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# Structure and magnetic properties of polynuclear chloro- and hydroxo-bridged copper(II) complexes formed by a tetramacrocyclic derivative of 1,4,7-triazacyclononane

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#### Abstract

Two new copper(II) complexes of the ligand 1,2,4,5-*tetrakis*(1,4,7-triazacyclononan-1-ylmethyl)benzene (L<sup>dur</sup>) have been synthesized and characterized by single crystal X-ray studies. The first,  $[Cu_4L^{dur}(\mu_2-OH)_4]Cl_2(PF_6)_2 \cdot 8H_2O$  (1), was isolated from a solution of L<sup>dur</sup> and Cu<sup>2+</sup> at pH 9. Under acidic conditions (pH 3), a polymeric complex, { $[Cu_4L^{dur}(\mu_2-Cl)_6](PF_6)_2 \cdot 10H_2O$ }, (2), crystallized from solution. In both complexes, each of the four triazacyclononane (tacn) rings of the L<sup>dur</sup> ligand facially coordinate to separate metal centres. Pairs of Cu(II) centres are then doubly-bridged by hydroxo groups in 1, leading to tetranuclear complex cation units featuring pairs of isolated copper(II) dimers with Cu<sub>2</sub>( $\mu_2$ -OH)<sub>2</sub> cores folded at the O···O lines. Two forms of the tetranuclear units, featuring slightly different Cu<sub>2</sub>( $\mu_2$ -OH)<sub>2</sub> core geometries, are present in equal amounts within the crystal lattice. In complex 2, chloro bridging ligands link pairs of Cu(II) centres from neighbouring tetranuclear units, forming a 1D helical polymeric structure. Variable-temperature magnetic susceptibility measurements suggest that the hydroxo-bridged copper(II) centres within one of the tetranuclear units in 1 are weakly antiferromagnetically coupled (J = -27 cm<sup>-1</sup>), whilst those in the other interact ferromagnetically (J = +19 cm<sup>-1</sup>). Similar measurements indicate weak ferromagnetic coupling (J = +16 cm<sup>-1</sup>) for the chloro-bridged copper(II) centres in 2.

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# 1. Introduction

Recent studies of polynucleating ligands incorporating multiple 1,4,7-triazacyclonone (tacn) units have led to the synthesis and characterization of a variety of bridged polynuclear copper(II) complexes [1–10]. One driving force for these studies has been interest in developing correlations between molecular structure and magnetic properties. In one recent study [7,8], a trimacrocyclic ligand consisting of three tacn units assembled around a single mesitylene unit was used to prepare trinuclear, hexanuclear and polymeric hydroxobridged copper(II) complexes with structural features of relevance to polynuclear metal sites found in metalloenzymes, while in a related study [9,10], a tetramacrocyclic ligand consisting of four tacn rings linked together by a central durene unit ( $L^{dur} = 1,2,4,5$ -*tetrakis*(1,4,7-triazacyclonon-1-ylmethyl)benzene) was used to prepare a series of complexes ranging from binuclear "sandwich" complexes, to tri- and tetra-nuclear non-bridged complexes, as well as tetranuclear bridged complexes in which pairs of metal centers are linked by two hydroxo,

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azido or alkoxo groups. Using the hydrobromide salt of L<sup>dur</sup> as the ligand source, it was found that the nonbridged tetracopper(II) complex, [Cu<sub>4</sub>L<sup>dur</sup>(H<sub>2</sub>O)<sub>8</sub>]- $(ClO_4)_8$ , was formed when the ligand was reacted with four molar equivalents of a copper salt at pH below 7 [9]. Adjustment of the pH of an aqueous solution of this complex to 9.5 resulted in the bridged hydroxo complex,  $[Cu_4L^{dur}(\mu_2-OH)_4](ClO_4)_4$ , which was found to transform into the methoxo-bridged derivative,  $[Cu_4L^{dur}(\mu_2 OMe_4$  (ClO<sub>4</sub>)<sub>4</sub>, on recrystallisation from methanol [10]. In these, and related bridged complexes, magnetic interactions between the Cu centers were found to vary systematically with key geometric descriptors of the Cu<sub>2</sub>O<sub>2</sub> core, e.g., Cu–O and Cu···Cu distance, Cu–O– Cu angle, and the dihedral angle between the two Cu<sub>2</sub>O units [10]. Our interest in the effect of pH on ligand binding to the copper has led to the synthesis and characterization of a new hydroxo-bridged copper(II) complex incorporating the L<sup>dur</sup> ligand at pH 9. At the lower pH of 3, a polymeric complex has been obtained in which pairs of Cu(II) centers are triply-bridged by three chloro ligands. We report here the characterization of these products by single crystal X-ray crystallographic and magnetochemical techniques. Interestingly, although the hydroxo-bridged complex has similar coordination features to the previously reported compound,  $[Cu_4L^{dur}(\mu_2-OH)_4](ClO_4)_4$ , it exhibits quite different magnetic properties.

# 2. Experimental

### 2.1. Materials

Reagent or analytical grade materials were obtained from commercial suppliers and used without further purification. Distilled water was used throughout. 1,4,7-triazatricyclo[5.2.1.0<sup>4,10</sup>]decane [3] and 1,2,4,5tetra(bromomethyl)benzene [11] were synthesized according to published methods.

