DALTON
COMMUNICATION

Synthesis of a series of novel binucleating ligands based on 1,4,7-triazacyclononane and *o*-, *m*- and *p*-xylene: crystal structure of the μ-hydroxy-bridged dicopper(II) complex $[Cu_2L^m(OH)_2][BPh_4]_2$ [L^m = α,α′-bis(*N*-1,4,7-triazacyclononane)-*m*-xylene]

Louis J. Farrugia,* Paul A. Lovatt and Robert D. Peacock*
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK

The crystal structure and magnetic properties of $[Cu_2L^m(OH)_2][BPh_4]_2$ has been determined; L^m is one of three new binucleating ligands based on 1,4,7-triazacyclononane and *o*-, *m*- or *p*-xylene.

There is considerable interest in ligands which can co-ordinate two metal ions at a suitable distance whereby a small molecule (or molecules) can bind between the metal centres. Such systems may show interesting magnetic behaviour[1] (antiferromagnetic or ferromagnetic coupling), may activate the bound molecule (phosphate ester hydrolysis) or may serve as models for metalloenzymes.[2]

Young and Chin[3] have recently reported a dinuclear copper(II) complex of L that catalyses the cleavage of adenylyl(3′-5′)adenosine and adenosine-2′:3′-cyclic monophosphate. The complex, prepared by the addition of 2 mol of $CuCl_2$ to L, was not crystallographically characterised but was presumed to have a $Cu(OH_2)_2$ unit bonded to the three nitrogen atoms of each 9[ane]N_3 (1,4,7-triazacyclononane) ring. An analogous complex $[Co(OH_2)_2L^1Co(OH_2)_2]^{6+}$ has been structurally characterised[4] and does indeed contain two $Co^{III}N_4(OH_2)_2$ units.

We report in this communication the preparation of three novel, potentially dinucleating ligands, based on *o*-, *m*- and *p*-xylene (L^o, L^m and L^p) which are similar to L in their co-ordinating ability, and the preparation and crystal structure of the μ-hydroxy bridged dicopper complex of L^m, $[Cu_2L^m(OH)_2]^{2+}$.

The macrocycles L^o, L^m and L^p were prepared by reaction of α,α′-dibromo-*o*-, -*m*- or -*p*-xylene respectively (0.946 g, 3.6 mmol) with 1,4,7-triazatricyclo[5.2.1.0$^{4.10}$]decane[5] (1 g, 7.2 mmol) in dry acetonitrile (10 cm^3), followed by base hydrolysis of the resulting salt (overall yields 50–60%).† The salt $[Cu_2L^m(OH)_2][BPh_4]_2$ **1** was prepared in ≈50% yield by reacting L^m with 2 mol equivalents of CuI and 2 mol equivalents of Na[BPh_4] followed by aerial oxidation. The resulting blue precipitate was recrystallised from MeCN. An overall view of the structure‡ of the cation of complex **1** is shown in Fig 1. Fig 2 shows two further views of the cation designed to demonstrate specific structural features.

The complex is, as expected, dimeric with bridging hydroxyl groups and its structure can be usefully compared with that of the 'unsupported' μ-hydroxy-bridged dimer $[L^2Cu(OH)_2CuL^2]^{2+}$ **2** (L^2 = *N*,*N*′,*N*″-trimethyl-1,4,7-triazacyclononane) which is the simplest μ-hydroxy-bridged dimer involving two 9[ane]N_3 units.[8] The environment round the copper is similar in the two complexes: pseudo-square pyramidal with two short and one long Cu–N bonds and two Cu–O bonds with average lengths for complex **1** (**2**), 2.026 (2.077), 2.359 (2.238) and 1.930 (1.938) Å respectively. A major difference, however, is seen in the geometry of the CuO_2Cu unit. In complex **2**, and other unsupported dimers[9] based on 9[ane]N_3, this unit is planar; in **1** it is bent out of plane by 6.5 ± 0.5° in the direction of the *m*-xylene [Fig. 2(*a*)]. The Cu–Cu and Cu–O bond lengths are slightly shorter in **1** than **2** [2.947 (2.971) and 1.930 (1.938) Å] while the Cu–O–Cu angles are essentially identical [99.6 (101.1)°]. The magnetic susceptibility of complex **1** has been obtained§ over the temperature range 1.8–300 K. It behaves, as expected, as a weak antiferromagnet with $-J = 159 \pm 8$ cm^{-1}. This value is in line with other μ-hydroxy-bridged dimers with similar $Cu(OH)_2Cu$ core geometries {$-J$ for **2** is 45 cm^{-1}; for $[CuL^3(OH)_2L^3]^{2+}$, L^3 = *N*,*N*′,*N*″-triallyl-1,4,7-triazacyclononane[10] it is 77 cm^{-1}}.

