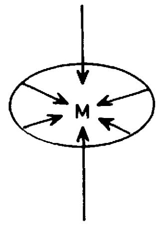
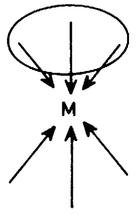
Studies on Transition-metal Macrocyclic Complexes. Single-crystal *X*-Ray Structure and Electrochemistry of the Bis-macrocyclic Complex $[Cu(L)_2][ClO_4]_2\cdot 2H_2O$ (L = 1,4,7-Triazacyclononane)†

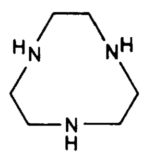
Andrew D. Beveridge, Aidan J. Lavery, Malcolm D. Walkinshaw, and Martin Schröder *
Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

A structural and electrochemical study of the bis-sandwich complex $[Cu(L)_2]^{2+}$ (L = 1,4,7-triazacyclononane) is reported. $[Cu(L)_2][ClO_4]_2\cdot 2H_2O$ crystallises in the monoclinic space group *Ca* (alternative setting for $P2_1/a$ with *c* axis unique), with $a = 9.533(3)$, $b = 16.909(8)$, $c = 13.653(9)$ Å, $\gamma = 89.22(3)°$, and $Z = 4$. The structure of the complex shows a centrosymmetric CuN_6^{2+} cation with a distorted octahedral copper(II) ion bound to each nitrogen donor atom of the macrocyclic ligands [Cu–N = 2.233(7), 2.176(6), and 2.087(6) Å]. The stereochemistry of $[Cu(L)_2]^{2+}$ is compared to the structures of related complexes of tridentate ligands. Cyclic voltammetry of $[Cu(L)_2][ClO_4]_2$ in acetonitrile (0.1 mol dm^{-3} $NBu^n_4ClO_4$) at platinum electrodes shows an irreversible oxidation at $E_{pa} = +0.95$ V *vs.* $[Fe(\eta\text{-}C_5H_5)_2]$–$[Fe(\eta\text{-}C_5H_5)_2]^+$ at a scan rate of 130 mV s^{-1} at 292 K; at an increased scan rate of 1.3 V s^{-1}, the redox couple becomes more reversible and $I_{pc}/I_{pa} = 0.80$. This Cu^{II}–Cu^{III} couple shows greater reversibility at 254 K with $E_{pa} = +0.91$ and $E_{pc} = +0.81$ V *vs.* $[Fe(\eta\text{-}C_5H_5)_2]$–$[Fe(\eta\text{-}C_5H_5)_2]^+$ and $I_{pc}/I_{pa} = 1$ at a scan rate of 260 mV s^{-1}. The electrochemical behaviour of $[Cu(L)_2]^{2+}$ is compared to that of the mono-macrocyclic species $[Cu(L)]^{2+}$.

Transition-metal complexes incorporating macrocyclic ligands are well known to represent kinetically inert, thermodynamically stable systems. A large amount of literature has built up around complexes of tetradentate macrocycles which usually show equatorial co-ordination around metal centres to leave two mutually *trans*, axially labile sites [see (A)].[1] Unlike their tetradentate analogues, however, tridentate macrocycles bind to metal ions in a facial manner leaving three mutually *cis* labile sites in the co-ordination sphere of the resulting complex [see (**B**)]. This opens up the possibility of using tridentate macrocycles as protecting groups for metal ions analogous to carbocyclic cyclopentadienyl and aryl ligands, and for the redox activation of co-ordination sites for catalytic reactivity. In addition, the binding of two macrocycles to one metal ion to form bis-sandwich species can be achieved with such minicycles.


(**A**)


(**B**)


L

The binding of 1,4,7-triazacyclononane (L) to form 1:1, M:L mononuclear[2–7] and binuclear[6–9] complexes and 1:2, M:L products[2–5,7,10–13] has been reported for a wide range of metal ions. Several potentiometric studies on the co-ordination of tridentate macrocyclic ligands to Cu^{2+} have been reported,[3,14–16] while more recently the role of such ligands in the modelling of copper protein and hemerythrin analogues has been described.[9,17] The single-crystal *X*-ray structures of $[CuBr_2(L)]$,[18] $[CuCl_2(L)]$,[19] and $[Cu(NO_3)(tcd)]NO_3$ (tcd = 1,4,7-triazacyclododecane)[17] confirm the facial co-ordination of the tridentate macrocycles in these five-co-ordinate complexes.