#### 2.2. Instrumentation

Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer as KBr pellets. Variable temperature magnetic susceptibilities were measured using a Quantum Design MPMS5 SQUID magnetometer operating in an applied field of 1 T. The powdered samples were contained in calibrated gelatine capsules held in the centre of a straw, the latter being attached to the end of the sample rod. The temperature and field were checked against a standard Pd sample and Cu-SO<sub>4</sub> · 5H<sub>2</sub>O. Fitting of the magnetic data employed a non-linear least-squares program called POLYMER, written at Monash University by Dr E. N. Bashki and Mr K. J. Berry. *Caution:* Although no problems were encountered in this work, transition metal perchlorates are potentially explosive. They should be prepared in small quantities and handled with care.

# 2.3. Syntheses

# 2.3.1. 1,2,4,5-Tetrakis(1,4,7-triazacyclonon-1ylmethyl)benzene dodecahydrohexafluorophosphate trihydrate ( $L^{dur} \cdot 12HPF_6 \cdot 3H_2O$ )

To a stirred solution of 1,4,7-triazatricyclo[5.2.  $1.0^{4,10}$  decane (0.79 g, 5.68 mmol) in CCl<sub>4</sub> was added dropwise a solution of 1,2,4,5,-tetra(bromomethyl)benzene (0.80 g, 1.78 mmol) in warm CCl<sub>4</sub>, resulting in the formation of a white precipitate after 10 min of stirring. This solution was stirred at room temperature for 15 h, the white solid collected by filtration, washed with CCl<sub>4</sub> and air-dried. The solid was then dissolved in H<sub>2</sub>O (50 mL) and refluxed for 2 h, the solution turning pale pink during this time. Upon cooling, a large excess of solid NaOH was added and the solution returned to reflux overnight. After this time, the solution had become pale yellow. The solvent was removed under reduced pressure, and the residual water removed via azeotropic distillation with toluene. The solution was then cooled, filtered, and the solvent removed under reduced pressure. The yellow oil was dissolved in 5 mL of EtOH and to this solution was added concentrated aqueous HPF<sub>6</sub> until no more solid precipitated. The solution was cooled, and the pale yellow precipitate of the product was collected at the pump and dried in the oven at 60 °C for 1 h. Yield: 1.94 g (45%). Anal. Calc. for C<sub>34</sub>F<sub>72</sub>H<sub>84</sub>N<sub>12</sub>O<sub>3</sub>P<sub>12</sub>: C, 16.7; H, 3.5; N, 6.9. Found: C, 16.5; H, 3.9; N, 6.7%. <sup>1</sup>H NMR (D<sub>2</sub>O, δ): 7.65 (s, 2H, ArCH), 4.09 (s, 8H, NCH<sub>2</sub>Ar), 3.61 (s, 16H, CH<sub>2</sub> tacn ring), 3.15 (t, 16H, CH<sub>2</sub> tacn ring), 2.98 (t, 16H, CH<sub>2</sub> tacn ring). IR and mass spectra equivalent to that reported by Graham et al. [10].

# 2.3.2. $[Cu_4L^{dur}(\mu_2-OH)_4]Cl_2(PF_6)_2 \cdot 8H_2O(1)$

To a stirred solution of  $L^{dur} \cdot 12HPF_6 \cdot 3H_2O(0.51 g,$ 0.21 mmol) in 50 mL H<sub>2</sub>O was added CuCl<sub>2</sub> · 2H<sub>2</sub>O (0.26 g, 1.51 mmol), affording a light blue solution. Dropwise addition of 2 M NaOH caused a colour change to deep blue. Continued addition of 2 M NaOH resulted in a fine precipitate of Cu(OH)<sub>2</sub>, which was redissolved with the minimum volume of 0.1 M HCl. Slow evaporation of the dark blue solution (pH 9) resulted in the formation of dark blue crystals of 1, which were collected by filtration and washed with the minimum volume of ice cold water (which resulted in some loss of product) and air-dried. The crystals lost solvent on drying. Yield: 0.18 g (56%). Anal. Calc. for C<sub>34</sub>Cl<sub>2</sub>Cu<sub>4</sub>F<sub>12</sub>H<sub>82</sub>N<sub>12</sub>O<sub>12</sub>P<sub>2</sub>: C, 27.8; H, 5.9; N, 11.4. Found: C, 27.6; H, 5.6; N, 11.0%. Selected IR bands (KBr, v cm<sup>-1</sup>): 3446 vs, br, 3290 s, 2931 m, 1654 m,

1498 m, 1363 m, 1093 m, 1004 m, 956 m, 843 vs, 626 s. Crystals suitable for the X-ray work were obtained from this sample, the composition of which corresponded to  $[Cu_4L^{dur}(\mu_2-OH)_4]Cl_2(PF_6)_2 \cdot 2.5H_2O.$ 