The other interesting structural feature of complex **1** is the disposition of the *m*-xylene unit over the CuO_2Cu core [depicted in Fig. 2(*b*)]. This clearly creates a hydrophobic pocket on one side of the CuO_2Cu 'plane' towards which one of the μ-hydroxy groups is directed. We have modelled the structure of **1** using the MM+ forcefield of HYPERCHEM.[11] The modelled structure is very close to the crystal structure, the major differences being the prediction of slightly shorter values for the Cu–Cu, Cu–N and Cu–O distances. The deviation from planarity of the CuO_2Cu core in the direction of the *m*-xylene is predicted, albeit by only 1°.

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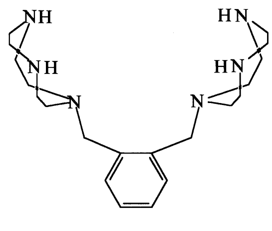
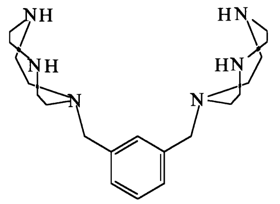
† NMR data (200 MHz, $CDCl_3$) for the macrocycles. L^o: ^{1}H, δ 7.29–7.07 (4 H, aromatic), 3.81 (4 H, $C_6H_4CH_2N$), 2.64 (8 H, CH_2N), 2.53 (16 H, CH_2NH), 2.07 (4 H, br, NH); ^{13}C, δ 138.43, 129.95, 126.76 (aromatic), 59.16 ($C_6H_4CH_2N$), 52.93 (CH_2N), 46.50 (CH_2NH). L^m: ^{1}H, δ 7.19–7.10 (4 H, aromatic), 3.62 (4 H, $C_6H_4CH_2N$), 2.67 (8 H, CH_2N), 2.55 (16 H, CH_2NH), 2.14 (4 H, br, NH); ^{13}C, δ 139.71, 129.51, 128.07, 127.59 (aromatic), 61.52 ($C_6H_4CH_2N$), 52.62 (CH_2N), 46.65, 46.37 (CH_2NH). L^p: ^{1}H, δ 7.18 (4 H, aromatic), 3.59 (4 H, $C_6H_4CH_2N$), 2.66 (8 H, CH_2N), 2.53 (16 H, CH_2NH), 2.11 (4 H, br, NH); ^{13}C, δ 138.5, 128.85 (aromatic), 61.32 ($C_6H_4CH_2N$), 52.7 (CH_2N), 46.75, 46.44 (CH_2NH).

‡ Crystal data for complex **1**. $C_{70}H_{81}B_2Cu_2N_7O_2$, *M* = 1201.12, triclinic, space group $P1$, blue prism, size 0.4 × 0.2 × 0.2 mm, *Z* = 2, *a* = 11.3259(9), *b* = 13.0874(5), *c* = 20.979(3) Å, α = 94.066(6), β = 97.590(8), γ = 93.169(5)°, *U* = 3068.1(5) Å^3, D_c = 1.300 g cm^{-3}, *F*(000) = 1268, μ (Mo-Kα) = 7.45 cm^{-1}. A total of 10 738 unique data were measured in bisecting geometry at 295 K on a CAD-4F diffractometer with graphite-monochromated X-radiation (λ = 0.710 73 Å). The structure was solved by direct methods (SIR 92)[6] and refined by full-matrix least squares on F^2 (SHELX 93).[7] The final *R*1 and *wR*2 (all data) were 0.0589 and 0.1373 for 649 parameters. Hydrogen atoms (apart from the OH hydrogen atoms which were directly located in the Fourier-difference map) were incorporated at fixed positions with C–H = N–H = 0.96 Å. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/411.

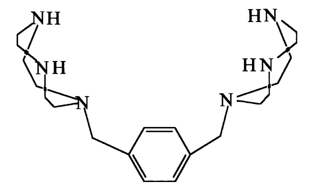
§ Magnetic measurements were obtained using a SQUID magnetometer. Six single crystals were attached (in random orientation) to a silica fibre and the magnetic susceptibility run over the range 1.8–300 K. The data between 50 and 300 K were fitted to a Bleaney–Bowers expression.