As part of a study of tridentate ligand co-ordination to transition-metal centres,[20] we have investigated the co-ordination of L to copper(II) and report herein the single-crystal *X*-ray structure and redox properties in acetonitrile of the bis-sandwich complex $[Cu(L)_2][ClO_4]_2$. We were interested particularly in comparing this system with the corresponding nickel complex $[Ni(L)_2]^{2+}$ which shows a trigonally distorted octahedral stereochemistry with Ni–N = 2.102, 2.098, and 2.111 Å.[10] Amine co-ordination to copper(II) under aqueous conditions is well known to occur readily with four or five nitrogen donor atoms, while the sixth nitrogen donor binds much more weakly.[21] We wished to confirm the co-ordination geometry of the bis-macrocylic copper(II) complex in which the symmetric facial co-ordination preferred by the tridentate ligands would be counterbalanced by Jahn–Teller distortion imposed by the d^9 metal ion. The complex $[Ni(L)_2]^{2+}$ shows a quasi-reversible oxidation at +0.95 V *vs.* a normal hydrogen electrode (n.h.e.) to yield the corresponding nickel(III) species $[Ni(L)_2]^{3+}$;[11,12] the nickel(III) complex of the related ligand 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetate has also been generated.[22] The half-lives of a series of unstable copper(III) complexes incorporating tetra- and penta-aza macrocycles have been determined and compared to corresponding Ni^{III} species;[23,24] the reversible oxidative

---

† Bis(1,4,7-triazacyclononane-*N*,*N*′,*N*″)copper(II) perchlorate dihydrate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Bond lengths (Å), and angles (°), and torsion angles (°) for $[Cu(L)_2][ClO_4]_2\cdot 2H_2O$

Cl(1)–O(1)	1.419(7)	N(1)–C(9)	1.472(11)
Cl(1)–O(2)	1.415(8)	C(2)–C(3)	1.525(12)
Cl(1)–O(3)	1.448(7)	C(3)–N(4)	1.447(11)
Cl(1)–O(4)	1.417(9)	N(4)–C(5)	1.459(10)
Cu(1)–N(1)	2.233(7)	C(5)–C(6)	1.535(12)
Cu(1)–N(4)	2.087(6)	C(6)–N(7)	1.468(11)
Cu(1)–N(7)	2.176(6)	N(7)–C(8)	1.480(10)
N(1)–C(2)	1.466(10)	C(8)–C(9)	1.554(11)

O(1)–Cl(1)–O(2)	108.6(4)	N(1)–C(2)–C(3)	111.6(7)
O(1)–Cl(1)–O(3)	110.6(4)	C(2)–C(3)–N(4)	111.3(7)
O(1)–Cl(1)–O(4)	110.0(5)	Cu(1)–N(4)–C(3)	105.7(5)
O(2)–Cl(1)–O(3)	109.1(4)	Cu(1)–N(4)–C(5)	111.2(5)
O(2)–Cl(1)–O(4)	109.2(5)	C(3)–N(4)–C(5)	114.8(6)
O(3)–Cl(1)–O(4)	109.4(5)	N(4)–C(5)–C(6)	112.9(7)
N(1)–Cu(1)–N(4)	80.73(25)	C(5)–C(6)–N(7)	110.4(7)
N(1)–Cu(1)–N(7)	80.22(24)	Cu(1)–N(7)–C(6)	102.9(5)
N(4)–Cu(1)–N(7)	81.97(25)	Cu(1)–N(7)–C(8)	111.1(5)
Cu(1)–N(1)–C(2)	107.9(5)	C(6)–N(7)–C(8)	111.6(6)
Cu(1)–N(1)–C(9)	103.5(5)	N(7)–C(8)–C(9)	110.9(6)
C(2)–N(1)–C(9)	116.0(6)	N(1)–C(9)–C(8)	109.7(6)

N(4)–Cu(1)–N(1)–C(2)	9.2(5)
N(4)–Cu(1)–N(1)–C(9)	−114.3(5)
N(7)–Cu(1)–N(1)–C(2)	92.6(5)
N(7)–Cu(1)–N(1)–C(9)	−30.9(5)
N(1)–Cu(1)–N(4)–C(3)	−32.7(5)
N(1)–Cu(1)–N(4)–C(5)	92.4(5)
N(7)–Cu(1)–N(4)–C(3)	−114.1(5)
N(7)–Cu(1)–N(4)–C(5)	11.1(5)
N(1)–Cu(1)–N(7)–C(6)	−114.4(5)
N(1)–Cu(1)–N(7)–C(8)	5.1(5)
N(4)–Cu(1)–N(7)–C(6)	−32.5(5)
N(4)–Cu(1)–N(7)–C(8)	87.0(5)
Cu(1)–N(1)–C(2)–C(3)	15.6(8)
C(9)–N(1)–C(2)–C(3)	131.2(7)
Cu(1)–N(1)–C(9)–C(8)	51.6(7)
C(2)–N(1)–C(9)–C(8)	−66.4(8)
N(1)–C(2)–C(3)–N(4)	−46.1(9)
C(2)–C(3)–N(4)–Cu(1)	52.3(7)
C(2)–C(3)–N(4)–C(5)	−70.6(9)
Cu(1)–N(4)–C(5)–C(6)	12.7(8)
C(3)–N(4)–C(5)–C(6)	132.6(7)
N(4)–C(5)–C(6)–N(7)	−42.9(9)
C(5)–C(6)–N(7)–Cu(1)	48.1(7)
C(5)–C(6)–N(7)–C(8)	−71.1(8)
Cu(1)–N(7)–C(8)–C(9)	21.2(7)
C(6)–N(7)–C(8)–C(9)	135.4(7)
N(7)–C(8)–C(9)–N(1)	−50.8(8)

