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Binuclear complexes of a new hexadentate macrocyclic ligand. The crystal and molecular structure of $[LCu_2(CH_3CO_2)_2](ClO_4)_2 \cdot 5H_2O$

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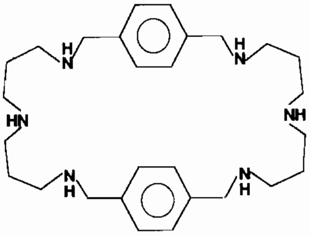
Abstract

The 30-membered hexaaza macrocylic ligand, L (L=3,7,11,18,22,26-hexaazatricyclo-[26.2.2.2^{13,16}]tetratriaconta-1(31),13(33),14,16(34),28(32),29-hexaene), is capable of forming binuclear complexes with the divalent transition metal ions Ni, Cu and Zn. The two metal ions are bound by the two dipropylenetriamine units of the macrocycle. Extra coordination sites on the metal ions can be occupied by exogenous ligands such as acetate, chloride and thiocyanate. The crystal structure of one of the di-copper complexes is described: $[LCu_2(CH_3CO_2)_2](ClO_4)_2 \cdot 5H_2O$ crystallizes in the monoclinic space group $P2_1/c$ (No. 14), with $a=9.369(2)$, $b=17.644(3)$, $c=27.466(3)$ Å, $\beta=92.90(1)°$, $U=4534.7$ Å^3 and $Z=4$. The Cu1···Cu2 separation is 8.40(3) Å. The access for potential exogenous bridging ligands, to the cavity between the copper ions, is somewhat restricted by the two phenyl units of the macrocycle which appear almost parallel in the structure. The redox potential of the couple $L(Cu^{2+})_2/L(Cu^+)_2$, recorded by cyclic voltammetry for the chloride adduct, $[LCu_2Cl_2]Cl_2 \cdot 5H_2O$, is −0.061 V versus SCE in DMF.

Introduction

There has been considerable interest in metal complexes of binucleating ligands as models for the coordination environments of the redox-active or Lewis acid sites in binuclear metalloenzymes [1–11]. Di-copper complexes of binucleating ligands incorporating *m*-xylyl bridging units have been reported as tyrosinase models [12–14]. Exposure of these Cu(I) complexes to oxygen results in rapid hydroxylation of the *m*-xylyl ring. Binuclear copper complexes of macrocyclic ligands have been demonstrated also to function as catalysts for the oxidation of organic substrates other than the ligand itself [15–17]. Some di-copper [18–20] and di-cobalt [21] complexes are capable of binding dioxygen reversibly, and are thus important as models for the metalloenzymes involved in O_2 transport.

The high-yield synthesis of the hexaaza macrocycle, L, has been described recently [22]. Here we report some binuclear transition metal complexes of L. A feature of this macrocyclic system is that the two sets of three nitrogen atoms are linked by *p*-phenylene units. The complexation of two metal ions by L should create a 'slot', between the ions, the *p*-phenylene units providing relatively rigid 'walls'. In this arrangement, it may be expected that the two metallic centres can be complimented in their coordination sphere by a small co-ligand. This co-ligand may be a substrate which, under the influence of the two metal ions, can be activated and eventually transformed into a product. The *p*-phenylene 'walls' may offer some degree of protection to this species from external reactants and therefore assist in the potential catalysis reaction. The observation of such reactions, promoted or catalyzed, by the dual activation effects of the di-metallic site in binuclear complexes has been relatively rare to date [23–27].