2.3.3. { $[Cu_4L^{dur}(\mu_2-Cl)_6](PF_6)_2 \cdot 9H_2O\}_n$  (2) A solution of  $L^{dur} \cdot 12HPF_6 \cdot 3H_2O$  (0.25 g, 0.10) mmol) was dissolved in 20 mL H<sub>2</sub>O and to this stirred solution was added  $CuCl_2 \cdot 2H_2O$  (0.12 g, 0.69 mmol) dissolved in the minimum volume of H<sub>2</sub>O, affording a light blue solution. The pH was increased to 6 using 2 M NaOH, the colour changing from light to dark blue. The addition was ceased upon formation of a faint pale blue precipitate. This precipitate was dissolved using 0.1 M HCl. After standing overnight, more pale blue precipitate had formed. This was dissolved using 0.1 M HCl, resulting in a decrease in pH to 3-4. Slow evaporation yielded green crystals of 2, which were collected at the pump, and washed with ice cold  $H_2O$  (resulting in significant loss of product). The crystals lost solvent on standing. Yield: 0.08 g (51%). Anal. Calc. for  $C_{34}Cl_6Cu_4F_{12}H_{86}N_{12}O_{10}P_2$ : C, 25.9; H, 5.4; N, 10.6. Found: C, 25.7; H, 4.9; N, 10.2%. Selected IR bands (KBr, v cm<sup>-1</sup>): 3450 vs, br, 3240 vs, br, 2927 m, 2876 m, 1625 m, 1492 m, 1454 m, 1360 m, 1097 s, 1004 m, 842 vs, br, 738 m, 559 s. Crystals suitable for the X-ray study were obtained from the mother liquor, the composition of which corresponded to  $\{[Cu_4L^{dur}]$  $(\mu_2 - \text{Cl})_6](\text{PF}_6)_2 \cdot \sim 9\frac{1}{3}\text{H}_2\text{O}_{n}$ 

#### 2.4. Structure determinations

For 1, a full sphere of CCD diffractometer data was measured at ca. 173 K using an Enraf-Nonius Kappa instrument  $(2\theta_{\text{max}} = 50^{\circ}, \omega \text{ scan mode; monochromatic})$ Mo K $\alpha$  radiation,  $\lambda = 0.7107_3$  Å). 21688 total reflections merged to 9266 unique ( $R_{int} = 0.25$ ), 4437 with  $F > 4\sigma(F)$ considered "observed", and refining to R = 0.13,  $R_{\rm w} = 0.25$  (weights:  $(\sigma^2(F^2) + 20F^2)^{-1}$ ), with only Cu, P, Cl and F displacement parameter forms anisotropic.

For 2, a unique data set, with symmetry equivalents, was measured at ca. 295 K using a single-counter/"four circle" instrument ( $2\theta_{\text{max}} = 50^\circ$ ,  $2\theta/\theta$  scan mode; monochromatic Mo K $\alpha$  radiation,  $\lambda = 0.7107_3$  Å). 11009 reflections merged, after gaussian absorption correction, to 5226 unique ( $R_{int} = 0.12$ ), 946 with  $I > 3\sigma(I)$  being considered "observed" and used in the full-matrix least-squares refinement, refining anionic displacement parameter forms for Cu, Cl only.  $(x,y,z,U_{iso})_{H}$  were included (where possible), constrained at estimated values. Conventional R,  $R_w$  (weights:  $(\sigma^2(F) + 0.0004F^2)^{-1})$  at convergence were 0.094, 0.107. Neutral atom complex scattering factors were employed within the XTAL 3.5 program system [12].

 $[Cu_4L^{dur}(\mu_2-OH)_4]Cl_2(PF_6)_2 \cdot 2.5H_2O \quad (1) \equiv C_{34}Cl_2 Cu_4F_{12}H_{75}N_{12}O_{6.5}P_2$ , M = 1371.3. Triclinic, space group  $P\bar{1}$  ( $C_{i_o}^1$ , No. 2), a = 12.086(2), b = 14.737(3), c = 15.900(3) Å,  $\alpha = 72.44(3)$ ,  $\beta = 82.73(3)$ ,  $\gamma =$ 82.69(3).  $V = 2666 \text{ Å}^3$ .  $D_c$   $(Z = 1) = 1.708 \text{ g cm}^{-3}$ .  $\mu_{Mo} = 18.4 \text{ cm}^{-1}$ .  $|\Delta \rho_{max}| = 2.9 \text{ e} \text{ Å}^{-3}$ . This compound presented considerable difficulties with data acquisition, the result serving only to define gross stoichiometry, stereochemistry and connectivity. Hydrogen atoms were not located, the bridges presumed hydroxyl; one difference map residue was modelled as 0.5 solvent (water) oxygen, the other fully weighted.