Table 2. Fractional atomic co-ordinates for $[Cu(L)_2][ClO_4]_2\cdot 2H_2O$, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cl(1)	−0.012 20(19)	0.397 29(11)	0.133 18(14)
O(1)	0.111 1(7)	0.437 2(4)	0.162 0(5)
O(2)	0.008 4(9)	0.315 3(4)	0.149 3(5)
O(3)	−0.131 6(7)	0.424 5(4)	0.190 1(5)
O(4)	−0.038 9(8)	0.410 6(6)	0.032 3(5)
Cu(1)	0.000	0.500	0.500
N(1)	−0.107 7(7)	0.450 8(4)	0.631 3(5)
C(2)	−0.005 3(9)	0.402 5(5)	0.685 6(5)
C(3)	0.144 5(9)	0.419 1(6)	0.653 0(6)
N(4)	0.155 6(7)	0.420 9(4)	0.547 4(5)
C(5)	0.142 2(9)	0.344 1(4)	0.499 7(6)
C(6)	0.040 9(10)	0.346 2(5)	0.412 3(6)
N(7)	−0.085 4(7)	0.392 8(4)	0.436 6(5)
C(8)	−0.175 1(9)	0.351 1(4)	0.507 9(5)
C(9)	−0.227 4(8)	0.408 4(5)	0.589 6(6)
O(5)	0.232 2(12)	0.245 5(5)	0.765 2(11)
H(1)	−0.147(6)	0.506(3)	0.651(4)
H(4)	0.212(10)	0.457(5)	0.522(6)
H(7)	−0.134(8)	0.417(4)	0.377(5)
H(21)	−0.011(8)	0.423(5)	0.743(7)
H(22)	−0.032(6)	0.348(3)	0.665(4)
H(31)	0.199(11)	0.394(5)	0.678(7)
H(32)	0.180(7)	0.465(4)	0.688(5)
H(51)	0.248(17)	0.323(9)	0.486(9)
H(52)	0.088(6)	0.303(3)	0.544(5)
H(61)	0.071(8)	0.382(5)	0.350(6)
H(62)	0.008(9)	0.299(5)	0.387(6)
H(81)	−0.113(6)	0.310(3)	0.532(4)
H(82)	−0.266(8)	0.321(4)	0.480(4)
H(91)	−0.291(8)	0.439(4)	0.556(5)
H(92)	−0.284(7)	0.399(4)	0.652(5)

redox behaviour of $[Cu(L)_2]^{2+}$ at reduced temperature in CH_3CN is reported herein.

Experimental

1,4,7-Triazacyclononane trihydrochloride was prepared by the literature method.[11,25]

Infrared spectra were measured as Nujol mulls, KBr and CsI discs using a Perkin-Elmer 598 spectrometer over the range 200—4 000 cm^{-1}. U.v.–visible spectra were measured in quartz cells using a Pye-Unicam SP8-400 spectrophotometer. Microanalyses were performed by the Edinburgh University Chemistry Department microanalytical service. E.s.r. spectra were recorded as solids or as glasses in appropriate solvent down to 77 K using a Bruker ER200D *X*-band spectrometer. Electrochemical measurements were performed on a Bruker E310 Universal Modular Polarograph. All readings were taken using a three-electrode potentiostatic system in acetonitrile containing 0.1 mol dm^{-3} $NBu^n_4ClO_4$ as supporting electrolyte. Cyclic voltammetric measurements were carried out using a double platinum electrode and an Ag–Ag$^+$ reference electrode. All potentials are quoted *versus* the ferrocene–ferrocenium couple.

Preparation of $[Cu(L)_2][ClO_4]_2$.—$[Cu(NO_3)_2]\cdot 3H_2O$ (0.24 g, 1 mmol) was treated with L (0.27 g, 2.1 mmol) in EtOH (50 cm^3) for 1 h at room temperature. Addition of excess of $NaClO_4$ to the clear deep blue solution gave the product which was collected and dried *in vacuo* (60% yield). Recrystallisation of the complex from *cold* water by addition of $NaClO_4$ gave blue monoclinic crystals of the dihydrate.