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Experimental

IR spectra were measured as KBr discs using a Hitachi 270-30 IR spectrometer. ^{1}H NMR spectra were recorded on a Bruker AC 250 FT NMR spectrometer. UV–Vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Positive-ion FAB mass spectra were recorded with a Kratos MS-50 instrument. Samples were dissolved in DMF/glycerol and bombarded with Xe (9 keV). ESR spectra were recorded on a Varian E104. Cyclic voltammetry was measured, under an argon atmosphere, in DMF with tetraethylammonium perchlorate as supporting electrolyte, using a glassy carbon working electrode. Magnetic susceptibilities were determined by the Gouy method. Diamagnetic corrections for the ligands were calculated by using Pascal's constants. Elemental analyses were carried out at the microanalytical laboratory of the H. C. Ørsted Institute, Copenhagen. 3,7,11,18,22,26-Hexaazatricyclo-[26.2.2.2^{13,16}]tetratriaconta-1(31),13(33),14,16(34),28(32),29-hexaene, L, was prepared by the reduction of the '2 + 2' condensation product of terephthalic aldehyde and bis(3-aminopropyl)amine as described previously [22].

Preparations

All the complexes can be crystallized in various solvated forms, as indicated by microanalytical data. To avoid confusion, we ignore the state of solvation when referring to the complexes throughout the text. The highly variable degree of solvation in these complexes most likely accounts for the difference between the calculated and measured densities of the crystals of $[LCu_2(CH_3CO_2)_2](ClO_4)_2 \cdot 5H_2O$.

$[LCu_2(CH_3CO_2)_2](ClO_4)_2$

The macrocycle (0.127 g, 0.27 mmol) dissolved in methanol (5 ml) was added to a solution of $Cu(CH_3CO_2)_2 \cdot H_2O$ (0.148 g, 0.74 mmol) in methanol (10 ml). The resultant deep blue solution was stirred under nitrogen for 1 h following which time $NaClO_4$ (0.047 g, 0.34 mmol) was added. Blue needles of the product were deposited on standing overnight. These were collected, washed with methanol and dried in vacuum at room temperature. Yield 0.175 g, 71%. $[LCu_2(CH_3CO_2)_2](ClO_4)_2$ could be recrystallized from methanol–water. *Anal.* Calc. for $C_{32}H_{52}N_6O_{12}Cl_2Cu_2 \cdot 2H_2O$: C, 40.59; H, 5.96; N, 8.88; Cl, 7.49. Found: C, 40.71; H, 5.60; N. 8.89; Cl, 7.32%. The crystal used for the X-ray structure determination was not dried and consequently shows more water present in the crystal lattice. IR (cm^{-1}): 3251 (ν_{NH}), 1569 (br, macrocycle + ν_{OCO}(asym)), 1430 (br, macrocycle + ν_{OCO}(sym)). UV–Vis (H_2O, λ_{max} (nm)): 685 (555 M^{-1} cm^{-1}). FAB-MS (*m/z*): 751 ($[L^{(ox)}Cu_2(CH_3CO_2)(ClO_4)]^+$); 691 ($[L^{(ox)}Cu_2(ClO_4)]^+$, 100%); 589 ($[LCu(CH_3CO_2)]^+$); 529 ($[LCu]^+$). $L^{(ox)}$ represents an oxidized form of the macrocycle in which one or more of the amine groups are converted to imine groups under the oxidizing conditions of the FAB experiment.

$[LZn_2(CH_3CO_2)_2](ClO_4)_2$

The macrocycle (0.4988 g, 1.1 mmol) and $Zn(CH_3CO_2)_2 \cdot 2H_2O$ (0.5112 g, 2.3 mmol) in methanol (10 ml) were heated under reflux in a N_2 atmosphere for 3 h. $NaClO_4$ (0.3289 g, 2.3 mmol) was added and the solution was filtered to remove a fine precipitate of zinc hydroxide. White crystals of the product grew from the filtrate over a period of one week. These were collected, washed with methanol and dried in vacuum at room temperature. Yield 0.1681 g, 17%. *Anal.* Calc. for $C_{32}H_{52}N_6O_{12}Cl_2Zn_2 \cdot CH_3OH$: C, 41.87; H, 5.96; N, 8.88; Cl, 7.49. Found: C, 41.70; H, 5.90; N, 8.83; Cl, 7.43%. IR (cm^{-1}): 3256 (ν_{NH}), 1592 (br, ligand + ν_{OCO}(asym)), 1392 (ν_{OCO}(sym)). ^{1}H NMR (ppm $(CD_3)_2SO$): 7.27 (m, 8H, Ar*H*); 3.35 (s, 8H, C*H*$_2$ArC*H*$_2$); 2.82 (br m, 16H, NC*H*$_2$); 3.35 (s, 6H, C*H*$_3$CO$_2$); 1.81 (br m, 8H, C–C*H*$_2$–C). FAB-MS (*m/z*): 815 ($[LZn_2(CH_3CO_2)_2(ClO_4)]^+$, 100%); 753 ($[L^{(ox)}Zn_2(CH_3CO_2)(ClO_4)]^+$); 629 ($[LZn(ClO_4)]^+$); 589 ($[LZn(CH_3CO_2)]^+$); 529 ($[L^{(ox)}Zn]^+$).

