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Synthesis, structure and magnetic properties of $[Cu_4(Hmbpp)_2(H_2NC(O)NH_2)_2(H_2O)_8]\cdot 4H_2O$

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Received 7th August 2003, Accepted 10th September 2003
First published as an Advance Article on the web 22nd September 2003

$[Cu_4(Hmbpp)_2(H_2NC(O)NH_2)_2(H_2O)_8]\cdot 4H_2O$ **1**, the first example of a discrete polynuclear copper phosphonate complex isolated from aqueous media was synthesised by the addition of urea to a solution of a copper(II) salt and the bisphosphonic acid ligand 4-methyl-2,6-bis(phosphonomethyl)phenol (H_5mbpp). **1** contains four distorted square pyramidal copper atoms and the Cu_4 units are linked by a complicated hydrogen bonded network involving co-crystallised water molecules.

Introduction

Earlier work[1–3] on the design of ligating groups to attach organic actives to metal oxide surfaces, and thus control properties such as corrosion inhibition or the adhesion of polymers and dyes has shown that molecules containing several donor atoms which can address an array of surface metals *via* 'multi-site attachment', form very stable complexes. A systematic approach to improving the efficacy of such ligands requires an understanding of their modes of binding. We have shown that the preparation and structure-determination of polynuclear cage compounds can assist in this process by providing information on the donor atom dispositions which can then be related to the requirements to address arrays of metal ions in oxide surfaces.[1,2] In this context, ligands containing several phosphonic acid groups are of great interest because they form very stable/insoluble metal complexes[4] which have received a great deal of attention in recent years due to the diverse range of potential applications for such materials. These include cation exchange,[5] catalysis/catalyst supports,[6] sorption,[7] sensors,[8] non-linear optics[9] and magnetic materials.[10]

Discrete cage complexes featuring phosphonate ligands are rare due to their propensity to form insoluble polymeric species. The few that have been structurally characterised include several vanadium,[11] zinc[12] and aluminium[13] complexes, a dodecanuclear copper cluster,[14] a tridecanuclear cobalt cage,[10] and manganese[10] and iron cages[15] where carboxylate triangles are linked through phosphonates. The aluminium, zinc and copper complexes were synthesised under rigorously anhydrous conditions to avoid hydrolysis and polymerization. Once formed the aluminium cages are stable to hydrolysis in air due to the protection afforded by the lipophilic sheath of organic ligands encapsulating the metal core.

Metal surfaces of commercial interest are usually coated by a thin oxide/hydroxide layer. Consequently, if we are to understand the ligand design features required for strong binding, model structures should ideally contain similar oxo or hydroxo bridged components. Two- and three-dimensional materials of this type are generally synthesised by hydrothermal methods. An alternative method used by Zhang and Clearfield[16] exploits the hydrolysis of urea which slowly generates NH_3, raising the pH of an aqueous solution containing a metal salt and the phosphonic acid. A variation on this method was used to produce $[Cu_4(Hmbpp)_2(H_2NC(O)NH_2)_2(H_2O)_8]\cdot 4H_2O$ **1**.

Experimental

Preparation of compounds

All reagents, metal salts and ligands were used as obtained from Acros or Aldrich. Analytical data were obtained on a Perkin-Elmer 2400 Elemental Analyser by the University of Edinburgh Microanalytical Service. Infrared spectra were obtained as potassium bromide discs using a Perkin-Elmer Paragon 1000 FT-IR spectrometer. EPR spectra were recorded on a Bruker ESP300E spectrometer Q-band (*ca.* 34 GHz) between 115 K and 300 K. Variable temperature magnetic measurements in the region 1.8–350 K were made using a SQUID magnetometer (Quantum Design) with samples sealed in gelatin capsules.