X-Ray Structure Determination of $[Cu(L)_2][ClO_4]_2\cdot 2H_2O$.—The crystals, which were fragile and sensitive to solvent loss, were mounted in Lindemann glass capillaries. Preliminary *X*-ray photographs were used to determine unit-cell dimensions. A non-standard *C*-centred unit cell with all angles near 90° was chosen in preference to the primitive $P2_1/a$ unit cell with dimensions $a = b = 9.53$, $c = 13.65$ Å, $\gamma \simeq 120°$. A crystal of dimensions 0.15 × 0.2 × 0.3 mm was selected for data collection on a CAD-4 diffractometer. Data were collected out to $\theta = 25°$ and of the 2 180 unique reflections measured 1 549 had $I \geqslant 2.5\sigma(I)$. An empirical absorption correction was applied.[26] There was no noticeable decay of intensity during data collection and no drift correction was required.

Crystal data. $C_{12}H_{30}Cl_2CuN_6O_8\cdot 2H_2O$, $M = 556.8$, space group *Ca* (alternative setting for $P2_1/a$ with *c* axis unique) [general equivalent positions (x, y, z): $x + \frac{1}{2}, y + \frac{1}{2}, z$; $x + \frac{1}{2}, y,$

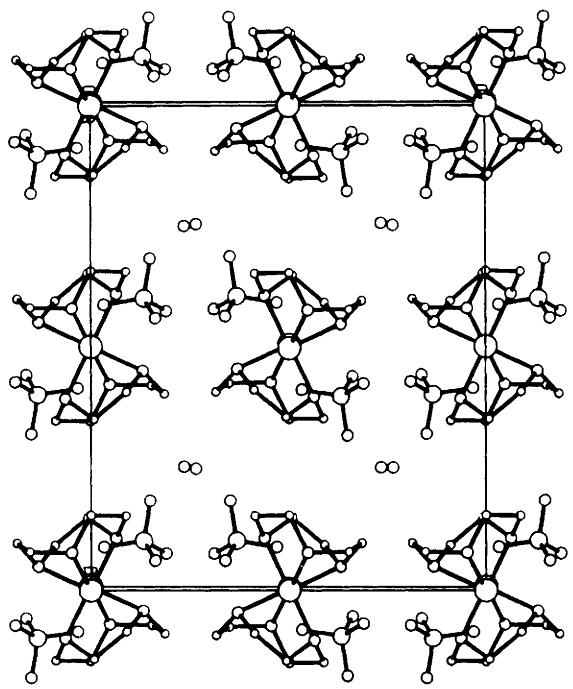


Figure 1. Crystal packing diagram for $[Cu(L)_2][ClO_4]_2{\cdot}2H_2O$

$\frac{1}{2} - z; x, y + \frac{1}{2}, \frac{1}{2} - z; \bar{x}, \bar{y}, \bar{z}; \frac{1}{2} - x, \frac{1}{2} - y, \bar{z}; \frac{1}{2} - x, \bar{y}, \frac{1}{2} + \bar{z}; \bar{x}, \frac{1}{2} - y, \frac{1}{2} + \bar{z}]$, $a = 9.533(3)$, $b = 16.909(8)$, $c = 13.653(9)$ Å, $\gamma = 89.22(3)°$, $U = 2\,200.8$ Å^3, $D_c = 1.68$ g cm^{-3}, $Z = 4$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 12.98 cm^{-1}, $F(000) = 1\,164$, $T = 20$ °C, $R = 0.068$ from 1 549 observed reflections.

The position of the copper atom was determined from a Patterson synthesis and all other atoms were located in subsequent Fourier-difference maps using the program SHELX76.[27] In the final cycles of full-matrix least-squares refinement all non-hydrogen atoms were refined with anisotropic thermal parameters giving a maximum shift/e.s.d. (estimated standard deviation) of 0.03. Positional and isotropic thermal parameters of all hydrogen atoms were also refined and gave an average shift over e.s.d. of 0.04. The maximum residual peak on the final difference-Fourier map was less than 0.8 Å^{-3}. The weighting scheme, which gave the best analysis of variance in ranges of $|F|$ and θ, was $w = 1/(\sigma^2 F + 0.0001F^2)$ and gave final residuals of $R = 0.068$ and $R' = 0.077$.

Bond lengths, angles, and torsion angles are given in Table 1 and fractional atomic co-ordinates in Table 2.

The pseudo-orthorhombic packing arrangement (Figure 1) provides channels running through the crystal which are occupied by loosely bound water solvent molecules. This accounts for the large thermal parameters of the water oxygen atoms and also explains the fragility and instability of the crystals to solvent loss. All C–H and N–H bond lengths lie between 0.9 and 1.1 Å.