$[LCu_2Cl_2]Cl_2$

The macrocycle (0.208 g, 0.46 mmol) dissolved in methanol (15 ml) was added to a solution of $CuCl_2 \cdot 2H_2O$ (0.168 g, 0.99 mmol) in water (5 ml). The resultant deep blue solution was heated for 1 h and on cooling yielded green crystals of the product. These were collected, washed with methanol and dried in vacuum at room temperature. Yield 0.149 g, 44%. *Anal.* Calc. for $C_{28}H_{46}N_6Cl_4Cu_2 \cdot 5H_2O$: C, 40.73; H, 6.84; N, 10.18; Cl, 17.17. Found: C, 40.27; H, 6.32; N, 10.52; Cl, 17.40%. IR (cm^{-1}): 3160 (ν_{NH}), 1631, 1434. UV–Vis (H_2O, λ_{max} (nm)): 685 (370 M^{-1} cm^{-1}). FAB-MS (*m/z*): 664 ($[LCu_2Cl_2]^+$); 627 ($[L^{(ox)}Cu_2Cl]^+$); 564 ($[LCuCl]^+$); 527 ($[L^{(ox)}Cu]^+$).

$[LNi_2(CH_3CO_2)_2(NCS)_2]$

The macrocycle (0.132 g, 0.28 mmol) was added to a solution of $Ni(CH_3CO_2)_2 \cdot 4H_2O$ (0.149 g, 0.60 mmol) in methanol (10 ml). The mixture was heated under nitrogen for a few minutes following which time a solution of NaSCN (0.061 g, 0.75 mmol) in methanol (10 ml) was added generating a blue solution. Blue needles of the product were deposited on standing overnight. These were collected, washed with methanol and dried in vacuum at room temperature. Yield 0.155 g, 68%. *Anal.* Calc. for $C_{34}H_{52}N_8O_4Ni_2 \cdot 2H_2O$: C, 47.79; H, 6.60; N, 13.12; S, 7.50. Found: C, 47.38; H, 6.19; N, 13.41; S, 7.08%. IR (cm^{-1}): 3215 (ν_{NH}), 2071

(ν_{NCS}(asym)), 1572 (br, ligand + ν_{OCO}(asym)), 1427 (br, ligand + ν_{OCO}(sym)). UV–Vis (CH_3CN, λ_{max} (nm)): 598.8 (127 M^{-1} cm^{-1}), 382.6 (428 M^{-1} cm^{-1}).

X-ray structural determination of $[LCu_2(CH_3CO_2)_2](ClO_4)_2 \cdot 5H_2O$

Crystal data

$C_{32}H_{52}N_6O_8Cl_2Cu_2 \cdot 5H_2O$, $M_r = 864.81$, crystallizes from methanol:water (5:1) as blue needles, monoclinic, $a = 9.369(2)$, $b = 17.644(3)$, $c = 27.466(3)$ Å, $\beta = 92.90(1)°$, $U = 4534.7$ Å^3, $F(000) = 1912$, space group $P2_1/c$ (No. 14), $Z = 4$, $D_c = 1.383$ g cm^{-1}, $D_m = 1.475(4)$ g cm^{-1}, Mo Kα radiation ($\lambda = 0.71073$ Å), $T = 295$ K, μ(Mo Kα) = 11.1 cm^{-1}, Enraf-Nonius CAD 4 diffractometer.