 $\{ [Cu_4 L^{dur}(\mu_2 - Cl)_6] (PF_6)_2 \cdot \sim 9 \frac{1}{3} H_2 O \}_n \quad (2) \equiv C_{34} Cl_6 - Cl_6 = C_{34} Cl_6 - Cl_6 + Cl_6 +$ Cu<sub>4</sub>F<sub>12</sub>H<sub>84.66</sub>N<sub>12</sub>O<sub>9.33</sub>P<sub>2</sub>, M = 1568. Rhombohedral, space group  $R\bar{3}c$  ( $D_{3d}^6$ , No. 167), a = 22.481(5), c = 60.76(2) Å, V = 26587 Å<sup>3</sup> (hexagonal setting).  $D_c$  $(Z = 18) = 1.76_2 \text{ g cm}^{-3}$ .  $\mu_{Mo} = 18.4 \text{ cm}^{-1}$ ; specimen:  $0.17 \times 0.25 \times 0.25$  mm;  $T_{\min,\max} = 0.64, 0.78. |\Delta \rho_{\max}| =$  $1.2 \text{ e} \text{ Å}^{-3}$ . Anions were subject to disorder/high displacement parameters and were modeled with constrained geometries. Residues were modeled as water molecule oxygen atoms (hydrogen atoms not located) and with unit site occupancies, O(07) excepted (0.5). The crystallographic study was of limited precision, consequent upon weak and limited diffraction data obtained from "difficult" material (presumably) consequent upon factors such as anion disorder, long axis, desolvation tendencies, and its polymeric nature. A second data set, measured at low temperature (110 K) at a CCD diffractometer/synchrotron radiation facility, gave no substantive improvement in data or model so that that derivative of the original data and model is recorded.

### 3. Results and discussion

#### 3.1. Synthesis and characterization

Addition of CuCl<sub>2</sub> · 2H<sub>2</sub>O to the hydrohexafluorophosphate salt of the L<sup>dur</sup> ligand, followed by adjustment of the pH to 9 yielded a product, 1 (Fig. 1), whose composition indicated formation of the expected tetranuclear  $[Cu_2(\mu_2-OH)_2]_2$  core. In contrast to the previously reported hydroxo-bridged copper(II) complex of L<sup>dur</sup>



Fig. 1. Complexes prepared in this study.

[10], where the complex cation was crystallized as a tetraperchlorate salt, in this case it was obtained as a dichloro-dihexafluorophosphate salt. A decrease in pH to ca. 3 in the presence of excess chloride resulted in rearrangement of the coordination geometry of the complex, with loss of the hydroxo bridges and subsequent formation of a polymeric structure incorporating trichlorobridged Cu<sub>4</sub>L<sup>dur</sup> cation units, which was isolated as its dihexafluorophosphate salt, 2 (Fig. 1). Microanalytical data supported the proposed formulations for 1 and 2. The UV–Vis reflectance spectrum of 1 showed a broad d-d band centred at 593 nm with a shoulder at ca. 890 nm, which is in accordance with the square-pyramidal geometry of the Cu(II) centres [13]. The green chlorobridged complex, 2, showed a broad d-d band at 608 nm, also consistent with pseudo-square pyramidal coordination geometry of the Cu(II) centres within the polymeric framework.

#### 3.2. Crystal structures

The crystal structures of complexes 1 and 2 were determined by single crystal X-ray studies. Projections of the cation units are presented in Figs. 2 and 3, whilst selected bond lengths and angles are listed in Tables 1 and 2.

As for the previously reported tetraperchlorate salt analogue [10], crystals of 1 contain the tetranuclear cation,  $[Cu_4L^{dur}(\mu_2-OH)_4]^{4+}$ , which features pairs of  $Cu_2(\mu_2-OH)_2$  dimeric units (Fig. 2). There are two very slightly different forms of the cation present in equal amounts within the crystal lattice, exhibiting small differences in the geometries of the  $Cu_2(\mu_2-OH)_2$  cores (see below). Both forms possess a crystallographic centre of symmetry, lying at the midpoint of the durene spacer, with the pairs of  $Cu_2(\mu_2-OH)_2$  dimeric units lying on opposite sides of the plane of the central aromatic ring of the L<sup>dur</sup> ligand in each case. These dimeric units are capped by pairs of tacn rings attached at meta positions relative to one another on the aromatic ring. The copper(II) centres all exhibit pseudo-square pyramidal coordination geometries, with two secondary amines and two oxygen donors occupying the four basal coordination sites and a tertiary bridgehead nitrogen residing in the apical position. The axial Cu–N bonds (2.26(2))– 2.34(2) A) are longer than the associated basal Cu–N bonds (2.01(2)-2.08(2) Å) due to the Jahn-Teller distortion associated with the d<sup>9</sup> copper(II) centres [13].

Comparison of the structure of the two tetranuclear cationic units in 1 with that in  $[Cu_4L^{dur}(\mu_2-OH)_4](ClO_4)_4$  reveals similar copper(II) coordination geometries. However there are slight differences in the geometries of the  $Cu_2(\mu_2-OH)_2$  cores (Table 3). In all cases, the  $Cu_2(\mu_2-OH)_2$  units are folded at their  $O \cdots O$  lines, as indicated by the fact that the dihedral angle ( $\delta$ ) between the two  $Cu_2O$  planes is reduced from 180°, although the

degree of bending varies between the different units (150° for the two cations in **1** versus 159° for the perchlorate salt). In addition, the Cu–O–Cu angles ( $\varphi$ ) in **1** are generally more acute than those in [Cu<sub>4</sub>L<sup>dur</sup>( $\mu_2$ -OH)\_4](ClO<sub>4</sub>)<sub>4</sub> (91.1(5)°, 96.5(7)°, 90.5(6)° and 94.2(7)° versus 95.7(4)° and 97.9(4)°). Consequently, shorter Cu···Cu distances are observed for complex **1** compared to the perchlorate salt (2.840(4) and 2.852(4) versus 2.939(9) Å). These differences are presumably attributable to the different anions and degrees of solvation for the complexes, and result in different magnetic behaviours (see Section 3.3).