Results and Discussion

The single-crystal structure of $[Cu(L)_2][ClO_4]_2{\cdot}2H_2O$ is illustrated in Figure 2 together with the atom-numbering scheme adopted; the structure confirms co-ordination of all six nitrogen donor atoms to the metal centre in the solid state. The $[Cu(L)_2]^{2+}$ cation is centrosymmetric with the copper(II) ion at the centre of symmetry co-ordinated to two macrocyclic ligands. The tridentate macrocycles are bound in a distorted facial manner with Cu–N(1) = 2.233(7), Cu–N(4) = 2.087(6), and Cu–N(7) = 2.176(6) Å and N–Cu–N angles of 80.7(3), 80.2(2), and 82.0(2)°. These features are a combination of the trigonal distortion along the elongated C_3 axis observed for the $[Ni(L)_2]^{2+}$ cation (N–Ni–N = 82.2, 82.5, and 83.1°),[10] and the expected distortion due to the d^9 metal ion as observed for the

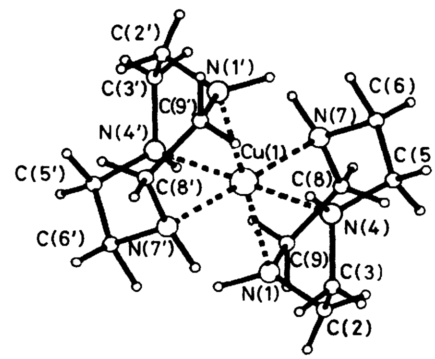


Figure 2. Crystal structure of the $[Cu(L)_2]^{2+}$ cation together with the atom-numbering scheme adopted

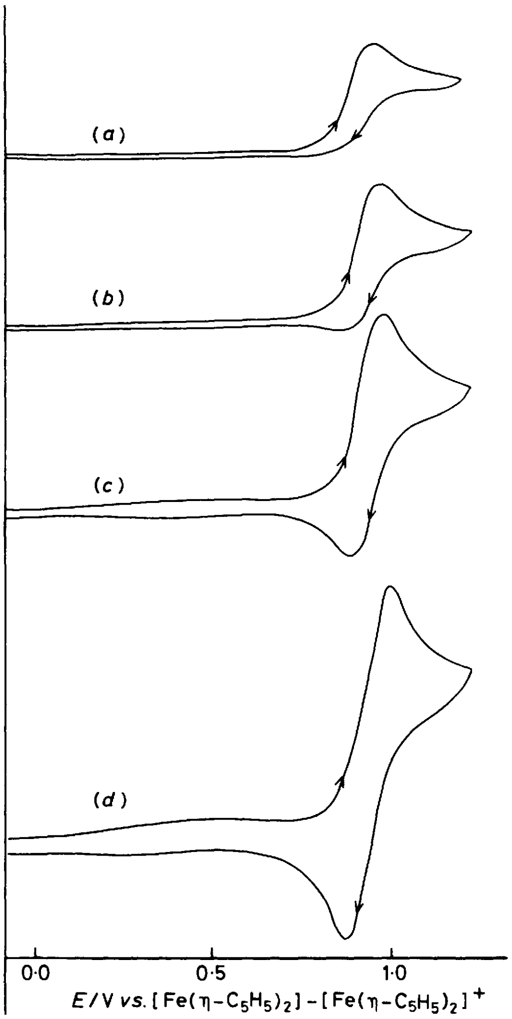


Figure 3. Cyclic voltammograms of $[Cu(L)_2][ClO_4]_2$ (oxidation) in acetonitrile (0.1 mol dm^{-3} $NBu^n{}_4ClO_4$) at platinum electrodes at 292 K. Scan rates: (a) 130 mV s^{-1}, (b) 260 mV s^{-1}, (c) 650 mV s^{-1}, (d) 1.3 V s^{-1}

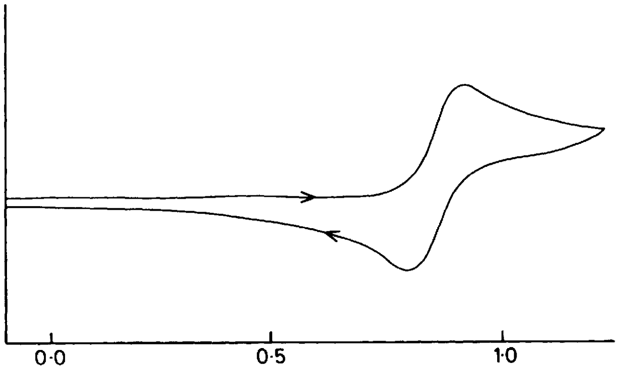


Figure 4. Cyclic voltammogram of $[Cu(L)_2][ClO_4]_2$ (oxidation) in acetonitrile (0.1 mol dm^{-3} $NBu^n_4ClO_4$) at platinum electrodes at 254 K. Scan rate = 260 mV s^{-1}