Data collection and processing

A single crystal having overall dimensions $0.36 \times 0.11 \times 0.08$ mm was mounted in a sealed Lindemann glass capillary tube and used for structure determination. Weissenberg photographs show that it belongs to the monoclinic system. The unit cell parameters were determined from least-squares refinement of the setting angles for 25 reflections. The ω-2θ ($\Delta\omega = 1.25 + 0.34 \tan\theta$) technique was used to measure 5958 (5112 unique) reflections in the range $4 \leqslant 2\theta \leqslant 44°$. Three standard reflections remeasured every 100 scans showed an approximately 7% loss in intensity during data collection. A correction for this intensity loss was included in the calculations. The orientation of the crystal was checked every 100 reflections. The intensity data were corrected for Lorentz and polarization effects. There were 2275 ($I = 2\sigma(I)$) reflections used in the refinement. The data were considered likely to be of relatively poor quality due to weak diffraction.

Structure analysis and refinement

The asymmetric unit contains the complex cation, two $[ClO_4]^-$ anions and lattice water. The Cu atoms and part of the macrocyclic framework (C7–C14, C21–C28) were located by direct methods. Alternating cycles of least-squares refinement and difference Fourier synthesis led to the identification of all non-hydrogen atoms. The perchlorate ion containing Cl(2) displayed rotational disordering with two perchlorate orientations being required to model the oxygen atoms. The occupancy of each position was initially refined but ultimately fixed at 0.5 for each O atom in the final cycles. The O atoms of the 5 lattice water molecules were found in 9 disordered positions. The occupancy of each position was refined. Only the Cu atoms and the atoms of the perchlorate anion which is not disordered (Cl1, O5–O8) were refined anisotropically. Peaks of high intensity near the four six-membered chelate rings indicated further disorder which could be accounted for by the presence of conformational isomers around these rings. Modelling of this disorder was not attempted. Attempts to refine the remaining non-hydrogen atoms with anisotropic thermal parameters resulted in many atoms with non-positive definite temperature factors. Hydrogen atoms could not be located in the final difference map. The final least-squares cycle included 309 parameters for 2275 variables, gave $R = 0.095$, $R_w = 0.112$, and did not shift any parameter by more than 0.09 times its estimated standard deviation. The largest peak in the final difference Fourier synthesis was 0.869 e Å^{-3}. Crystallographic computations were performed on a Micro VAX II computer using the Enraf-Nonius Structure Determination Package. Atomic scattering factors and anomalous dispersion corrections were taken from ref. 28 and used as contained in the program system. Fractional atomic coordinates for the non-hydrogen atoms are listed in Table 1. See also ‘Supplementary material’.

Results and discussion

The reaction of the macrocyclic ligand with two equivalents of $M(CH_3CO_2)_2$ (M = Cu, Zn) and $NaClO_4$ gives the binuclear complexes, $[LM_2(CH_3CO_2)_2](ClO_4)_2$, (M = Cu, Zn). The IR spectra of these complexes are nearly identical; the acetato ν_a(OCO) and ν_s(OCO) bands are included in broad ligand-associated bands. The separation and slight shift to lower frequency of the ν_s(OCO) for the Zn(II) complex (1392 cm^{-1}) is probably indicative of monodentate acetato groups (cf. the Cu complex which shows bidentate acetato groups in the X-ray structure, *vide infra*). The ^1H NMR spectrum of the Zn complex supports the proposed formulation.