Despite the deficiencies of the data, the single crystal X-ray study of 2 is consistent with the stoichiometry and connectivity as given above and in Fig. 1. The uncoordinated hexafluorophosphate anions and solvent residues fill the voids between strands of the cationic polymer,  $[Cu_4L^{dur}(\mu-Cl)_6]_n^{2n+}$  (Fig. 2), which wind as helices about the crystallographic 3-axis. The repeating unit of the polymer is disposed about a crystallographic inversion center, which lies at the centre of the aromatic ring of the  $L^{dur}$  ligand, with the {(CH<sub>2</sub>)tacn} substituents in adjacent pairs attached at the 1,2- and centrosymmetrically-related 4,5-positions, and disposed on opposite sides of the aromatic ring plane. Each tacn ring coordinates facially in the coordination sphere of a six-coordinate Cu(II) centre, the other three sites being occupied by a fac-Cl<sub>3</sub> array, the latter also fac to a further symmetryrelated Cu(II) centre of the other type (i.e., Cu(2) cf. Cu(1)), leading to a trichloro-bridged dimer  $(Cu(1)\cdots$ Cu(2) = 3.192(9) Å). About each Cu(II) centre, the sixcoordinate array, as is frequently the case, is dominated by a cis-N<sub>2</sub>Cl<sub>2</sub> array, the other trans pair of "axial" sites occupied by the remaining nitrogen (N(n1)) and the remaining bridging chlorine (Cl(2)/Cu(1); Cl(3)/Cu(2)). The Cu(1)-Cl(2) and Cu(2)-Cl(3) distances (2.86(2)) and 2.95(1) Å) are significantly longer than the Cu(n)-N(n1) distances (2.26(3) and 2.30(2) Å) so that the aspect of the coordination sphere is perhaps more accurately described as "square-pyramidal" (the angle sums in the pair of "square-planar" arrays are 350 and 349°). As a consequence also, two of the chlorine atoms (Cl(2,3))may better be described as "semi-bridging", Cl(1) being the only symmetrically-bridging chlorine.

Despite the wealth of binuclear and polynuclear copper(II) halide complexes containing di-bridged chloro units [14], there are relatively few crystallographically characterized examples of dicopper units bridged by three chlorides, the majority containing polymeric  $[Cu(\mu_2-Cl)_3]$  chains [15]. Within these structures, the Cu(II) centres reside in distorted octahedral geometries, with Cu···Cu separations of the order of 3.2–3.5 Å, and the Cu–Cl separations range from about 2.2 to 2.9 Å. The Cu<sub>2</sub>( $\mu_2$ -Cl)<sub>3</sub> core geometries are thus quite similar to those found in **2**. There are only two descriptions of trichloro-bridged copper amine complexes, namely





Fig. 2. (a) Plot of one of the tetranuclear cations in  $[Cu_4L^{dur}(\mu_2-OH)_4]Cl_2(PF_6)_2 \cdot 2.5H_2O(1)$ . (b) Unit cell contents of 1, projected down the *a* axis.

 $[Cu_2(\mu_2-Cl)_3(Me_3tacn)_2]Cl \quad (Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane) [16] and [Cu_2(\mu_2-Cl)_3(tmen)_2]$  $[B{(C_6H_3(CF_3)_2)}_4] (tmen = Me_2N(CH_2)_2NMe_2) [17], of which only the latter has been crystallographically characterised. Of note is that, unlike$ **2**, both these complexes were prepared under non-acidic conditions, $[Cu_2(\mu_2-Cl)_3(tmen)_2]<sup>+</sup> being prepared using fluoroben-$  zene as the solvent, and  $[Cu_2(\mu_2-Cl)_3(Me_3tacn)_2]^+$  from an addition of an aqueous solution of the free base of Me<sub>3</sub>tacn to a methanolic solution of CuCl<sub>2</sub> · 2H<sub>2</sub>O. Whilst the capping ligands in  $[Cu_2Cl_3(tmen)_2] [B\{(C_6H_3(CF_3)_2)\}_4]$  are bidentate as compared to tridentate in **2**, this complex also features a distorted  $[Cu(\mu_2-Cl)_3]$  core, with one chlorine lying further from



Fig. 3. Plot of a section of the polymeric complex  $\{[Cu_4L^{dur}(\mu_2-Cl)_6](PF_6)_2 \cdot \sim 9^1/_3H_2O\}_n$  (2).

