Macrocyclic Cu$^{II}_4$ and Cu$^{II}_2$M^{II} Complexes. Structure of a Heterotrinuclear Cu$^{II}_2$Zn^{II} Complex exhibiting a Helical Twist†

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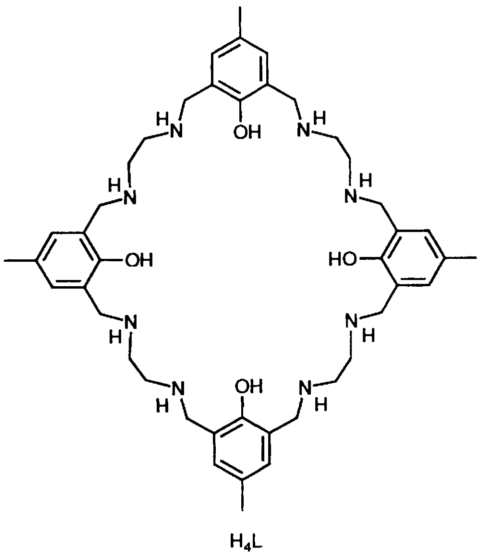
Three heterotrinuclear complexes $[Cu_2Zn(HL)][ClO_4]_3{\cdot}3H_2O$ **1**, $[Cu_2Mg(HL)][ClO_4]_3{\cdot}2H_2O$ **2** and $[Cu_2Mg(HL)][NO_3]_3{\cdot}3H_2O$ **3** and two tetranuclear complexes $[Cu_4L][ClO_4]_4{\cdot}4H_2O$ **4** and $[Cu_4L(\mu_3\text{-}OH)][ClO_4]_3{\cdot}MeOH$ **5** have been synthesized from a 38-membered macrocycle (H_4L) having eight amine and four phenol functionalities. The compounds have been characterized on the basis of IR, UV/VIS and ESR spectroscopy and magnetic susceptibility measurements. Their redox chemistry has been studied by cyclic voltammetry and differential pulse voltammetry. The crystal structure of **1** has been determined. The two copper centres have N_2O_2 square-planar co-ordination environments and the zinc has a trigonal-bipyramidal geometry with N_3O_2 donors; one of the copper(II) ions is bridged to the zinc(II) ion by two phenolate oxygens. The cation in **1** has a helically twisted configuration.

The formation of organized structures through self-assembly of ligands in the presence of metal ions is a topic of considerable current interest in supramolecular chemistry.[1–4] In particular, extensive studies have been made on the spontaneous organization of ligands around one or more metal centres to produce single-, double- and triple-stranded helical structural motifs.[5–17] Although metal ions showing preference for tetrahedral and octahedral co-ordination environments facilitate the formation of metal helicates, in one case a non-directional influence of the sodium ion has produced a double-helical complex.[14] The majority of the metal helicates reported so far are derived either from oligomultidentate ligands[6,8] with well defined metal-binding sites separated by spacers, or oligopyridines containing four to six pyridine rings.[7,9] Until recently, macrocyclic ligands were not used in deliberate synthesis of metal helicates, presumably due to their preorganized configuration. Nevertheless, at least three studies have been reported[15–17] on the formation of macrocyclic complexes with helical structures.

We have recently reported[18] the synthesis of a flexible 38-membered macrocyclic ligand H_4L having eight secondary amines and four phenol moieties and have studied[19] magnetostructural relationships in a series of tetranuclear nickel(II) complexes derived from it. We now report the chemistry of tetracopper(II) and heterotrinuclear Cu_2M (M^{II} = Zn or Mg) complexes. Of particular interest is the structure of $[Cu_2Zn(HL)][ClO_4]_3{\cdot}3H_2O$, which exhibits a helically twisted configuration.



H_4L

Experimental

Materials.—All chemicals were obtained from commercial sources and used as received. The macrocycle H_4L was prepared according to the reported method.[18]

Synthesis.—$[Cu_2Zn(HL)][ClO_4]_3{\cdot}3H_2O$ **1**. To a MeOH solution (100 cm^3) of H_4L (0.77 g, 1 mmol) was added $[Cu(acac)_2]$ (Hacac = acetylacetone) (0.52 g, 12 mmol) and the solution refluxed for 0.5 h, when a bright green solution resulted. Although the dinuclear complex $[Cu_2L]{\cdot}H_2O$ could be isolated almost in quantitative yield, the solution was directly treated with a MeOH solution of $Zn(ClO_4)_2{\cdot}4H_2O$ (0.34 g, 1 mmol) and reflux continued for 0.5 h. The resulting dark green solution was filtered hot to remove any solid material and the filtrate concentrated to *ca.* 50 cm^3, which on standing deposited dark green crystals of complex **1**. These were filtered off and recrystallized from MeCN–MeOH (3:2); yield 1.1 g (85%) (Found: C,40.0; H,5.0; Cu, 9.8; N, 8.65. $C_{44}H_{67}Cl_3Cu_2N_8O_{19}Zn$ requires C, 40.3; H, 5.1; Cu, 9.7; N, 8.55%). $\tilde{\nu}$/cm^{-1} (KBr) 3400s (br) [ν(OH), H_2O], 3230w [ν(NH)], 1610m [δ(NH)], 1470s [ν(C=C), aryl], 1100s (br) and 630m [$\nu(ClO_4^-)$]. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) in MeCN 580 (450), 400 (3000), 290 (15 100) and 247 (30 200).