CuN_6 chromophores of $[Cu(dien)_2]^{2+}$ (dien = diethylenetriamine),[28] $[Cu(Him)_6]^{2+}$ (Him = imidazole),[29] and $[Cu(terpy)_2]^{2+}$ (terpy = 2,2′:6′,2″-terpyridyl).[30] Interestingly, the trithia analogue $[Cu(L')_2]^{2+}$ (L′ = 1,4,7-trithiacyclononane) shows no apparent tetragonal distortion around Cu with the Cu–S bond lengths varying only by 0.040 Å from the shortest to the longest [Cu–S = 2.423(4) and 2.459(3) Å, S–Cu–S = 87.8(6) and 92.2(6)°], suggesting a time-averaged octahedral structure for this complex.[31]

1,4,7-Triazacyclononane has been shown previously[11,12] to stabilise the metal(III) oxidation state for M = Cr, Mn, Fe, Co, or Ni in the complexes $[M(L)_2]^{3+}$; it was therefore of interest to ascertain whether the formation of Cu^{III} could be achieved from the distorted octahedral precursor $[Cu(L)_2]^{2+}$. $[Cu(L)_2][ClO_4]_2$ shows an irreversible oxidation at 292 K in anhydrous acetonitrile (0.1 mol dm^{-3} $NBu^n_4ClO_4$ as base electrolyte) at E_{pa} = +0.95 V *vs.* $[Fe(\eta-C_5H_5)_2]-[Fe(\eta-C_5H_5)_2]^+$ at a scan rate of 130 mV s^{-1}. Increasing the scan rate leads to an increase in the return wave of the couple such that at a scan rate of 1.3 V s^{-1}, I_{pc}/I_{pa} = 0.80 and ΔE_p = 117 mV (Figure 3). It would appear that this oxidative couple is unlikely to be a ligand-based process due to the saturated nature of the macrocyclic ligand, and therefore we tend to assign it to a Cu^{II}–Cu^{III} redox couple. Related copper(II) complexes of tetra- and penta-dentate aza macrocycles show similar irreversible redox behaviour with half-lives of the copper(III) products ranging from 0.004 to 60 s;[23] we estimate the half-life of the copper(III) species generated in our experiments to be *ca.* 0.8 s at 292 K.

Cyclic voltammetry of $[Cu(L)_2][ClO_4]_2$ at 254 K shows a more fully reversible redox behaviour (I_{pc}/I_{pa} = 1.0) with E_{pa} = +0.91 and E_{pc} = +0.81 V (ΔE_p = 100 mV) at a scan rate of 260 mV s^{-1}, indicative of increased stability of the copper(III) product at reduced temperatures (Figure 4); at a lower scan rate of 140 mV s^{-1}, I_{pc}/I_{pa} reduces to 0.86. Quantitative electrogeneration of the copper(III) product at 254 K has failed thus far to produce an isolable d^8 species. Fabbrizzi and co-workers[24] have noted the increased stability of Cu^{III} under acidic conditions; preliminary attempts to stabilise Cu^{III} with L in the presence of $HClO_4$ have been unsuccessful.

The relative kinetic instability of the copper(III) complexes with polyaza macrocycles contrasts with the corresponding low-spin d^7 nickel(III) complexes which tend to show a strong preference for octahedral stereochemistry.[32] This is not the case for d^8 copper(III) species which appear to have a lower affinity for octahedral geometries;[23,24,33] our results are in accordance with this observation. The mechanism of decomposition of the copper(III) complex is likely to involve metal-mediated oxidative dehydrogenation of the triamine macrocycle, a mechanism that has been proposed[23,32] previously for copper(III) tetra-aza macrocycles.

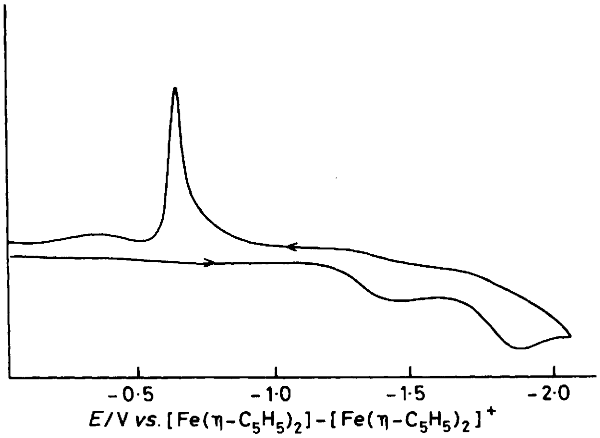


Figure 5. Cyclic voltammogram of $[Cu(L)_2][ClO_4]_2$ (reduction) in acetonitrile (0.1 mol dm^{-3} $NBu^n_4ClO_4$) at platinum electrodes at 292 K. Scan rate = 500 mV s^{-1}