The frozen-glass ESR spectrum of $[LCu_2(CH_3CO_2)_2](ClO_4)_2$ in DMF/water/methanol (1:1:5) shows no indication of exchange coupling between the Cu^{2+} centres, however a broad signal around $g = 2$ indicates significant dipolar interaction. The room temperature magnetic moment, μ_{eff}, of 2.49 BM for $[LCu_2(CH_3CO_2)_2](ClO_4)_2$ (1.76 BM per Cu(II) ion) indicates also the lack of magnetic interaction between the copper ions. This lack of exchange coupling between the copper ions is not surprising in view of the lack of suitable exchange pathways via the *p*-xylene moiety [29] and the through space interatomic separation between the copper atoms of $[LCu_2(CH_3CO_2)_2](ClO_4)_2$ observed in the solid state (Cu1 $\cdots$ Cu2 = 8.40 Å), *vide infra*.

The reaction of copper chloride with the macrocycle produces the chloride adduct, $[LCu_2Cl_2]Cl_2$. The structure of the methanol solvate of this complex has been

TABLE 1. Atomic coordinates for $[LCu_2(CH_3CO_2)_2](ClO_4)_2 \cdot 5H_2O$

Atom	x	y	z
Cu1	0.5506(3)	0.7496(2)	0.61426(6)
Cu2	0.9470(3)	0.7515(2)	0.89583(6)
N1	0.345(2)	0.7567(8)	0.6229(4)
N2	0.544(2)	0.6524(8)	0.5741(5)
N3	0.735(2)	0.7259(9)	0.6469(5)
N4	1.168(2)	0.765(1)	0.8876(5)
N5	0.947(2)	0.6504(8)	0.9308(5)
N6	0.750(2)	0.7245(7)	0.8582(4)
O1	0.567(2)	0.8629(7)	0.6211(4)
O2	0.931(2)	0.8637(8)	0.8873(4)
O3	0.919(2)	0.8280(8)	0.9626(5)
O4	0.556(2)	0.8302(9)	0.5440(5)
C1	0.242(2)	0.745(1)	0.5782(6)
C2	0.279(2)	0.656(1)	0.5608(6)
C3	0.421(3)	0.645(1)	0.5389(7)
C4	0.672(2)	0.647(1)	0.5484(6)
C5	0.804(2)	0.634(1)	0.5821(6)
C6	0.864(3)	0.702(1)	0.6159(6)
C7	0.787(2)	0.792(1)	0.6809(6)
C8	0.905(2)	0.760(1)	0.7206(6)
C9	0.994(2)	0.823(1)	0.7411(5)
C10	1.089(2)	0.810(1)	0.7788(6)
C11	1.104(2)	0.7311(9)	0.7978(5)
C12	1.014(3)	0.671(1)	0.7778(8)
C13	0.912(2)	0.692(1)	0.7381(6)
C14	1.208(3)	0.712(1)	0.8399(7)
C15	1.249(2)	0.726(1)	0.9290(6)
C16	1.213(3)	0.649(1)	0.9482(8)
C17	1.064(3)	0.654(1)	0.9716(7)
C18	0.801(3)	0.644(1)	0.9599(7)
C19	0.677(3)	0.635(1)	0.9222(6)
C20	0.649(2)	0.707(1)	0.8946(6)
C21	0.705(2)	0.791(1)	0.8263(6)
C22	0.591(2)	0.7737(9)	0.7882(5)
C23	0.513(3)	0.836(1)	0.7690(6)
C24	0.411(3)	0.822(1)	0.7300(7)
C25	0.392(2)	0.751(1)	0.7114(6)
C26	0.465(2)	0.685(1)	0.7316(6)
C27	0.558(2)	0.697(1)	0.7695(6)
C28	0.286(3)	0.731(1)	0.6678(6)
C29	0.580(2)	0.877(1)	0.5778(6)
C30	0.593(3)	0.966(1)	0.5642(8)
C31	0.924(3)	0.883(1)	0.9349(7)
C32	0.893(3)	0.962(1)	0.9470(8)
Cl1	0.9331(8)	0.4415(4)	0.8934(2)
O5	1.023(3)	0.3793(9)	0.9071(7)
O6	0.859(4)	0.394(1)	0.8615(7)
O7	0.978(3)	0.5056(9)	0.8676(6)
O8	0.885(3)	0.474(1)	0.9333(6)
Cl2	0.5762(9)	0.4327(3)	0.5974(2)
O9	0.636(4)	0.464(2)	0.558(1)
O10	0.443(4)	0.401(2)	0.575(1)
O11	0.701(5)	0.419(2)	0.629(1)
O12	0.626(5)	0.391(2)	0.632(1)
O13	0.524(4)	0.503(2)	0.621(1)
O14	0.504(6)	0.470(3)	0.635(1)
O15	0.496(9)	0.371(4)	0.578(2)
O16	1.296(5)	0.930(2)	0.928(1)
Ow1	0.716(6)	1.005(2)	0.802(1)
Ow2	0.796(7)	0.999(3)	0.727(2)
Ow3	1.195(5)	1.013(2)	0.799(1)
Ow4	0.269(3)	1.028(1)	0.7078(8)
Ow5	0.272(3)	0.450(1)	0.3039(7)
Ow6	0.316(5)	0.457(2)	0.194(1)
Ow7	0.969(3)	0.512(1)	0.3201(6)
Ow8	0.571(3)	0.508(1)	0.1885(8)
Ow9	0.975(6)	1.016(3)	0.837(2)