$[Cu_2Mg(HL)][ClO_4]_3{\cdot}2H_2O$ **2**. The reaction was carried out

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI units employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, G = 10^{-4} T.

in the same way as for complex **1** but with the addition of $Mg(ClO_4)_2 \cdot 6H_2O$ when **2** deposited as dark green crystals (90%). The product was recrystallized from MeCN (Found: C, 42.6; H, 5.1; Cu, 10.0; N, 8.8. $C_{44}H_{65}Cl_3Cu_2MgN_8O_{18}$ requires C, 42.2; H, 5.2; Cu, 10.15; N, 8.95%). $\tilde{\nu}$/cm^{-1} (KBr) 3400s (br) [ν(OH), H_2O], 3240w [ν(NH)], 1620m [δ(NH)], 1475s [ν(C=C), aryl], 1100s (br) and 630m [$\nu(ClO_4^-)$]. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) in MeCN 585 (460), 402 (3150), 290 (15 800) and 247 (28 500).

$[Cu_2Mg(HL)][NO_3]_3 \cdot 3H_2O$ **3**. This compound was obtained (60%) in the same way as for **2** but using $Mg(NO_3)_2$ (Found: C, 45.45; H, 5.6; Cu, 10.85; N, 13.25. $C_{44}H_{67}Cu_2MgN_{11}O_{16}$ requires C, 45.65; H, 5.8; Cu, 11.0; N, 13.3%). $\tilde{\nu}$/cm^{-1} (KBr) 3440s (br) [ν(OH), H_2O], 3230w [ν(NH)], 1620m [δ(NH)], 1475s [ν(C=C), aryl] and 1385s [$\nu(NO_3^-)$]. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) in MeCN 590 (445), 398 (2850), 292 (15 200) and 245 (26 800).

$[Cu_4L][ClO_4]_4 \cdot 4H_2O$ **4**. A mixture of H_4L (0.77 g, 1 mmol) and NEt_3 (0.4 g, 4 mmol) in MeOH (100 cm^3) was refluxed for 10 min and to the resulting clear solution was added $Cu(ClO_4)_2 \cdot 6H_2O$ (1.48 g, 4 mmol) and reflux continued for 1 h. The greenish brown crystals deposited were filtered off and recrystallized from MeOH–MeCN (1 : 1); yield 1.2 g (80%) (Found: C, 35.7; H, 4.5; Cu, 16.95; N, 7.65. $C_{44}H_{68}Cl_4Cu_4N_8O_{24}$ requires C, 35.5; H, 4.55; Cu, 17.1; N, 7.5%). $\tilde{\nu}$/cm^{-1} (KBr) 3400s (br) [ν(OH), H_2O], 3230w [ν(NH)], 1610m [δ(NH)], 1470s [ν(C=C), aryl], 1100s (br) and 630m [$\nu(ClO_4^-)$]. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) in MeCN 620 (440), 400 (3250), 290 (16 400) and 245 (30 1000).

$[Cu_4L(\mu_3\text{-}OH)][ClO_4]_3 \cdot MeOH$ **5**. To a MeCN solution (60 cm^3) of complex **4** (0.75 g, 0.5 mmol) an aqueous solution (5 cm^3) of NaOH (20 mg, 0.5 mmol) was added dropwise with stirring. The greenish brown solution changed to emerald green and was stirred for 0.5 h and then filtered to remove any suspended material. The filtrate on rotary evaporation gave shiny green crystals, which were filtered off and recrystallized from MeCN–MeOH (1 : 1); yield 0.61 g (90%) (Found: C, 39.3; H, 4.6; Cu, 18.5; N, 8.1. $C_{45}H_{65}Cl_3Cu_4N_8O_{18}$ requires C, 39.55; H, 4.75; Cu, 18.6; N, 8.2%). $\tilde{\nu}$/cm^{-1} (KBr) 3460s [ν(OH)], 3220m [ν(NH)], 1610m [δ(NH)], 1470s [ν(C=C), aryl], 1100s (br) and 630m [$\nu(ClO_4^-)$]. λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) in MeCN–MeOH (1 : 1) 660 (515), 407 (2900), 295 (15 800) and 248 (28 900).

CAUTION: all the perchlorate salts reported here are potentially explosive and therefore should be handled with care.

Physical Measurements.—Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer using KBr discs and electronic spectra on a Shimadzu UV-160 A spectrophotometer. The electrochemical measurements were carried out under O_2-free conditions using a Bioanalytical Systems BAS 100B electrochemical analyser. A three-electrode assembly (BAS) comprising a platinum working electrode, platinum auxiliary electrode and Ag–AgCl reference electrode with a salt bridge separated by a porous Vycor tip and heat-shrinkage tubing was used. Tetraethylammonium perchlorate (0.1 mol dm^{-3}) was used as the supporting electrolyte. The potentials recorded were automatically corrected for *iR* drop in solution. Variable-temperature magnetic susceptibility data were obtained in the range 90–300 K by using a PAR 155 vibrating-sample magnetometer in combination with a Janis 153N cryostat and a Lake Shore DRC-70C controller. The magnetometer was calibrated with $[HgCo(NCS)_4]$ and susceptibility data were corrected for diamagnetism using Pascal constants. X-Band ESR spectra of solutions at 77 K were recorded on a Bruker 2000D spectrometer using dipicrylhydrazyl (dpph, $g = 2.0037$) as the calibrant. The C, H and N analyses were performed on a Perkin-Elmer model 240 C elemental analyser; copper was determined gravimetrically.