Table 1 Selected bond distances (Å) and angles (°) for  $[Cu_4L^{dur}(\mu_2\text{-}OH)_4]Cl_2\text{-}(PF_6)_2\cdot 2.5H_2O$  (1)

Bond lengths	
Cu(1) - N(11)	2.34(2), 2.30(2)
Cu(1)–N(14)	2.05(2), 2.03(2)
Cu(1)–N(17)	2.05(2), 2.06(2)
Cu(1)–O(1)	1.95(2), 1.99(8)
Cu(1)–O(2)	2.03(1), 1.96(2)
Cu(2) - N(21)	2.29(2), 2.26(2)
Cu(2) - N(24)	2.05(2), 2.08(2)
Cu(2) - N(27)	2.01(2), 2.02(2)
Cu(2)–O(1)	1.88(2), 2.01(2)
Cu(2)–O(2)	1.97(2), 1.91(1)
Bond angles	
Cu(1)–O(1)–Cu(2)	96.5(7), 90.5(6)
O(1)-Cu(1)-O(2)	80.3(6), 82.9(6)
O(1)-Cu(1)-N(11)	104.8(7), 116.9(6)
O(1)-Cu(1)-N(14)	171.4(6), 159.6(6)
O(1)-Cu(1)-N(17)	95.6(8), 99.4(7)
O(2)–Cu(1)–N(11)	114.2(6), 101.3(7)
O(2)-Cu(1)-N(14)	96.3(7), 92.8(7)
O(2)-Cu(1)-N(17)	162.4(6), 174.4(6)
N(11)-Cu(1)-N(14)	83.8(7), 83.5(6)
N(11)-Cu(1)-N(17)	83.4(7), 82.2(7)
N(14)-Cu(1)-N(17)	85.3(7), 83.2(7)
Cu(1)-O(2)-Cu(2)	91.1(5), 94.2(7)
O(1)–Cu(2)–O(2)	83.4(6), 83.9(6)
O(1) - Cu(2) - N(21)	100.1(7), 113.7(6)
O(1) - Cu(2) - N(24)	175.6(7), 162.6(7)
O(1)-Cu(2)-N(27)	93.2(7), 95.7(8)
O(2) - Cu(2) - N(21)	115.6(6), 105.1(6)
O(2) - Cu(2) - N(24)	97.4(7), 93.0(7)
O(2) - Cu(2) - N(27)	160.8(7), 171.2(7)
N(21)-Cu(2)-N(24)	83.4(7), 83.7(7)
N(21)-Cu(2)-N(27)	83.6(7), 83.2(7)
N(24)-Cu(2)-N(27)	84.6(7), 84.7(8)

The two values in each entry are the counterpart values for the two independent forms of the tetranuclear cation present in the crystal lattice. Centrosymmetrically-related atoms are italicized.

Table 2 Selected bond distances (Å) and $\{[Cu_4L^{dur}(\mu_2\text{-}Cl)_6](PF_6)_2 \cdot \sim 9\frac{1}{3}H_2O\}_n$ (2)	angles	(°)	for
Bond lengths			
Cu(n)– $Cl(1)$	2.33	(1), 2.2	29(2)
Cu(n)– $Cl(2)$	2.86	(2), 2.2	2(3)
Cu(n)– $Cl(3)$	2.18	(2), 2.9	5(1)
Cu(n)-N(n1)	2.26	(3), 2.3	0(2)
Cu(n)-N(n4)	2.00	(4), 2.0	6(3)
Cu(n)-N(n7)	1.98	(3), 2.0	1(4)
Bond angles			
N(n4)-Cu(n)-Cl(1)	92(1	), 93(1)	
N(n4)-Cu(n)-N(n7)	83(1	), 83(1)	
$N(n7)-Cu(n)-Cl(x)^{a}$	99(1	), 98(1)	
$Cl(1)-Cu(n)-Cl(x)^{a}$	76.3	(5), 75.	1(5)
$Cu(1)$ – $Cl(1)$ – $Cu(2^i)$	87.3	(3)	
$Cu(1)$ – $Cl(2)$ – $Cu(2^i)$	76.7	(6)	
$Cu(1)-Cl(3)-Cu(2^{i})$	75.3	(5)	

The two values in each entry are for the two distinct copper centres (n = 1, 2).

<sup>a</sup> For n = 1, x = 2; for n = 2,  $x = 3^{i}$  (i = 2/3 - x; 1/3 - x + y; 5/6 - z).

the copper(II) centres than the other two. The longest Cu–Cl bonds, however, are significantly shorter than those observed in **2** (2.600(1) and 2.640(1) Å versus 2.86(2) and 2.95(1) Å), resulting in a shorter Cu···Cu separation (2.9517(7) versus 3.192(9) Å), perhaps because formation of the polymeric structure in **2** imposes additional constraints on the geometry of the Cu<sub>2</sub>( $\mu_2$ -Cl)<sub>3</sub> core.

# 3.3. Magnetic properties

Variable-temperature magnetic susceptibility measurements were carried out on powdered samples of complexes 1 and 2 in the 2–300 K temperature range.