4-Methyl-2,6-bis(phosphonomethyl)phenol (H_5mbpp). 2,6-Bis(hydroxymethyl)-*p*-cresol (8.4 g, 50 mmol) and trimethyl phosphite (13.0 g, 105 mmol) were heated under reflux for four hours. The solution was cooled to room temperature and the excess trimethyl phosphite removed on a rotary evaporator to give a colourless oil. Diethyl ether was added to the flask and the solution placed in the fridge overnight. The white precipitate that formed was filtered off and dried under vacuum to give [3-(dimethoxy-phosphorylmethyl)-2-hydroxy-5-methyl-benzyl]-phosphonic acid dimethyl ester as a white crystalline solid. This was dissolved in water (100 ml) and methanol (100 ml) and the solution heated under reflux overnight. The solution was cooled to room temperature and the solvent removed on a rotary evaporator to give a white solid which was recrystallised from methanol/ethyl acetate, washed with ethyl acetate then diethyl ether and dried under vacuum to give 4-methyl-2,6-bis(phosphonomethyl)phenol as a white solid (9.1 g, 61%); mp ≈250 °C (Found: C, 36.7; H, 4.6%; $C_9H_{14}O_7P_2$ requires C, 36.5; H, 4.7%); ^1H NMR (D_2O, 200 MHz) δ 6.88–6.85 (m, 2H), 3.07 (d, 4H, 2 × CH_2), 2.10 (d, 3H, CH_3); ^{13}C NMR (D_2O, 63 MHz) δ 149.45 (1C), 131.24 (1C), 130.54 (2C), 121.64 (2C), 29.36 (d, 2C, 2 × CH_2), 19.41 (1C, CH_3); ^{31}P NMR (D_2O, 101 MHz) δ 26.92 (2P); FABMS *m*/*z* 297 (LH); IR (cm^{-1}, KBr disc) ν 2926m (CH), 1636w, 1485s, 1398w, 1377w, 1310m, 1264m (P=O), 1229s, 1159s, 1116s, 1013s, 952s, 927s, 868w, 845w, 731m, 688w, 606w, 541w, 510m, 464w.

$[Cu_4(Hmbpp)_2(H_2NC(O)NH_2)_2(H_2O)_8]\cdot 4H_2O$ 1. Copper perchlorate hexahydrate (1.0 g, 2.7 mmol) and 4-methyl-2,6-bis(phosphonomethyl)phenol (H_5mbpp) (0.40 g, mmol) were

DOI: 10.1039/b309475h

dissolved in distilled water (40 ml) and sodium hydroxide (2.75 ml of a 1 M solution) was added dropwise. The solution colour changed from blue through yellow to brown. The solution was filtered into a 100 ml thick walled test tube, urea (0.40 g) was added and the tube was sealed and heated (65 °C) overnight. A small quantity of brown precipitate was removed, more urea (0.40 g) was added and the sealed tube left to stand at room temperature. Brown crystals of **1** were collected after four days, yield 0.23 g, 29% (Found: C, 20.5; H, 4.4; N, 4.8%; $C_{20}H_{52}Cu_4N_4O_{28}P_4$ requires C, 20.4; H, 4.4; N, 4.8%); IR (cm^{-1}, KBr disc) *v* 3456s (OH), 3325s (NH), 3246s, 2922m (CH), 1657s (C=O), 1578m, 1503w, 1460m, 1409w, 1310w, 1240m (P=O), 1218w, 1207w, 1141s, 1110s, 1083s, 1026s, 984s, 941m, 866w, 860w, 782w, 751m, 627w, 581m, 557m, 502m. Crystals of **1** suitable for X-ray analysis were grown from a similar reaction substituting copper sulfate pentahydrate in place of copper perchlorate hexahydrate.

Crystallography

Data collection and processing. Data for **1** were collected at 150(2) K on a Bruker SMART APEX CCD diffractometer equipped with an Oxford Cryosystems low-temperature device using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Formula $C_{20}H_{52}Cu_4N_4O_{28}P_4$, *M* 1174.70, monoclinic, space group *P*21/*c*, a = 7.9478(18), b = 14.715(3), c = 17.977(4) Å, β = 99.129(4)°, V = 2075.9(8) Å^3, Z = 2, μ = 2.275 mm^{-1}, 4219 unique data, $R1$ = 0.0227, $wR2$ = 0.0665.

Structure analysis and refinement. The structure was solved by direct methods (SHELXTL[17]) and refined against F^2 using a full matrix least squares procedure (SHELXTL[17]). An absorption correction was applied using the multi-scan method of Blessing[18] (SADABS[19]).