Crystal Structure Determination of $[Cu_2Zn(HL)][ClO_4]_3 \cdot 3H_2O$ **1**.—Crystals suitable for structure determination were obtained by diffusing Et_2O into a solution of complex **1** in MeCN–MeOH (1 : 1). Intensity data were collected with a Siemens R3m/V diffractometer in the ω–2θ scan mode at 293 K using graphite-monochromated Mo-Kα radiation. Pertinent crystallographic data are summarized in Table 1. Three standard reflections were periodically monitored and no crystal decay was observed. The intensity data were corrected for Lorentz-polarization effects and a semiempirical absorption correction was made from ψ scans. The structure was solved by direct and Fourier methods and refined by full-matrix least squares based on F^2 using the programs SHELXTL PLUS[20] and SHELXL 93.[21] The atomic scattering factors were taken from ref. 22. The non-hydrogen atoms were refined anisotropically, except for N(1) and C(12) which are disordered over two sites [N(11) and N(12), and C(121) and C(122)] each with an occupancy of 0.5. The hydrogen atoms were fixed at the calculated positions. The anions are severely disordered. The perchlorate oxygens belonging to Cl(1) and Cl(2) lie on a special position; the oxygen atoms of the third ClO_4^- ion mostly remained unlocated. The water molecules O(w2) and O(w3) are also disordered. Owing to these problems the *R* indices [$I > 2\sigma(I)$] $R1 = 0.1002$ and $wR2 = 0.2490$ were rather high. In the final stage of refinement (on F^2) the goodness of fit was 1.032 and the minimum and maximum peak heights in the Fourier-difference map were -0.655 and $+1.449$ e Å^{-3}.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis.—The reaction between 2 equivalents of copper(II) acetylacetonate and 1 equivalent of the macrocycle H_4L produces a neutral dinuclear complex of composition $[Cu_2L] \cdot H_2O$ in almost quantitative yield. The two metal centres are most likely occupying diagonally opposite sides of the macrocycle. Corey–Pauling–Koltun (CPK) models revealed that if the metal centres have square-planar geometry then the macrocycle adopts a helically twisted configuration. However, this structure remains unconfirmed due to the lack of single crystals. The complex readily reacts with the perchlorate or nitrate salts of zinc and magnesium giving the heterotrinuclear complexes $[Cu_2Zn(HL)][ClO_4]_3 \cdot 3H_2O$ **1**, $[Cu_2Mg(HL)][ClO_4]_3 \cdot 2H_2O$ **2** and $[Cu_2Mg(HL)][NO_3]_3 \cdot 3H_2O$ **3**. In all three the ligand is monoprotonated at an unco-ordinated secondary amine nitrogen. When $[Cu_2L] \cdot H_2O$ is treated with copper(II) perchlorate the tetranuclear complex $[Cu_4L][ClO_4]_4 \cdot 4H_2O$ **4** is obtained instead of the expected tricopper species. Complex **4** can be directly synthesized from 4 equivalents of copper(II) perchlorate, 1 equivalent of H_4L and 4 equivalents of triethylamine. This compound on treatment with 1 equivalent of sodium hydroxide affords a hydroxide-bridged complex of composition $[Cu_4L(\mu_3\text{-}OH)][ClO_4]_3 \cdot MeOH$ **5**. We have previously reported[18] the structure of $[Ni_4L(\mu_3\text{-}OH)(\mu\text{-}H_2O)_2(ClO_4)][ClO_4]_2 \cdot Me_2CO$.

Characterization.—The IR spectra of the complexes have several common features. For example, the NH stretching and bending modes due to the ligand are observed at 3240–3220 and 1620–1610 cm^{-1}, respectively, and a strong band due to C=C stretching of the aryl rings appears at about 1470 cm^{-1}. A broad band due to ν(OH) of the water molecules in **1**–**4** is seen at about 3400 cm^{-1}, while for **5** the hydroxide bridge ν(OH) is sharper and shifted to higher wavenumber, 3460 cm^{-1}. All the perchlorate salts show a strong broad band near 1100 (antisymmetric stretch) and a sharp band at 630 cm^{-1} (antisymmetric bend), indicative of unco-ordinated perchlorate anions. The occurrence of a strong band at 1385 cm^{-1} for **3** similarly indicates the presence of free ionic nitrates.