Table 3

Structural and magnetic data for selected	complexes	containing folded	$Cu_2(\mu_2-OH)_2$ units
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Complex		Cu–O–Cu $(\varphi)$ (°)	Cu···Cu (Å)	$\delta^{\mathrm{a}}$ (°)	$J ({ m cm})^{-1}$
1	Cation A	90.5(6)	2.840(4)	150	+19
		94.2(7)			
	Cation B	96.5(7)	2.852(4)	150	-27
		91.1(5)			
$[Cu_{3}L^{mes}(\mu_{2}\text{-}OH)_{2}(H_{2}O)_{2}](ClO_{4})_{4}{}^{b}$		98.9(2)	2.9041(8)	152	-24
		92.1(1)			
$[Cu_4L^{dur}(\mu_2\text{-}OH)_4](ClO_4)_4^{\ c}$		97.9(4)	2.939(9)	159	-27
		95.7(4)			
$[Cu_2L^{mx}\!(\mu_2\text{-}OH)_2]\!(BPh_4)_2{}^d$		99.6(1)	2.9464(5)	174	-80

<sup>a</sup> Dihedral angle between two CuO<sub>2</sub> planes.

<sup>b</sup> Ref. [8],  $L^{mes} = 1,3,5$ -tris(1,4,7-triazacyclononan-1-ylmethyl)benzene.

<sup>c</sup> Ref. [10].

<sup>d</sup> Ref. [5],  $L^{mx} = 1,3$ -bis(1,4,7-triazacyclonon-1-ylmethyl)benzene.

The plots of magnetic susceptibility ( $\chi$ ) and  $\chi T$  versus temperature (T) are shown in Fig. 4.

The magnetic susceptibility of **1** shows a gradual increase with decreasing temperature (Fig. 4(a)). The corresponding plot of  $\chi T$  versus temperature shows a staggered decrease from 0.476 cm<sup>3</sup> mol<sup>-1</sup> K at 300 K, to 0.325 cm<sup>3</sup> mol<sup>-1</sup> K at 8 K, and then to 0.282 cm<sup>3</sup> mol<sup>-1</sup> K at 2 K. Unlike the case for the previously reported compound, [Cu<sub>4</sub>L<sup>dur</sup>(µ<sub>2</sub>-OH)<sub>4</sub>](ClO<sub>4</sub>)<sub>4</sub> [10], attempts to fit the data for **1** to a simple model assuming

the presence of only a single type of  $Cu_2(\mu_2\text{-}OH)_2$  dimer were unsuccessful. A very good fit was obtained, however, when the data were fitted to a modified Bleaney– Bowers equation (Eq. (1)) that assumes the presence of equimolar amounts of two distinct types of magnetically-independent  $Cu_2(\mu_2\text{-}OH)_2$  dimeric units with different exchange coupling contants,  $J_1$  and  $J_2$ :

$$\chi = 0.5 (N\beta^2 g^2 / kT) [3 + \exp(-2J_1 / kT)]^{-1} + 0.5 (N\beta^2 g^2 / kT) [3 + \exp(-2J_2 / kT)]^{-1} + N_{\alpha}.$$
(1)



Fig. 4. Plot of  $\chi(\Box)$  and  $\chi T(\bigcirc)$  (per Cu) versus temperature for **1** (a) and **2** (b). Solid lines show best fits to Eqs. (1) and (2), yielding the following: for **1**: g = 2.28,  $J_1 = -27$  cm<sup>-1</sup>,  $J_2 = +19$  cm<sup>-1</sup>,  $N_{\alpha} = 50 \times 10^{-6}$  cm<sup>3</sup> mol<sup>-1</sup>; for **2**: g = 1.95, J = +16 cm<sup>-1</sup>, x = 0.026,  $\theta = -3.51$  K,  $N_{\alpha} = 52 \times 10^{-6}$  cm<sup>3</sup> mol<sup>-1</sup>.

In Eq. (1),  $\chi$  is expressed per mole of copper, the parameters N,  $\beta$  and k have their usual meanings, and  $N_{\alpha}$  is the temperature-independent paramagnetism. The parameters obtained on fitting the data by leastsquares regression were g = 2.28,  $J_1 = -27 \text{ cm}^{-1}$ ,  $J_2 = +19 \text{ cm}^{-1}$  and  $N_{\alpha} = 50 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ . This suggests that the Cu<sub>2</sub>(µ<sub>2</sub>-OH)<sub>2</sub> units within one of the tetranuclear [Cu<sub>4</sub>L<sup>dur</sup>(µ<sub>2</sub>-OH)<sub>4</sub>]<sup>4+</sup> cations present in **1** feature pairs of antiferromagnetically-coupled copper(II) centres ( $J_1 = -27 \text{ cm}^{-1}$ ), whilst those in the other cation feature ferromagnetically-coupled copper(II) centres ( $J_2 = +19 \text{ cm}^{-1}$ ). The coupling across the aromatic ring is zero, as expected.

