Chiral channels in a 3-D network of self-assembled tetranuclear copper(II) aggregates†

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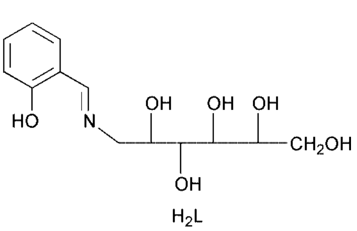
A sugar-substituted ligand allowed for the synthesis of chiral Cu(II) tetranuclear aggregates which assemble *via* H-bonding in a 3D-network containing hydrophobic helical channels.

Polynuclear complexes attract much interest. They are the subject of extensive studies regarding their magnetic properties[1–4] as well as in the field of bioinorganic chemistry.[5–7] The most common strategy to obtain these complexes involves metal self-association induced by bridging ligands like alkoxyde, thiolate or carboxylate.[8–12] Alternatively, polyfunctional ligands have been used in directing construction of polynuclear architectures.[13–16] However, little attention has been paid to the construction of supramolecular networks by the association of these polynuclear entities through non-covalent interactions between their organic ligand shells. Such a supramolecular arrangement might be desirable for controlling the bulk physical properties arising from the inorganic subunits. One way to achieve the self-assembly of discrete units into a more organised network would be to take advantage of the ability of specific functional groups (*e.g.* hydroxy groups) to link the molecular unit by H-bonding.[17,18] We report here that a sugar functionalised Schiff-base may induce polymetallic aggregation. Moreover, the resulting tetranuclear complexes associate *via* H-bonding into a 3-D network.

The ligand (H_2L, Scheme 1) was synthesised in 91% yield by the condensation of salicylaldehyde and 1-amino-1-deoxy-D-sorbitol.§ The reaction of H_2L and $Cu(MeCO_2)_2$ in hot water afforded a green complex of formula $\{Cu_4L_4\}\cdot 2H_2O$¶ which it was possible to recrystallize almost quantitatively by slow diffusion of THF to a DMF solution. X-Ray structural determination revealed a molecule consisting of an inorganic core formed by four Cu(II) ions surrounded by four ligands in a head-to-tail arrangement (Fig. 1), two water molecules being associated to the molecular unit.‖ Each $\{Cu_4L_4\}$ molecule has a central core formed by an eight-membered $\{Cu_4O_4\}$ ring folded in a boat-like conformation. The phenyl rings and the polyhydroxy chains point outward from the core in an alternate disposition in all directions, giving the molecule a globular shape. The molecule is chiral, the optically pure ligand leading to the formation of a single enantiomer of the polynuclear compound. Intracluster H-bonds stabilise the structure, notably the bond formed between H(21) and O(11) with an H··O distance of 2.13 Å. The copper atoms are five-coordinate in a distorted square-pyramidal geometry and are bridged by alkoxy groups formed by the deprotonation of the sorbitol C-2 hydroxy group. The base of each pyramid consists of the imine nitrogen, the phenolate oxygen atom and the two bridging alkolate oxygen atoms. Notably, for Cu(1) the hydroxy group bound in axial position is borne by C-3 of the sorbitol chain [O(40)], while for Cu(2) it is borne by C-4 [O(21)]. Thus alternate Cu atoms are chelated by 6/5/5 and 6/5/6 ring systems.

The $\{Cu_4L_4\}$ molecules are assembled in a 3D-network by intermolecular hydrogen bonding involving the hydroxy groups of the side chains and the two water molecules located between neighbouring $\{Cu_4L_4\}$ units. This H-bonded pattern can be described as a network of supramolecular helices interconnected by H-bonds. In the *c* direction the packing generates a three-fold screw axis and parallel channels (Fig. 2). Based upon van der Waals radii, the width of the channels is 5 Å for the smaller lobes and up to 7 Å wall to wall. These channels are