The electronic spectra of complexes **1**–**5** in solution exhibit four absorption bands in the range 200–900 nm. The first two at 245–248 and 290–295 nm are due to the internal ligand transitions. The third peak occurring between 398 and 407 nm is assignable to $PhO^- \rightarrow Cu^{II}$ ligand-to-metal charge transfer.[23–25] The fourth band, which is evidently due to a d–d transition, occurs at 580–590 for **1**–**3**, 620 for **4** and 660 nm for **5**. The fairly high intensity (ε = 445–515 $dm^3 mol^{-1} cm^{-1}$) of this band for all these complexes probably indicates a low symmetry for the chromophores. As will be seen from the crystal structure of **1**, the two non-interacting copper(II) centres in this compound have approximately square-planar geometry with some displacement from the respective basal planes. Similar structures are expected also for **2** and **3**. By contrast, the adjacent metal centres in **4** are linked by phenolate bridges and each of the copper(II) ions is presumably bound to a water molecule and therefore they probably have square-pyramidal geometry. In complex **5** the three copper(II) centres anchored to the hydroxide ion are likely to be more displaced from the square plane and have a different stereochemistry from that of the remaining copper(II) centre which, in turn, probably is bound to the methanol molecule. It has been reported[26] that the energy of the $d_{z^2} \longrightarrow d_{x^2-y^2}$ transition in copper(II) complexes can be correlated with the extent of tetragonal distortion of the metal centre, and is higher for a square-planar species. Although in the present series of compounds no definite assignment can be made for the d–d transition, assuming it to be $d_{z^2} \longrightarrow d_{x^2-y^2}$, the decreasing order of energy **1**–**3** > **4** > **5** can be rationalized.

Variable-temperature (90–300 K) magnetic susceptibility measurements have been carried out for complex **1**. In the entire temperature range the magnetic moment remains essentially unchanged [1.88–1.92 μ_B per copper(II)], showing that the two copper(II) centres are magnetically non-interacting.

The ESR spectrum of complex **1** in frozen (77 K) MeCN–MePh solution (Fig. 1) is typical of an axially symmetric copper(II) complex with $g_{\parallel} > g_{\perp}$ and $d_{x^2-y^2}$ ground state. The spectrum is well resolved for the copper hyperfine lines in the lower-field region, but not in the higher-field region. As will be seen in the structure of **1**, while both the copper(II) centres have N_2O_2 co-ordination environment, one is linked to the zinc atom by two phenolate bridges. Thus, the two copper(II) centres are magnetically non-equivalent because the localized electron densities are not the same. This is clearly evident in the ESR spectrum which shows two sets of four-line $A_{\parallel}$ features for the two copper(II) centres with $A_{\parallel}(1) = 185$, $A_{\parallel}(2) = 170$ G, $g_{\parallel}(1) = 2.254$ and $g_{\parallel}(2) = 2.192$. In the higher-field region only $g_{\perp} = 2.060$ was reliably estimated. The ESR spectrum of **2** is very similar, with $g_{\parallel}(1) = 2.260$, $g_{\parallel}(2) = 2.196$, $A_{\parallel}(1) = 190$, $A_{\parallel}(2) = 180$ G and $g_{\perp} = 2.056$, suggesting it is isostructural with **1**.

The redox behaviour of complexes **1** and **4** have been studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) using Me_2SO solutions and a glassy carbon working electrode for scanning in the negative potential ranges, while MeCN solutions and a platinum electrode were employed at positive potentials. In the case of **1**, reduction of both the copper(II) centres takes place irreversibly, however the copper that is bridged with zinc is reduced more easily ($E_{p,c} = 0.41$ V *vs.* Ag–AgCl) relative to the other ($E_{p,c} = -0.90$ V). The CV of **4** (Fig. 2) shows that in the cathodic sweep two closely spaced waves with peaks at -0.58 and -0.70 V are followed by a third wave at -1.32 V. In the reverse scan, however, instead of three, only two peaks are observed at -1.08 and -0.46 V. Apparently, the anodic peak at -0.46 V is unresolved for the cathodic components occurring at -0.58 and -0.70 V. The current heights of the waves in CV and DPV indicate that two one-electron charge-transfer processes are succeeded by a single-step two-electron transfer (Scheme 1). The addition of the first electron to one of the copper(II) centres, for example $Cu^{II}(1)$, is closely followed by the addition of the second electron to the diagonally opposite metal centre, $Cu^{II}(3)$. Further addition of electrons is more difficult because the positive charge of the complex cation is now depleted. Since the probabilities of electron transfer to $Cu^{II}(2)$ and $Cu^{II}(4)$ are equal, sequential addition of two electrons to these two metal centres occurs either at the same or nearly same potentials. There are precedents for similar two-electron charge transfers occurring at the same potential in dinuclear copper(II) complexes.[26,27]

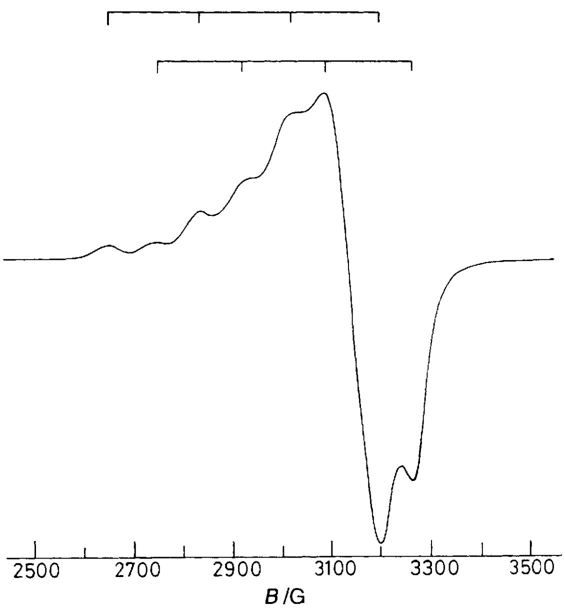

Fig. 1 The ESR spectrum of $[Cu_2Zn(HL)][ClO_4]_3{\cdot}3H_2O$ **1** in acetonitrile–toluene at 77 K. Microwave frequency 9.231 GHz