All hydrogen atoms bound to oxygen atoms were located on the difference map and refined with distance restraints of 0.85 Å. All twelve of these hydrogen atoms refined to distances between 0.789(16) and 0.877(17) Å. All other hydrogen atoms were placed at calculated positions and refined as riding groups or rotating groups. All non-H atoms were included with anisotropic displacement parameters.

CCDC reference number 217024.

See http://www.rsc.org/suppdata/dt/b3/b309475h/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis and structure of [Cu_4(Hmbpp)$_2$($H_2NC(O)NH_2$)$_2$(H_2O)$_8$]·4H_2O 1

The ligand 4-methyl-2,6-bis(phosphonomethyl)phenol (H_5mbpp) was synthesised in two steps *via* a modified literature[20] method. Slowly raising the pH of an aqueous solution of copper perchlorate hexahydrate, H_5mbpp and sodium hydroxide using urea, on standing gave brown crystals that were identified by a combination of X-ray and elemental analysis as the tetranuclear copper complex [Cu_4(Hmbpp)$_2$($H_2NC(O)NH_2$)$_2$(H_2O)$_8$]·4H_2O **1** (Fig. 1). Initially, due to the poor quality of the crystals, identification of the terminal ligands as urea groups was made on the basis of elemental analysis data. Changing the copper salt to copper sulfate resulted in higher quality crystals, but lower yield (15%), enabling the structure to be definitively assigned (*R*-factor 0.0227). Elemental analysis for both products was identical.

Complex **1** contains four, distorted square pyramidal copper atoms with all oxygen donor sets. The equatorial Cu–O bond lengths range from 1.9371(13) to 1.9931(15) Å (see Table 1) and the axial bonds to the oxygen donors of water, which are longer due to Jahn–Teller distortion, are Cu(1)–O(1) 2.2060(15) Å and Cu(2)–O(2) 2.3685(17) Å. The angles between the axial oxygen and the equatorial oxygens range from 89.61(6) to 101.62(6)°. The distance between the central copper atoms is 3.0886(8) Å while that between Cu(1) and the outer copper, Cu(2), is 5.2289(9) Å. The central core of the complex can be described as a Cu_2O_2 dimer, in which the two Cu(1) centres are bridged [Cu(1)–O(11)–Cu(1) 103.79(6)°] by the phenolate oxygens of two Hmbpp ligands. Two phosphonate oxygens, one from each Hmbpp ligand and a water molecule in the axial position complete the coordination of the Cu(1) sites, which are crystallographically identical.

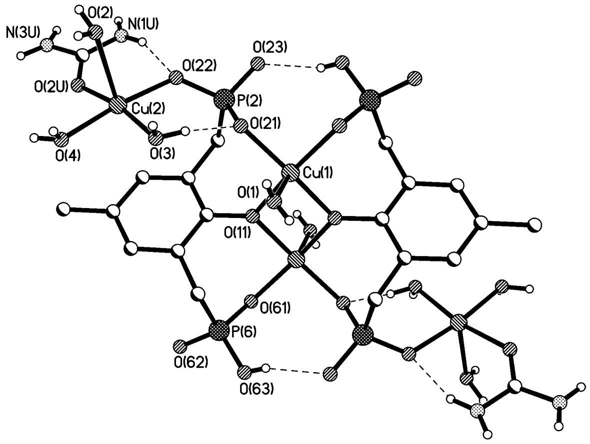

Fig. 1 Structure of **1** in the crystal.

The outer copper atom, Cu(2), is coordinated to one phosphonate oxygen, three water molecules, one of which is in the axial coordination site, and the oxygen atom of a urea molecule. The presence of a urea ligand was unexpected as this has not been reported in other polynuclear complexes which have been prepared using urea as a base. Coordinated urea is not uncommon in copper complexes,[21] particularly in copper carboxylate dimers[22] where it occupies the terminal sites. The involvement of the urea in both intra- and inter-molecular hydrogen bonding within complex **1** may explain its presence in this case.