Scheme 1

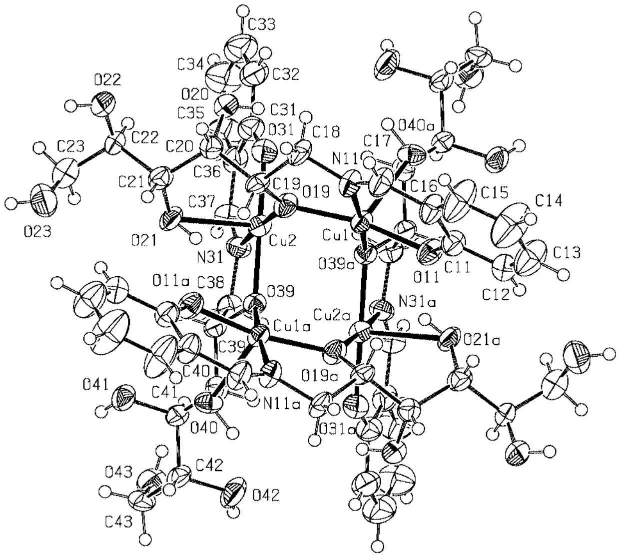


Fig. 1 Perspective view and atom labelling of the molecule $\{Cu_4L_4\}$ (ORTEP diagram, ellipsoids at 50% probability level). Selected bond length (Å) and angles (°): Cu(1)–O(11) 1.945(5), Cu(1)–O(19) 1.955(5), Cu(1)–O(39) 1.929(5), Cu(1)–O(40) 2.410(5), Cu(1)–N(11) 1.930(7), Cu(1)··Cu(2) 3.2962(15), Cu(1)··Cu(2a) 3.4462(15), Cu(1)··Cu(1a) 3.808(2), Cu(2)–O(19) 1.958(5), Cu(2)–O(21) 2.493(5), Cu(2)-O(31) 1.934(5), Cu(2)–O(39a) 1.973(5), Cu(2)–N(31) 1.945(6); Cu(1)–O(19)–Cu(2) 114.8(2), Cu(2)–O(39a)–Cu(1a) 124.1(2).

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† This paper is dedicated to the memory of Professor O. Kahn who passed suddenly away on December 8, 1999.

‡ Author for enquiries relating to the crystallographic study.

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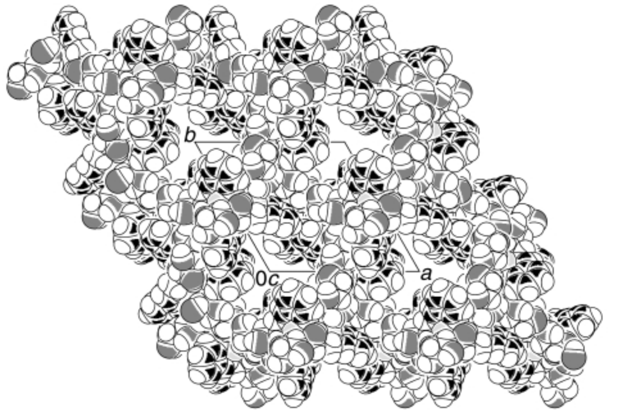

Fig. 2 CPK model view of the molecular packing along the *c* axis showing the channels (H_2O located in the channels have been omitted for clarity). H-Bonds involved in the intermolecular association (Å): OH(22)··O(42)[#1] 2.11, OH(40)··O(1)[#3] 1.99, OH(41)··O(20)[#4] 1.98, OH(42)··O(22)[#5] 2.20, OH(1B)··O(42)[#4] 2.45, OH(23)··H(41)[#2] 2.43 (Symmetry used: #1 $x - y + 1, -y + 1, -z + 2/3$; #2 $-x + 1, -x + y, -z + 1/3$; #3 $-y + 1, x - y + 1, z + 1/3$; #4 $-x + y, -x + 1, z - 1/3$; #5 $x - y, -y + 1, -z + 2/3$).

hydrophobic because the hydrogen atoms of the phenyl moieties and those in positions 2 and 3 of the sorbitol chains point towards the cavities. The X-ray structure analysis suggested that these channels are occupied by highly mobile water molecules distinct from those included in the formula $\{Cu_4L_4\}\cdot 2H_2O$.‖ However, after drying the crystalline compound *in vacuo* at room temperature, these labile water molecules are removed as found by the elemental analysis.

The magnetic interaction between the Cu(II) ions in the inorganic core was investigated, the plot of $\chi_M T$ *vs.* T being shown in Fig. 3. The observed behaviour indicates that substantial antiferromagnetic interactions among the spin carriers tend to cancel the magnetic moment of the Cu(II) cluster. It is very unlikely that they include significant intermolecular interactions, because the inorganic cores are well shielded by the organic ligands. Therefore, the magnetic data have been analysed using a model for interaction between Cu(II) ions bridged by an O-atom within the $\{Cu_4O_4\}$ ring ($H = -J(\boldsymbol{S}_1 \cdot \boldsymbol{S}_2 + \boldsymbol{S}_2 \cdot \boldsymbol{S}_3 + \boldsymbol{S}_3 \cdot \boldsymbol{S}_4 + \boldsymbol{S}_4 \cdot \boldsymbol{S}_1)$)[19] yielding an interaction parameter, $J = -87.8$ cm^{-1}.