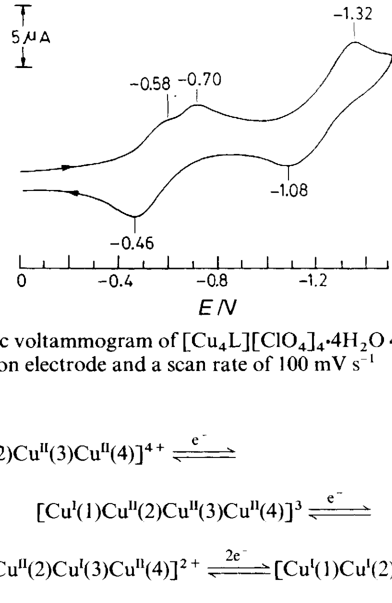

Fig. 2 Cyclic voltammogram of $[Cu_4L][ClO_4]_4{\cdot}4H_2O$ **4** in Me_2SO at a glassy carbon electrode and a scan rate of 100 mV s^{-1}

$$[Cu^{II}(1)Cu^{II}(2)Cu^{II}(3)Cu^{II}(4)]^{4+} \overset{e^-}{\rightleftharpoons}$$

$$[Cu^{I}(1)Cu^{II}(2)Cu^{II}(3)Cu^{II}(4)]^{3} \overset{e^-}{\rightleftharpoons}$$

$$[Cu^{I}(1)Cu^{II}(2)Cu^{I}(3)Cu^{II}(4)]^{2+} \overset{2e^-}{\rightleftharpoons} [Cu^{I}(1)Cu^{I}(2)Cu^{I}(3)Cu^{I}(4)]$$

Scheme 1

The electrochemical behaviour of complexes **1** and **4** with regard to oxidation at the metal centres is characterized by slow rates of heterogeneous electron-transfer processes. Consequently, up to +1.5 V a single irreversible wave occurs with a peak at 0.95 V for **1** and 1.27 V for **4**.

Molecular Structure of $[Cu_2Zn(HL)][ClO_4]_3{\cdot}3H_2O$ **1**.—A perspective view of the cation in complex **1** is shown in Fig. 3 along with the atom-labelling scheme for the asymmetric unit. The atomic coordinates are given in Table 2, selected bond distances and angles in Table 3.