The Hmbpp ligands have not been fully deprotonated in **1** and as a result are unsymmetrical with one phosphonate group doubly deprotonated and the second only singly deprotonated. The phenolic oxygen is also deprotonated. As might be expected it is the doubly deprotonated phosphonate which performs the bridging function between Cu(1) and Cu(2). The phenyl rings of the Hmbpp ligands are twisted out of the plane formed by the Cu_2O_2 core by an angle of 62.8°. Interestingly the ligands adopt the same *trans* conformation of the methylene phosphonic acid arms as seen in the structure[23] of the free ligand.

The tetranuclear complex contains six strong inter-ligand hydrogen bonds. The central [Cu_2(Hmbpp)$_2$(H_2O)$_2$]$^{4-}$ unit in **1** is enclosed by hydrogen bonding between the terminal phosphonate oxygens O(63)–H ··· O(23) 2.4941(19) Å. A similar effect is believed to impart stability[24,25] to the bis-salicylaldoximatocopper(II) complexes formed in the commercial solvent extraction of copper, where a ring structure is generated by inter-ligand hydrogen bonding between the oxime protons and phenolate oxygen atoms. The two outer coppers are coordinated to the cage *via* a single bond to a phosphonate oxygen but are further stabilised by two additional hydrogen bonds, the first between an equatorial water molecule coordinated to Cu(2) and a phosphonate oxygen coordinated to Cu(1), O(3)–H ··· O(21) 2.6160(19) Å, and the second between a nitrogen donor from the coordinated urea and a phosphonate oxygen coordinated to Cu(1), N(1U)–H ··· O(22) 2.797(2) Å. The crystal structure determination also reveals a very complicated intermolecular hydrogen bond network involving

Table 1 Selected bond lengths (Å) and angles (°) for **1**

Cu(1)–O(21)	1.9371(13)	Cu(2)–O(22)	1.9637(13)
Cu(1)–O(11)#1	1.9426(13)	Cu(2)–O(2U)	1.9420(13)
Cu(1)–O(11)	1.9825(12)	Cu(2)–O(3)	1.9635(15)
Cu(1)–O(61)#1	1.9819(13)	Cu(2)–O(4)	1.9931(15)
Cu(1)–O(1)	2.2060(15)	Cu(2)–O(2)	2.3685(17)
O(21)–Cu(1)–O(11)#1	165.56(5)	O(2U)–Cu(2)–O(3)	169.16(6)
O(21)–Cu(1)–O(11)	94.45(5)	O(2U)–Cu(2)–O(22)	97.19(6)
O(11)#1–Cu(1)–O(11)	76.21(6)	O(3)–Cu(2)–O(22)	89.72(6)
O(21)–Cu(1)–O(61)#1	91.22(5)	O(2U)–Cu(2)–O(4)	88.83(6)
O(11)#1–Cu(1)–O(61)#1	95.29(5)	O(3)–Cu(2)–O(4)	83.85(6)
O(11)–Cu(1)–O(61)#1	164.81(5)	O(22)–Cu(2)–O(4)	173.14(6)
O(21)–Cu(1)–O(1)	90.53(6)	O(2U)–Cu(2)–O(2)	89.61(6)
O(11)#1–Cu(1)–O(1)	101.62(6)	O(3)–Cu(2)–O(2)	98.36(6)
O(11)–Cu(1)–O(1)	98.43(6)	O(22)–Cu(2)–O(2)	93.25(5)
O(61)#1–Cu(1)–O(1)	95.60(5)	O(4)–Cu(2)–O(2)	90.06(6)
Cu(1)#1–O(11)–Cu(1)	103.79(6)		

Symmetry transformations used to generate equivalent atoms: #1 $-x,-y,-z$.

hydrogen bond acceptors/donors in the complex and the four water molecules within the unit cell. The packing of the complex in the crystal is shown (Fig. 2). Within the crystal the molecules of $[Cu_4(Hmbpp)_2(H_2NC(O)NH_2)_2(H_2O)_8]$ are linked both *via* direct hydrogen bonds and through the water molecules within the crystal lattice. Each water molecule is situated at the hub of four hydrogen bonds, one of which is to the other water and the remaining three to oxygens or nitrogens on the complex. A full list of all intra- and inter-molecular hydrogen bonds in **1** is given (Table 2).