We find the electrochemistry of the bis-sandwich complex $[Cu(L)_2][ClO_4]_2$ in acetonitrile to be very similar to that of the mono-macrocyclic species $[Cu(L)(ClO_4)]ClO_4$ in acetonitrile. This suggested that some dissociation of the $[Cu(L)_2]^{2+}$ cation was occurring in solution. Such dissociation to the mono-macrocyclic species *via* solvation of the metal ion has been noted previously,[2,3,15] and is consistent with the solid-state structure which shows two particularly elongated Cu–N distances of 2.233(7) Å. U.v.–visible and e.s.r. spectroscopy of $[Cu(L)_2]^{2+}$ in the solid state and in solution indicate an important role for the solvent in the co-ordination sphere of the copper(II) cation in solution. U.v.–visible data for $[Cu(L)_2][ClO_4]_2$ show λ = 596 (as Nujol mull), 618 (in CH_3CN), and 615 nm (in H_2O), while addition of one equivalent of L to a solution of $[Cu(L)(ClO_4)]ClO_4$ in CH_3CN (λ = 622 nm) caused a shift in absorption from 622 to 614 nm. E.s.r. data show g_{av} = 2.104 (as solid, 293 K); $g_{\parallel}$ = 2.171, $g_{\perp}$ = 2.061 (as solid, 133 K); g_1 = 2.253, g_2 = 2.064, g_3 = 2.025 (in H_2O glass, 193 K); $g_{\parallel}$ = 2.226, $g_{\perp}$ = 2.023 [in $(CH_3)_2SO$ glass, 193 K]: g_{av} = 2.102 (in CH_3CN glass, 77 K). These results are consistent with partial dissociation of $[Cu(L)_2]^{2+}$ in solution to yield solvated bis-macrocyclic products, in which L behaves as a bi- and unidentate ligand, and solvated mono-macrocyclic species (Scheme, S = solvent). 1,4,7-Triazacyclononane has been shown to be capable of binding to metal centres as a bi- or unidentate ligand.[5,34]

$$[Cu(L)_2]^{2+} + S \rightleftharpoons [Cu(L)_2S]^{2+}$$

$$[Cu(L)_2S]^{2+} + S \rightleftharpoons [Cu(L)_2S_2]^{2+}$$

$$[Cu(L)_2S_2]^{2+} + S \rightleftharpoons [Cu(L)S_3]^{2+} + L$$

Scheme.

Cyclic voltammetry of $[Cu(L)_2]^{2+}$ in CH_3CN shows two irreversible reductions at E_{pc} = −1.41 and −1.90 V *vs.* $[Fe(\eta-C_5H_5)_2]-[Fe(\eta-C_5H_5)_2]^+$ (Figure 5), corresponding presumably to the formation of unstable copper(I) and copper(0) species respectively. Repeated reductive scans to −2.0 V, or electrogeneration at −1.4 V causes deposition of copper metal at the platinum electrode. Copper(I) would be expected to prefer tetrahedral stereochemistry; although the species $[Cu(L)_2]^+$ (with bidentate L) and $[Cu(L)(NCCH_3)]^+$ (with tridentate L) might be expected to be produced in the electrochemical reduction of the copper(II) complex, stronger π-acceptor ligands are clearly required to stabilise copper(I). We have reported recently such a stabilisation using a related trithia moiety.[35]

Further studies on the stabilisation of copper(III) and copper(I) species using tridentate macrocycles are underway.

Acknowledgements

We thank the S.E.R.C. for financial support (to A. J. L.) and Professor E. Pedersen for helpful discussions.

