spin) cation.¶

Cyclic voltammetry (c.v.) of the $[Cu^{II}\cdot(1)](ClO_4)_2$ complex in 10 M $HClO_4$ solution, using a platinium working electrode, showed a fully reversible (ΔE_p = 60 mV, $i_{p.a.}/i_{p.c.}$ = 1) one-electron oxidation process profile centred at an $E_{1/2}$ value of 1.09 V vs. normal hydrogen electrode (N.H.E.). A silver wire was used as pseudo-reference electrode, which was standardized against the Fe^{3+}/Fe^{2+} redox couple. In this connection iron metal was allowed to dissolve in the solution of the Cu^{II} complex and the two wave profile (Fe^{2+}/Fe^{3+} and CuL^{2+}/CuL^{3+}) was recorded. The $E_{1/2}$ (Fe^{3+}/Fe^{2+}) value in 10 M $HClO_4$ (0.750 V vs. N.H.E.) was obtained by extrapolation using the equation reported by Ciavatta and Bieder-

mann.**[11] The effect of acidity on the kinetic stability of the $[Cu^{III}\cdot(1)]^{3+}$ complex was investigated by recording the c.v. curves for solutions of decreasing concentration of $HClO_4$. A reversible c.v. behaviour was maintained down to 2—3 M $HClO_4$ solution, indicating that for an acid concentration lower than this limiting value the trivalent species is no longer stable even on the time scale of c.v. experiments (performed at a potential scan rate of 100 mV s^{-1}).

Reversible c.v. responses were also obtained in 10 M $HClO_4$ solution for the one-electron oxidation of Cu^{II} complexes with the saturated analogues (2) and (3): corresponding $E_{1/2}(Cu^{III}/Cu^{II})$ values are reported in the diagram in Figure 2. The most stable Cu^{III} complex, in a thermodynamic sense, is that with the unsubstituted fully saturated macrocycle (3), for which the less positive value of $E_{1/2}$ was found. In spite of its greater thermodynamic stability, the $[Cu^{III}\cdot(3)]^{3+}$ complex is much less stable than that of the unsaturated analogue (1). In fact, in the controlled potential coulometry experiment performed in a 10 M $HClO_4$ solution of $[Cu^{II}\cdot(3)](ClO_4)_2$, the current did not decrease to zero and the integrated signal continued to increase indefinitely with a constant slope: this behaviour is indicative of a decomposition process occurring on a time scale considerably lower than that of the coulometric experiment. Moreover, c.v. studies at varying concentrations of acid showed a reversibility limit at 8.5/8.0 M $HClO_4$ concentration.

For comparison the Ni^{III}/Ni^{II} couples in the same tetra-aza macrocyclic systems were investigated in 10 M $HClO_4$ solution and the $E_{1/2}$ values of the reversible redox changes are reported in Figure 2. On the basis of the values of the third ionization potential, the formation of Ni^{III} species is expected to occur at a less positive potential than Cu^{III}: this happens in the case of the unsubstituted macrocycle (3), even though the difference in the redox potential values, 0.12 V, is much lower than that observed in the gas phase process, ΔI_3 = 1.6 V. The behaviour of the metal complexes with the hexamethyl substituted ligands (1) and (2) is surprising: in the case of the saturated macrocycle (2), the expected trend was observed, $E_{1/2}(Ni^{III}/Ni^{II})$ being less positive than $E_{1/2}(Cu^{III}/Cu^{II})$. In contrast, for the unsaturated macrocycle (1), the inverse tendency was found: the formation of the trivalent copper complex being favoured with respect to that of nickel. A

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† Cu^{II} complexes with the 14-membered macrocycles investigated here are inert with respect to acid attack (owing to the so-called *kinetic macrocyclic effect*) and persist in solution, as monitored through the intensity of the d–d absorption band.

‡ There is some evidence that kinetic stability of the electrochemically generated Cu^{III} complexes described here depends upon the purity of the acidic medium employed. Among the concentrated perchloric acid solutions commercially available that we have tested, the most satisfactory behaviour was with $HClO_4$ 70% Riedel-DeHaën, RG für Analyse, which was used without further purification.

§ Oxidation of $[Cu^{II}\cdot(1)]^{2+}$ to the trivalent state can also be accomplished chemically using $Na_2S_2O_8$ as oxidizing agent. However this oxidation process is fairly slow and is complicated by the decay process of the so-formed Cu^{III} complex.

¶ The absence of the e.s.r. signal does not demonstate the low-spin nature of the Cu^{III} complex. We assume that the Cu^{III} tetra-aza macrocyclic complexes investigated here are diamagnetic in analogy with the planar Cu^{III} complexes with polypeptides, which display a similar spectral pattern and for which diamagnetism has been ascertained both in solution and in the solid state (ref. 10).

** We preferred to use an extrapolated value, rather than to perform a direct measurement of the half-wave potential of the Fe^3/Fe^{2+} redox couple vs. a standard reference electrode (e.g. the standard calomel electrode), since this value would definitely include a large contribution due to the junction potential. In any case, the choice of the reference electrode potential does not affect the significance of the comparison of $E_{1/2}$ values for the M^{III}/M^{II} complex systems investigated here (vide infra).

possible explanation lies in the different donor properties of the macrocycles and in the selective crystal field stabilisation energy (C.F.S.E.) contribution of the M^{III}/M^{II} redox change. The unsaturated ligand (1) exerts stronger co-ordinative interaction (possibly owing to constrictive effects) towards the encircled cation than (2), as shown by the energy of the d–d absorption band of the Ni^{II} (low-spin) and Cu^{II} complexes: $\{[Ni^{II}\cdot(1)]^{2+}$ 23580, $[Ni^{II}\cdot(2)]^{2+}$ 21550, $[Cu^{II}\cdot(1)]^{2+}$ 21380, $[Cu^{II}\cdot(2)]^{2+}$ 20830 cm^{-1}, measured in 10 M $HClO_4$ solutions$\}$. On the other hand, the Cu^{III}/Cu^{II} conversion ($d^9 \rightarrow d^8$ low-spin, in a square planar geometry) profits from a C.F.S.E. contribution owing to an increase of the donor tendencies of the ligand (12.28 Dq units) whereas the Ni^{II} (d^8 low-spin, square planar) to Ni^{III} (d^7 low-spin, octahedral) process is disfavoured by 6.56 Dq units, cancelling the favourable contribution due to the increase of electrical charge of the cation. An inversion of the gaseous stability trend of Ni^{III} and Cu^{III} states has previously been found in complexes with strongly donating ligands such as those containing deprotonated peptido/amido groups (polypeptides[12] and diamido macrocycles[13]).

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