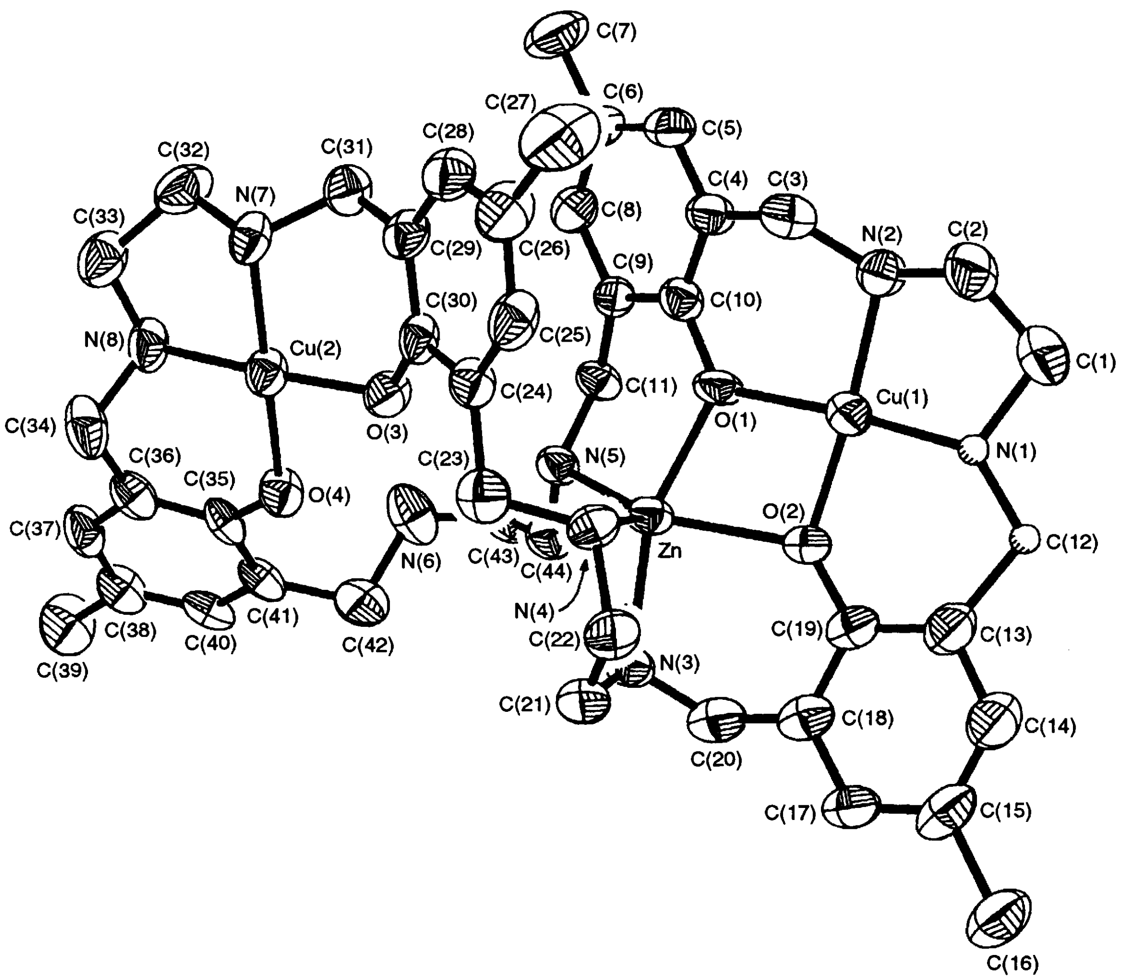

Fig. 3 An ORTEP[28] view of the cation $[Cu_2Zn(HL)]^{3+}$ in complex **1**

Table 1 Crystal data for $[Cu_2Zn(HL)][ClO_4]_3 \cdot 3H_2O$ **1**

Formula	$C_{44}H_{67}Cl_3Cu_2N_8O_{19}Zn$
M	1310.9
Crystal size/mm	0.33 × 0.27 × 0.25
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	14.262(4)
b/Å	15.745(4)
c/Å	16.072(4)
α/°	117.22(2)
β/°	111.03(2)
γ/°	90.28(2)
U/Å^3	2932.8(13)
Z	2
D_c/g cm^{-3}	1.484
λ(Mo-Kα)/Å	0.710 73
μ/mm^{-1}	1.390
Transmission (%)	92–22
θ range/°	2.42–27.56
Reflections measured	14 451
Independent reflections	13 565
Index ranges	$-18 \leqslant h \leqslant 17, -20 \leqslant k \leqslant 18, 0 \leqslant l \leqslant 20$
F(000)	1454
R [$I > 2\sigma(I)$]*	$R1 = 0.1002, wR2 = 0.2490$
R (all data)	$R1 = 0.2122, wR2 = 0.3275$

* $R1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|^2$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ where $w^{-1} = [\sigma^2(F_o^2) + (0.146P)^2 + 10.56P]$ and $P = (F_o^2 + 2F_c^2)/3$.

The structure consists of co-ordination polyhedra around a heterodinuclear Cu(1)Zn core and an isolated copper site Cu(2). In the heterodinuclear unit the two metal centres are bridged by the phenolate oxygens O(1) and O(2). Atom Cu(1) lies in a distorted square plane provided by N(1)N(2)O(1)O(2), while Zn has a trigonal-bipyramidal geometry involving the donors N(3)N(4)N(5)O(1)O(2). Atom Cu(2) also obtains a square-planar geometry by co-ordinating with the amine nitrogen atoms N(7) and N(8) and the phenolate oxygen atoms O(3) and O(4). The composition of **1** suggests that the remaining unco-ordinated amine nitrogen atom N(6) is protonated. The atoms O(3)O(4)N(7)N(8) from almost an exact plane (±0.017 Å), below which Cu(2) is displaced by 0.066 Å. The Cu(2)–O distances are nearly equal [1.93(1) Å], as are the Cu(2)–N distances [2.01(1) Å]. A consideration of the long-range perturbation involving the oxygen atom O(w1) and Cu(2) [Cu(2) ··· O(w1) 2.75(1) Å] leads to the description of the co-ordination sphere as square pyramidal. In contrast, the two other water molecules O(w2) and O(w3) do not show any interaction with the metal ions and both are disordered over at least two crystallographic sites. The *cis* angles around Cu(2) in the basal plane, which vary in the range 84.9(3)–93.3(3)°, do not differ much from idealized geometry. Turning to Cu(1), the plane formed by O(1)O(2)N(1)N(2) is rather irregular as its atoms are displaced alternatively above and below the mean plane by about 0.12 Å. Atom Cu(1) also lies 0.168 Å above this plane. The average Cu(1)–O [1.90(2) Å] and Cu(1)–N [1.97(1) Å] bond distances are shorter relative to those involving Cu(2). Moreover, the *cis* angles, which vary in the range 81.5(3)–