Each oxygen atom of the disordered perchlorate ion (O9–O16) refined to an average occupancy of 50%. The oxygen atoms of the disordered water molecules (Ow1–Ow9) refined to an average occupancy of 55%.

solved [30] and shows a similar arrangement to the structure of $[LCu_2(CH_3CO_2)_2](ClO_4)_2$ presented here. Each copper atom is bound by a dipropylenetriamine unit of the macrocycle and one chloride atom (Cu···Cl, 2.25 and 2.22 Å). A second chloride ion is only weakly associated with each copper atom (Cu···Cl, 3.41 and 3.58 Å) suggesting that the complex is cationic in solution.

The positive-ion FAB mass spectra of $[LCu_2(CH_3CO_2)_2](ClO_4)_2$, $[LZn_2(CH_3CO_2)_2](ClO_4)_2$ and $[LCu_2Cl_2]Cl_2$, all show peaks corresponding to the loss of one or two counter anions combined with the loss of one or two of the anionic exogenous ligands. The shift to lower masses by 1 to 4 units of some of these peaks indicates oxidation of the macrocyclic ligand, most probably oxidation of one or two of the amine groups to form imine groups. All the assigned peaks are substantiated further by comparison to the theoretical isotopic pattern required for the respective molecular formulae. Addition of trichloroacetic acid to the samples liberates the macrocyclic ligand to give a pattern for LH^+ centred at *m/z* 467.

A nickel complex, $[LNi_2(CH_3CO_2)_2(NCS)_2]$, was prepared by the reaction of the macrocycle with nickel acetate in the presence of the thiocyanate anion. The IR spectrum shows one ν_a(NCS) at 2071 cm^{-1} which indicates that the thiocyanate ions are most likely terminally N-coordinated, one to each Ni atom [31]. Coordination of three amino nitrogen atoms of the macrocycle and a bidentate acetato ligand, or monodentate acetate and a water molecule, at each Ni ion satisfies the preferred six-coordination of Ni^{2+}. The solubility properties and the poor quality FAB mass spectrum of this complex suggest it is a neutral inner sphere complex. The room temperature magnetic moment, $\mu_{eff}=4.79$ BM, for $[LNi_2(CH_3CO_2)_2(NCS)_2]$ (3.03 BM per Ni(II) ion) indicates also that the metal ions are probably not bridged by the thiocyanate ligands. The possibility of thiocyanate bridging between the nickel atoms in adjacent molecules thereby forming sandwich or polymeric type complexes can probably be eliminated also on the basis of the magnetic and spectroscopic measurements.

An objective of the present work has been to incorporate an exogenous ligand in the cavity created in the binuclear metal complexes of L. As evident in the X-ray structure of $[LCu_2(CH_3CO_2)_2](ClO_4)_2$ the exogenous acetate ligands act as bidentate chelating ligands rather than bridging between the two copper atoms. This is probably also the case in $[LNi_2(CH_3CO_2)_2(NCS)_2]$ which was synthesized in order to test whether it was possible for a ligand with a larger bite distance than a carboxylate, in this case, thiocyanate coordinating through its two terminal atoms, to bridge between the metal atoms.