References

1 'Co-ordination Chemistry of Macrocyclic Compounds,' ed. G. A. Melson, Plenum Press, New York, 1979.
2 R. Yang and L. J. Zompa, *Inorg. Chem.*, 1976, **15**, 1499.
3 L. J. Zompa, *Inorg. Chem.*, 1978, **17**, 2531.
4 M. Nonoyama and K. Sakai, *Inorg. Chim. Acta*, 1983, **72**, 57; P. Chaudhuri, K. Wieghardt, Y. H. Tsai, and C. Krüger, *Inorg. Chem.*, 1984, **23**, 427.
5 K. Wieghardt, M. Köppen, W. Swiridoff, and J. Weiss, *J. Chem. Soc., Dalton Trans.*, 1983, 1869.
6 K. Wieghardt, W. Herrmann, M. Köppen, I. Jibril, and G. Huttner, *Z. Naturforsch., Teil B*, 1984, **39**, 1335; P. Chaudhuri, K. Wieghardt, I. Jibril, and G. Huttner, *ibid.*, p. 1172.
7 K. Wieghardt, W. Schmidt, B. Nuber, B. Prikner, and J. Weiss, *Chem. Ber.*, 1980, **113**, 36.
8 K. Wieghardt, W. Schmidt, B. Nuber, and J. Weiss, *Chem. Ber.*, 1979, **112**, 2220; K. Wieghardt, W. Schmidt, H. Endres, and C. R. Wolfe, *ibid.*, p. 2837; K. Wieghardt, M. Hahn, W. Swiridoff, and J. Weiss, *Inorg. Chem.*, 1984, **23**, 94; K. Wieghardt, U. Bossek, K. Volckmar, W. Swiridoff, and J. Weiss, *ibid.*, p. 1387; M. Hahn and K. Wieghardt, *ibid.*, p. 3977.
9 K. Wieghardt, K. Pohl, and W. Gebert, *Angew. Chem.*, 1983, **95**, 739; *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 727; P. Chaudhuri, K. Wieghardt, B. Nuber, and J. Weiss, *Angew. Chem.*, 1985, **97**, 774; K. Wieghardt, U. Bossek, D. Ventur, and J. Weiss, *J. Chem. Soc., Chem. Commun.*, 1985, 347; A. Spool, I. D. Williams, and S. J. Lippard, *Inorg. Chem.*, 1985, **24**, 2156.
10 L. J. Zompa and T. N. Margulis, *Inorg. Chim. Acta*, 1978, **28**, L157.
11 A. McAuley, P. R. Norman, and O. Olubuyide, *Inorg. Chem.*, 1984, **23**, 1938.
12 K. Wieghardt, W. Schmidt, W. Herrmann, and H-J. Küppers, *Inorg. Chem.*, 1983, **22**, 2953.
13 J. C. A. Boeyens, A. G. S. Forbes, R. D. Hancock, and K. Wieghardt, *Inorg. Chem.*, 1985, **24**, 2926; H. Koyama and T. Yoshino, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 48.
14 M. Nonoyama, *Transition Met. Chem.*, 1976, **1**, 70.
15 T. J. Riedo and T. A. Kaden, *Helv. Chim. Acta*, 1979, **62**, 1089.
16 M. Kodama and E. Kimura, *J. Chem. Soc., Dalton Trans.*, 1977, 1473; 1978, 1081; P. G. Graham and D. C. Weatherburn, *Aust. J. Chem.*, 1981, **34**, 291; 1984, **37**, 2243; M. DeRonde, D. Driscoll, R. Tang, and L. J. Zompa, *Inorg. Nucl. Chem. Lett.*, 1975, **11**, 521; L. Fabbrizzi and L. J. Zompa, *ibid.*, 1977, **13**, 287.
17 H. Gampp, M. M. Roberts, and S. J. Lippard, *Inorg. Chem.*, 1984, **23**, 2793.
18 R. D. Bereman, M. R. Churchill, P. M. Schaber, and M. E. Winkler, *Inorg. Chem.*, 1979, **18**, 3122.
19 W. F. Schwingdinger, T. G. Fawcett, R. A. Lalancette, J. A. Potenza, and H. J. Schugar, *Inorg. Chem.*, 1980, **19**, 1379.
20 M. N. Bell, A. J. Blake, M. Schröder, and T. A. Stephenson, *J. Chem. Soc., Chem. Commun.*, 1986, 471.
21 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 4th edn., J. Wiley and Sons, New York, 1980, p. 815.
22 M. J. Van der Merwe, J. C. A. Boeyens, and R. D. Hancock, *Inorg. Chem.*, 1983, **22**, 3490.
23 P. Zanello, R. Seebar, A. Cinquantini, G. A. Mazzocchin, and L. Fabbrizzi, *J. Chem. Soc., Dalton Trans.*, 1982, 893; L. Fabbrizzi, A. Poggi, and P. Zanello, *ibid.*, p. 2191; L. Fabrizzi, M. Licchelli, A. Perotti, A. Poggi, and S. Soresi, *Isr. J. Chem.*, 1985, **25**, 112.
24 C. B. Castellani, L. Fabrizzi, M. Licchelli, A. Perotti, and A. Poggi, *J. Chem. Soc., Chem. Commun.*, 1984, 806.
25 J. E. Richman and T. J. Atkins, *J. Am. Chem. Soc.*, 1974, **96**, 2268.
26 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
27 G. M. Sheldrick, SHELX76, University of Cambridge, 1976.
28 F. S. Stephens, *J. Chem. Soc. A*, 1969, 883, 2233.
29 D. L. McFadden, A. T. McPhail, C. D. Garner, and F. E. Mabbs, *J. Chem. Soc., Dalton Trans.*, 1975, 263.
30 M. Mathew and G. J. Palenik, *J. Coord. Chem.*, 1971, **1**, 243.
31 W. N. Setzer, C. A. Ogle, G. S. Wilson, and R. S. Glass, *Inorg. Chem.*, 1983, **22**, 266.
32 A. Bencini, L. Fabbrizzi, and A. Poggi, *Inorg. Chem.*, 1981, **20**, 2544.
33 D. C. Olsen, and J. Vasilevskis, *Inorg. Chem.*, 1971, **10**, 463.
34 A. J. Holder, M. Schröder, and T. A. Stephenson, unpublished work.
35 R. O. Gould, A. J. Lavery, and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1985, 1492.

Received 11*th March* 1986; *Paper* 6/493