Table 2 Atomic coordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for $[Cu_2Zn(HL)][ClO_4]_3\cdot 3H_2O$ **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Zn	6 328(1)	3 243(1)	2 017(1)	C(26)	9 768(8)	2 489(9)	1 508(8)
Cu(1)	7 345(1)	2 689(1)	3 696(1)	C(27)	10 787(9)	2 480(12)	2 250(9)
Cu(2)	6 440(1)	1 941(1)	−1 907(1)	C(28)	9 278(8)	1 726(9)	507(8)
O(1)	7 007(5)	2 232(4)	2 297(5)	C(29)	8 382(7)	1 679(7)	−184(7)
O(2)	6 400(5)	3 512(5)	3 493(5)	C(30)	7 791(7)	2 441(7)	132(6)
O(3)	6 859(5)	2 408(5)	−469(5)	C(31)	7 905(8)	874(8)	−1 250(7)
O(4)	5 202(5)	2 461(5)	−1 952(10)	C(32)	7 366(9)	532(9)	−3 047(8)
N(11)[a]	8 003(14)	3 463(11)	5 211(10)	C(33)	6 833(9)	1 001(10)	−3 702(9)
N(12)[a]	7 494(30)	3 157(24)	5 098(21)	C(34)	5 580(8)	2 086(10)	−3 744(9)
N(2)	8 346(6)	1 844(6)	3 821(6)	C(35)	4 427(7)	2 329(7)	−2 820(7)
N(3)	5 539(7)	4 401(6)	2 186(6)	C(36)	4 542(8)	2 156(8)	−3 697(8)
N(4)	7 584(6)	4 229(5)	2 411(6)	C(37)	3 694(9)	2 063(8)	−4 545(7)
N(5)	5 494(6)	2 163(5)	440(5)	C(38)	2 724(8)	2 123(8)	−4 552(8)
N(6)	3 627(8)	1 591(7)	−1 777(7)	C(39)	1 866(10)	2 058(11)	5 458(9)
N(7)	7 629(6)	1 272(6)	−1 996(6)	C(41)	3 437(7)	2 354(7)	−2 834(7)
N(8)	5 999(7)	1 375(7)	−3 421(6)	C(42)	3 268(8)	2 453(9)	−1 918(9)
C(1)	8 456(11)	2 736(10)	5 547(9)	C(43)	3 612(9)	1 583(8)	−908(8)
C(2)	9 062(9)	2 325(8)	4 923(7)	C(44)	4 435(7)	2 320(7)	108(7)
C(3)	8 867(8)	1 667(7)	3 113(8)	Cl(1)	5 518(2)	627(2)	3 195(2)
C(4)	8 146(7)	1 121(7)	2 015(7)	O(11)[a]	5 783(18)	62(14)	3 663(15)
C(5)	8 350(7)	297(7)	1 330(8)	O(12)[a]	6 084(15)	1 627(11)	3 964(14)
C(6)	7 683(8)	−221(7)	286(8)	O(13)[a]	4 498(17)	787(24)	3 015(30)
C(7)	7 950(11)	−1 106(10)	−455(10)	O(14)[a]	5 773(21)	406(18)	2 382(15)
C(8)	6 801(8)	91(7)	−48(8)	O(15)[a]	5 137(35)	612(32)	3 904(33)
C(9)	6 538(7)	909(6)	626(7)	O(16)[a]	5 867(37)	1 340(39)	3 135(41)
C(10)	7 253(7)	1 433(6)	1 668(7)	O(17)[a]	6 569(24)	313(21)	3 535(22)
C(11)	5 500(7)	1 149(6)	301(7)	O(18)[a]	4 861(18)	−251(16)	2 293(17)
C(121)[a]	7 861(30)	4 202(28)	5 658(27)	Cl(2)	0	5 000	5 000
C(122)[a]	7 216(14)	3 854(13)	5 627(13)	O(21)	−880(40)	4 637(39)	4 575(40)
C(13)	6 839(8)	4 609(8)	5 279(8)	O(22)	711(25)	4 311(23)	4 662(21)
C(14)	6 794(9)	5 501(8)	6 019(9)	O(23)	−151(19)	5 362(18)	4 113(16)
C(15)	6 265(9)	6 134(8)	5 803(9)	O(24)	761(24)	5 864(15)	5 767(16)
C(16)	6 230(11)	7 133(8)	6 655(9)	Cl(3)[b]	2 462(15)	4 046(16)	601(16)
C(17)	5 728(8)	5 841(7)	4 775(8)	O(31)[b]	3 489(2)	4 408(18)	598(19)
C(18)	5 747(7)	4 961(7)	3 994(8)	O(34)[b]	2 355(67)	4 708(67)	59(69)
C(19)	6 352(7)	4 352(7)	4 252(8)	Cl(41)[b]	10 090(20)	1 643(23)	−2 376(25)
C(20)	5 043(9)	4 623(8)	2 896(9)	Cl(42)[b]	9 958(13)	850(15)	−3 373(17)
C(21)	6 262(9)	5 235(7)	2 430(8)	O(w1)	7 751(16)	3 496(15)	−1 508(16)
C(22)	7 368(9)	5 205(7)	2 980(8)	O(w21)[b]	5 503(15)	4 179(14)	−186(14)
C(23)	7 810(8)	4 118(7)	1 533(8)	O(w22)[b]	5 738(16)	4 444(16)	−388(16)
C(24)	8 277(7)	3 239(7)	1 145(7)	O(w31)[b]	2 129(15)	89(14)	−3 700(15)
C(25)	9 235(8)	3 245(8)	1 791(7)	O(w32)[b]	1 697(18)	260(16)	−3 415(18)

[a] Site occupancy 0.5. [b] Disordered.

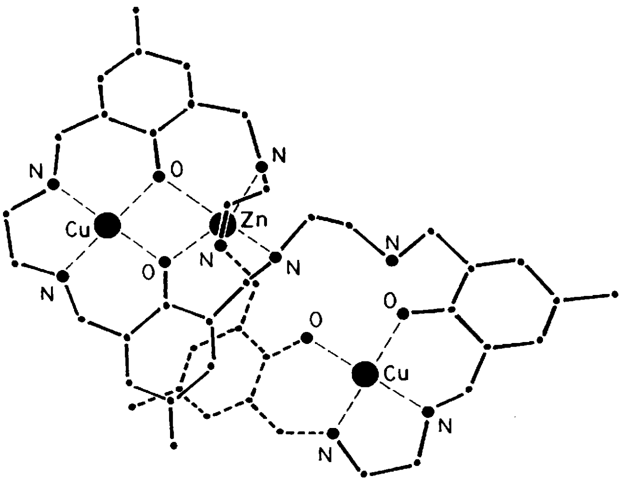

Fig. 4 A perspective view of the cation in complex **1**

Table 3 Selected bond distances (Å) and angles (°) for $[Cu_2Zn(HL)][ClO_4]_3\cdot 3H_2O$ **1**