L^o



L^m



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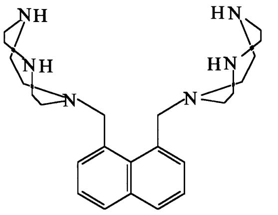

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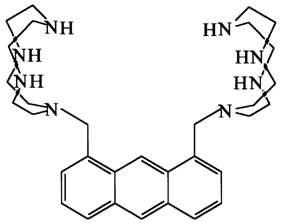

L^1

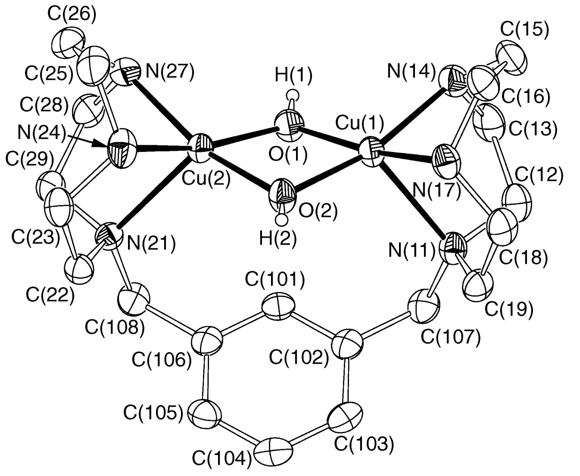

Fig. 1 Molecular structure and atomic labelling scheme for the cation of complex **1**. Important bond lengths (Å) and angles (°) are: Cu(1)–Cu(2) 2.9464(5), Cu(1)–O(2) 1.928(2), Cu(1)–O(1) 1.931(2), Cu(1)–N(17) 2.022(3), Cu(1)–N(14) 2.024(3), Cu(1)–N(11) 2.351(3), Cu(2)–O(1) 1.928(3), Cu(2)–O(2) 1.931(2), Cu(2)–N(24) 2.018(3), Cu(2)–N(27) 2.039(3), Cu(2)–N(21) 2.366(2); Cu(1)–O(1)–Cu(2) 99.55(10), Cu(1)–O(2)–Cu(2) 99.56(10), O(1)–Cu(1)–O(2) 79.00(10), O(1)–Cu(2)–O(2) 79.01(10), O(2)–Cu(1)–N(17) 96.52(11), O(1)–Cu(1)–N(14) 97.33(11), N(17)–Cu(1)–N(14) 84.32(11), N(17)–Cu(1)–N(11) 81.69(10), N(14)–Cu(1)–N(11) 81.82(11), O(1)–Cu(1)–N(11) 110.73(10), O(2)–Cu(1)–N(11) 111.78(10), O(2)–Cu(2)–N(24) 95.08(11), O(1)–Cu(2)–N(27) 96.95(12), N(24)–Cu(2)–N(27) 84.76(13), N(24)–Cu(2)–N(21) 81.52(10), N(27)–Cu(2)–N(21) 79.64(10), O(1)–Cu(2)–N(21) 115.30(10), O(2)–Cu(2)–N(21) 114.96(10)

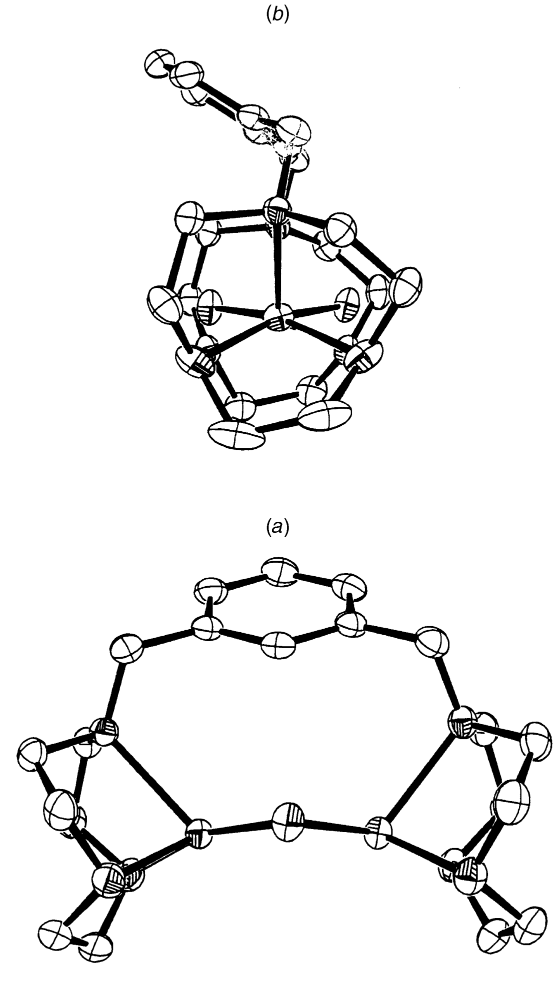

Fig 2. Views of the cation of complex **1** showing (*a*) the bending of the μ-OH groups towards the xylene and (*b*) the orientation of the xylene over the CuO_2Cu core

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