Table 3 compares selected structural and magnetic data for complex 1 with those of related complexes containing  $Cu_2(\mu_2-OH)_2$  moieties. All of the listed complexes feature similar supporting ligand structures, with the pairs of tacn rings that cap the  $Cu_2(\mu_2-OH)_2$ units attached to the meta positions of a benzene ring via methylene groups. Despite this, there is variation in the geometries of the  $Cu_2(\mu_2-OH)_2$  units, which translate into different magnetic behaviours. Several studies have examined how angular distortions to the  $Cu_2(\mu_2$ - $OH_{2}$  unit may attenuate the value of J. Empirically, Crawford et al. [18] found that for complexes with planar or near-planar  $Cu_2(\mu_2-OH)_2$  cores, J varies linearly with the Cu–O–Cu angle  $(\phi)$  according to  $2J = -74.53\varphi + 7270 \text{ cm}^{-1}$ . However, Charlot et al. [19] have shown the magnetic interaction becomes less antiferromagnetic at a given angle of  $\varphi$  as the dihedral angle ( $\delta$ ) between the two Cu<sub>2</sub>O planes is reduced from 180°, i.e., as the  $Cu_2(\mu_2 \text{-OH})_2$  core is folded into a "roofshaped" structure. Consistent with this, the complex in Table 3 with the most planar  $Cu_2(\mu_2-OH)_2$  unit,  $[Cu_2L^{mx}(\mu_2-OH)_2](BPh_4)_2$  [5], exhibits the strongest antiferromagnetic interaction  $(J = -80 \text{ cm}^{-1})$ . At the other extreme, complex 1, featuring the most folded  $Cu_2(\mu_2$ -OH)2 units, features the only ferromagnetically-interacting copper centres  $(J = +19 \text{ cm}^{-1})$ , which are most likely those present in the tetranuclear cation with the smallest  $\varphi$  angles (cation A). [Cu<sub>4</sub>L<sup>dur</sup>( $\mu_2$ -OH)<sub>4</sub>](ClO<sub>4</sub>)<sub>4</sub> [10],  $[Cu_3L^{mes}(\mu_2-OH)_2(H_2O)_2](ClO_4)_4$  [8] and cation B in 1 have more similarly folded  $Cu_2(\mu_2-OH)_2$  units and all display intermediate J values of the order of  $-25 \text{ cm}^{-1}$ .

The plot of  $\chi T$  versus temperature for 2 (Fig. 4(b)) shows a steady increase with decreasing temperature, reaching a maximum of 0.398 cm<sup>3</sup> mol<sup>-1</sup> K at ca. 40 K. This behaviour is indicative of ferromagnetic coupling. Below 40 K,  $\chi T$  decreases, reaching a value of 0.155 cm<sup>3</sup> mol<sup>-1</sup> K at 2 K, which could be due to the combined effects of zero-field splitting of the triplet ground state and intermolecular antiferromagnetic interactions. The data for 2 were successfully fitted to a modified Bleaney–Bowers equation (Eq. (2)), which assumes the system to consist of magnetically-independent  $Cu_2(\mu_2-Cl)_3$  dimeric units, all with the same exchange coupling contant, *J*:

$$\chi = (1 - x) [N\beta^2 g^2 / k(T - \theta)] [3 + \exp(-2J/kT)]^{-1} + xN\beta^2 g^2 / 4kT + N_{\alpha}.$$
(2)

The susceptibility equation includes a Curie term to allow for a fraction of monomeric impurity (x), seen commonly in such systems, and  $\chi$  is again expressed per mole of copper. A Weiss constant ( $\theta$ ) was introduced into the temperature term to account for both intermolecular effects and zero-field splitting. The parameters obtained on fitting the data were g = 1.95, J = +16 cm<sup>-1</sup>, x = 0.026,  $\theta = -3.51$  K, and  $N_{\alpha} = 52 \times 10^{-6}$  cm<sup>3</sup> mol<sup>-1</sup>. The low g value is most likely indicative of dimer-dimer interactions.

Detailed magneto-structural correlations have been carried out on dichloro-bridged binuclear and polynuclear copper(II) complexes [14,20], whilst there is limited data available for tribridged systems [15,21]. It has been observed that the dichloro linkage can lead to either ferromagnetic or antiferromagnetic coupling, depending on the geometry of the  $Cu_2(\mu_2-Cl)_2$  core (e.g., Cu-Cl-Cu angles) and the orientation of the two polygons formed by each half of the binuclear complex. For trichloro-bridged systems, on the other hand, magnetic coupling has been invariably found to be ferromagnetic in nature. Notably, the Cu-Cl-Cu angles in **2** are quite acute.

# 4. Concluding remarks

Two new bridged polynuclear complexes of a tacnbased tetranucleating ligand, L<sup>dur</sup>, have been prepared: a further tetranuclear hydroxo-bridged complex, 1, and a novel chloro-bridged helical polymeric complex, 2. The type and strength of magnetic coupling observed between the pairs of dihydroxo-bridged metal centres in 1 and trichloro-bridged centres in 2 can be rationalized in terms of the geometries of the  $Cu_2(\mu_2-OH)_2$  and  $Cu_2(\mu_2-Cl)_3$  cores present within the structures. Comparison of the structure of 1 with that of its perchlorate salt analogue,  $[Cu_4L^{dur}(\mu_2-OH)_4](ClO_4)_4$ , indicate that the geometry of the  $Cu_2(\mu_2-OH)_2$  units is dictated predominantly by the  $L^{dur}$  ligand, but is also influenced by the counter anion and/or solvent molecules present in the crystal lattice, leading to changes in the strength of the magnetic coupling between the two copper(II) centres.

#### 5. Supplementary material

Crystallographic data for 1 and 2 have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 271989 (1) and 262745 (2). Copies may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk).

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