Cu(1)–O(1)	1.883(6)	Cu(1)–O(2)	1.922(6)
Cu(1)–N(11)	1.98(1)	Cu(1)–N(12)	1.95(3)
Cu(1)–N(2)	1.976(8)	Zn–O(1)	2.007(7)
Zn–O(2)	2.174(6)	Zn–N(3)	2.109(8)
Zn–N(4)	2.069(8)	Zn–N(5)	2.146(7)
Cu(2)–O(3)	1.920(6)	Cu(2)–O(4)	1.941(6)
Cu(2)–N(7)	2.010(8)	Cu(2)–N(8)	2.007(8)
Cu(1) · · · Zn	3.08	Cu(1) · · · Cu(2)	8.13
Zn · · · Cu(2)	5.61		
O(1)–Cu(1)–N(11)	162.9(6)	O(1)–Cu(1)–N(12)	172.1(11)
O(2)–Cu(1)–N(2)	175.5(3)	O(2)–Cu(1)–N(11)	96.8(4)
O(2)–Cu(1)–N(12)	92.7(8)	O(1)–Cu(1)–N(2)	94.6(3)
N(2)–Cu(1)–N(11)	86.2(4)	N(2)–Cu(1)–N(12)	96.8(4)
O(1)–Cu(1)–O(2)	81.5(3)	O(1)–Zn–N(3)	159.9(3)
O(1)–Zn–N(4)	101.3(3)	O(1)–Zn–N(5)	90.1(3)
O(2)–Zn–N(3)	87.3(3)	O(2)–Zn–N(4)	103.1(3)
O(2)–Zn–N(5)	137.0(3)	N(3)–Zn–N(4)	85.5(3)
N(3)–Zn–N(5)	103.2(3)	N(4)–Zn–N(5)	119.1(3)
Cu(1)–O(1)–Zn	104.8(3)	Cu(1)–O(2)–Zn	97.5(3)
O(3)–Cu(2)–N(8)	176.7(3)	O(4)–Cu(2)–N(7)	174.2(3)
O(3)–Cu(2)–N(7)	93.3(3)	O(4)–Cu(2)–N(8)	91.8(3)
N(7)–Cu(2)–N(8)	84.9(3)	O(3)–Cu(2)–O(4)	89.7(3)

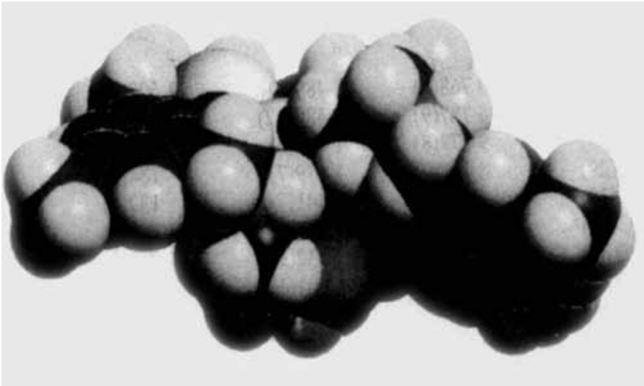

Fig. 5 Space-filling diagram of the $[Cu_2Zn(HL)]^{3+}$ cation

96.8(4)°, also deviate more from the idealized orthogonal geometry. The donor atoms N(4), N(5) and O(2), in the form of a non-isosceles triangle, provide the basal plane of the trigonal-bypyramidal co-ordination sphere of Zn(1), the axial donors being O(1) and N(3). All the Zn–N and Zn–O distances are unequal, Zn–O(1) 2.007(7) Å] being the shortest and Zn–O(2) 2.174(6) Å the longest. The in-planar angles involving Zn deviate from 120° and the axial N(3)–Zn–O(1) angle is 159.9(3)°. Further, compared to the distance of 3.08 Å between Cu(1) and Zn, Cu(2) is separated from Cu(1) and Zn by 8.13 and 5.61 Å, respectively.

A different perspective of the cation in complex **1** (Fig. 4) shows that in the process of co-ordinating with the metal ions the macrocycle is extensively twisted and has attained an incomplete helical structure. Clearly, in the metal–ligand self-assembly the helical twist occurs as a result of the steric requirement of the square plane orienting the copper(II) centres, and the role of zinc (or magnesium) is to stabilize this configuration by anchoring the available donor sites. A space-filling diagram of the cation in **1** is shown in Fig. 5. The extent of helical twist in compound **1** may be judged by considering the following dihedral angles between the planes of the phenyl rings: C(4)–C(10)/C(13)–C(19) 155.1, C(4)–C(10)/C(24)–C(30) 7.6, C(4)–C(10)/C(35)–C(41) 132.6, C(13)–C(19)/C(24)–C(30) 152.6, C(13)–C(19)/C(35)–C(41) 58.9 and C(24)–C(30)/C(35)–C(41) 126.0°.

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