Attempts to introduce possible bridging species capable of spanning larger distances than the acetate and thiocyanate ions, such as imidazolate, oxalate and fumarate were unsuccessful. The size of any potential bridging species is probably greatly restricted by the presence of the *p*-phenylene units of the macrocycle. However species such as oxalate are capable of bridging between the metal atoms of adjacent binuclear units to form sandwich-type complexes [32]. Work is continuing in this area.

Description of the structure of $[LCu_2(CH_3CO_2)_2](ClO_4)_2 \cdot 5H_2O$

The structure revealed by X-ray crystallography (Fig. 1) consists of discrete binuclear cations of formula $[LCu_2(CH_3CO_2)_2]^{2+}$ together with $[ClO_4]^-$ ions and lattice water. Selected bond lengths and angles are listed in Table 2.

The two Cu(II) atoms are bound by the dipropylenetriamine units of the 30-membered macrocyclic ligand. Each Cu ion is further coordinated by a bidentate acetate ligand thus achieving overall pentacoordination. The acetato coordination is unsymmetric, one Cu–O bond at each Cu being significantly longer than the other (Cu1–O4, 2.40(1), Cu2–O3, 2.30(1) Å; cf. Cu1–O1, 2.01(1), Cu2–O2, 1.99(1) Å). The remaining Cu–donor bond distances are normal. The aromatic rings of the macrocycle are nearly coplanar with a dihedral angle between the planes through the benzene rings of 19(1)°. The approximate distance between the planes (e.g. C8···C22) is 3.82 Å. Some of the disordered, hydrogen bonded, water molecules are located inside the cavity. The Cu···Cu distance of 8.40 Å probably precludes the incorporation of bridging species such as imidazolate, oxalate, fumarate and the pseudohalide ions in the cavity of the macrocycle in the present configuration. For example this distance is significantly greater than those measured for similar imidazole-bridged di-copper macrocyclic complexes (5.87–5.99 Å) [33, 34]. However, molecular models suggest that the $[LCu_2]^{4+}$ moiety may be flexible enough to adopt more appropriate configurations for the incorporation of a bridging anion.

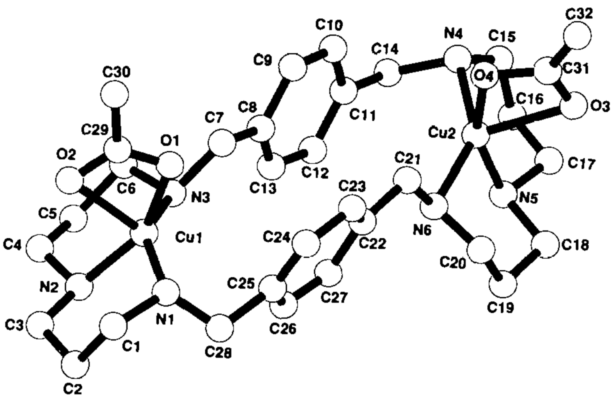

Fig. 1. Structural view of $[LCu_2(CH_3CO_2)_2]^{2+}$ together with the atomic numbering scheme.

TABLE 2. Selected interatomic distances (Å) and bond angles (°) for $[LCu_2(CH_3CO_2)_2](ClO_4)_2 \cdot 5H_2O$