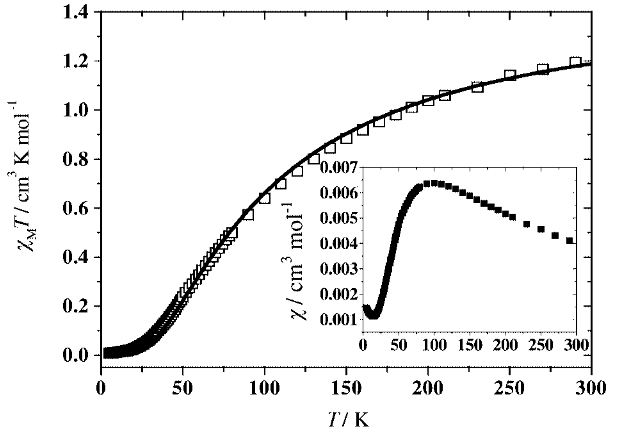

Fig. 3 Experimental (□) and calculated (—) $\chi_M T$ *vs.* T curve; χ_M *vs.* T is depicted in the insert.

The $\{Cu_4L_4\}$ compound illustrates the ability of a polyol-substituted Schiff base to induce the formation of an inorganic core. Moreover the functional groups of the ligand are able to associate the polynuclear aggregates by hydrogen bonding, so constructing a very stable network. The possibility of varying the nature of the metal ions as well as the size of the inorganic core is under investigation. The solubility of the $\{Cu_4L_4\}$ compound in hot water or alcohols suggest the possibility of trapping organic molecules in the hydrophobic cavities while still maintaining the hydrogen bond network.

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Notes and references

§ H_2L:[21] salicylaldehyde (5 mmol) was added dropwise to a vigorously stirred suspension of 1-amino-1-deoxy-D-sorbitol (5 mmol) in MeOH (100 mL). The reaction mixture turned yellow and stirring was continued for 1 h. The yellow precipitate was filtered off and washed several times with MeOH followed by Et_2O and dried *in vacuo* (yield: 91%); mp 161–162 °C (decomp.). IR(KBr, cm^{-1}): 1636($\nu_{C=N}$). δ_H(200 MHz, DMSO-d$_6$): 3.60 (m, 6H, CH), 6.87 (m, 2H, H$_{arom}$), 7.37 (m, 2H, H$_{arom}$), 8.49 (s, 1H, HC=N). δ_C(DMSO-d$_6$) 61.3 (C-1), 63.4 (C-6), 70.0, 71.5, 71.7, 72.2 (C-2,3,4,5), 116.6, 118.1, 118.7, 131.6, 132.2, 161.2 (C$_{arom}$), 166.6 (HC=N). Anal.: Calc. for $C_{13}H_{19}O_6N$: C, 54.7; H, 6.7; N, 4.9. Found: C, 54.4; H, 6.3; N, 5.0%.

¶ $\{Cu_4L_4\}\bullet 2H_2O$: $Cu(Me_3CO_2)_2$ (0.5 mmol) in water (1 mL) was warmed to 90 °C and added with stirring to a hot solution of the ligand HL_2 (0.5 mmol). Green plate crystals of the title compound suitable for X-ray crystallography were obtained after the hot solution cooled down to room temperature. Anal. Calc. for $C_{52}H_{68}N_4O_{24}Cu_4\bullet 2H_2O$: C, 43.9; H, 5.1; N, 4.0; Cu, 17.9. Found: C, 43.6; H, 5.4; N, 4.1; Cu, 17.6%. IR(KBr, cm^{-1}): 3350s, 2927m, 1639s, 1600m, 1542m, 1471m, 1449s, 1304m, 1081m, 761m.

‖ *Crystal data* for $C_{52}H_{72}N_4O_{26}Cu_4$: M = 1423.30, trigonal, space group $P3_12_1$ (no. 152), a = 18.551(3), b = 18.551(3), c = 18.0135(16) Å, U = 5368.9(15) Å^3, T = 293 K, Z = 3, μ(Cu-Kα) = 1.54184 Å, 4227 reflections measured, 4227 unique (R_{int} = 0.0) which where used in all calculations. The final $R(F^2)$ was 0.0541. The structure was solved using direct methods and refined by full-matrix least squares on F^2. The absolute configuration was established according to published procedures.[20] Two density peaks of *ca.* 1.36 e A^3 at (−0.9163, −0.7074, −0.3644) and (−0.7885, −9601, −0.3749) were found which appear to correspond to water molecules that are highly disordered because of their great mobility in the channels. These molecules were not included in the structure refinement.

CCDC 182/1710. See http://www.rsc.org/suppdata/cc/b0/b002360o/ for crystallographic files in .cif format.

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