Cu1···Cu2	8.40(1)	Cu2–N4	2.12(2)
Cu1–N1	1.97(1)	Cu2–N5	2.03(1)
Cu1–N2	2.03(1)	Cu2–N6	2.13(1)
Cu1–N3	1.96(2)	Cu2–O2	1.99(1)
Cu1–O1	2.01(1)	Cu2–O3	2.30(1)
Cu1–O4	2.40(1)		
N1–Cu1–N2	96.5(6)	N4–Cu2–N5	100.0(7)
N1–Cu1–N3	144.6(5)	N4–Cu2–N6	144.2(5)
N1–Cu1–O1	89.9(6)	N4–Cu2–O2	86.8(7)
N1–Cu1–O4	97.6(5)	N4–Cu2–O3	99.3(6)
N2–Cu1–N3	94.1(6)	N5–Cu2–N6	90.8(6)
N2–Cu1–O1	152.4(5)	N5–Cu2–O2	157.8(5)
N2–Cu1–O4	93.6(5)	N5–Cu2–O3	98.2(5)
N3–Cu1–O1	96.1(6)	N6–Cu2–O2	96.0(6)
N3–Cu1–O4	115.9(6)	N6–Cu2–O3	112.9(5)
O1–Cu1–O4	58.8(5)	O2–Cu2–O3	59.9(5)

The rather high values for *R* and R_w (0.095 and 0.112) are not unexpected in view of the poor quality data and the disorder, not only of one perchlorate ion and solvent molecules but also of the saturated chelate rings. Some of the residual electron density in the final difference map close to the macrocyclic framework can be accounted for by the possibility of disordered conformations around the six-membered chelate rings. A better model would require an unreasonable number of parameters.

Electrochemistry

Cyclic voltammetry and potentiometry were used to characterize $[LCu_2Cl_2]Cl_2$ electrochemically. A typical cyclic voltammogram is presented in Fig. 2. The solid line corresponds to a 2*e* nearly reversible wave with

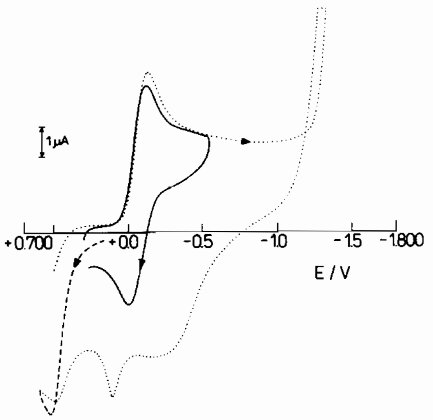

Fig. 2. Cyclic voltammetric curves $[LCu_2Cl_2]Cl_2$ in DMF containing 0.1 M TEAP, measured with a glassy carbon electrode vs. SCE at a sweep rate of 20 mV s^{-1} (22 °C): 1mM $LCu(II)_2$, solid and dotted lines; 1 mM Cu(I), dashed line.

the ratio of cathodic peak to anodic peak current slightly higher than 1. This curve indicates that both Cu(II) atoms in the complex are reduced to Cu(I) with a potential for the couple, $LCu(II)_2/LCu(I)_2$, of -0.061 V versus SCE. The second reduction peak at -1.2 V (dotted curve) is connected with the reduction of Cu(I) to Cu(0). This can be concluded from the large anodic charge during the reverse scan.

The potentiometric study carried out in DMF solutions was based on the assumption that both the Cu(I) and the Cu(II) complexes contain two copper atoms. A copper electrode was employed in the potential measurements, which involved measuring the potential of the Cu electrode in a solution containing either Cu(I) or Cu(II) and increasing the concentration of the ligand. The range of available concentrations was limited by the low solubility of the ligand. Only one step in the metal uptake was observed for both oxidation states. The following 2:1 formation constants were found: $\log K_{Cu(II)} = 26.3 \pm 0.6$, $\log K_{Cu(I)} = 17.7 \pm 1.0$.

The observed formation constant, $K_{Cu(II)}$, is two orders of magnitude less than that expected if no interaction between the copper ions is assumed, i.e. if the formation constant is compared to that for the 1:1 Cu(II) complex of 3,3′-iminobis(propylamine) [35]. This suggests that the two Cu(II) ions in the macrocyclic ligand may feel an electrostatic repulsion.

Supplementary material

Tables of positional and anisotropic thermal parameters, interatomic distances and angles and torsion angles, and listings of observed and calculated structure amplitudes are available from the authors on request.

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