Table 2 Hydrogen bond contacts within **1**

Bond type	Donor atom	Acceptor atom	Bond length/Å
O–H ··· O	O(63)	O(23)	2.4941(19)
O–H ··· O	O(3)	O(21)	2.6160(19)
N–H ··· O	N(1U)	O(22)	2.797(2)
N–H ··· O	N(1U)	O(3)	3.042(2)
N–H ··· O	N(3U)	O(4)	3.334(2)
N–H ··· O	N(3U)	O(1W)	2.909(2)
O–H ··· O	O(1)	O(23)	2.722(2)
O–H ··· O	O(1)	O(2W)	2.805(2)
O–H ··· O	O(2)	O(61)	3.091(2)
O–H ··· O	O(2)	O(63)	3.017(2)
O–H ··· O	O(3)	O(62)	2.558(2)
O–H ··· O	O(4)	O(61)	2.781(2)
O–H ··· O	O(4)	O(2W)	2.678(2)
O–H ··· O	O(1W)	O(2)	2.838(2)
O–H ··· O	O(1W)	O(22)	2.849(2)
O–H ··· O	O(2W)	O(62)	2.697(2)
O–H ··· O	O(2W)	O(1W)	2.781(2)

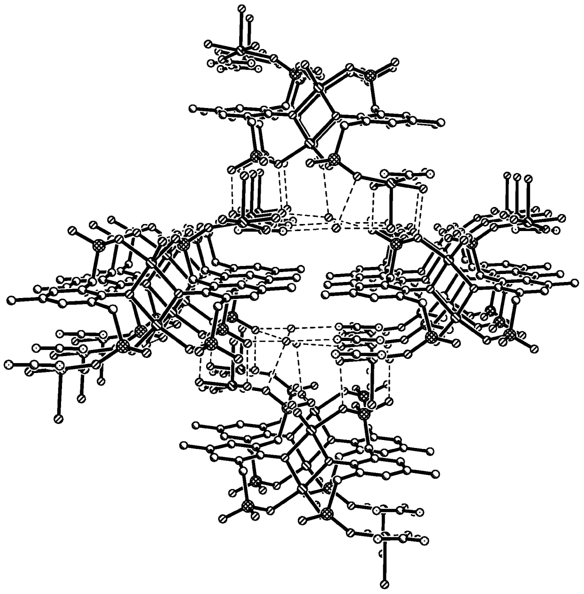

Fig. 2 Packing of **1** in the crystal.

EPR Studies

The EPR spectrum (Fig. 3) of a solid sample of **1** at room temperature is broad and typical of a spectrum due to an $S = ½$ spin state. At 115 K the powder spectrum is much sharper, with three *g*-values resolved at *g* = 2.335, 2.020 and 2.009. This is therefore typical for a Cu(II) centre with an unpaired electron in the $d_{x^2-y^2}$ orbital. No copper hyperfine structure is resolved. The EPR behaviour suggests that there is very strong antiferromagnetic exchange within the central Cu_2O_2 ring of the complex, causing this part of the compound to be EPR silent. The two external Cu(II) centres are non-interacting, and the EPR signal is presumably due to these copper sites.

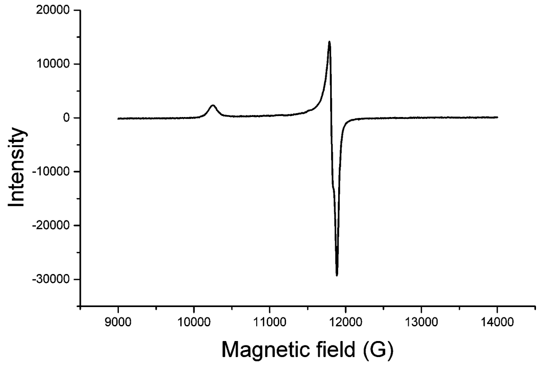

Fig. 3 EPR spectrum of **1** at 115 K.

Magnetic behaviour

The magnetic behaviour of **1** was studied in the range 1.8 to 350 K. The susceptibility per mole of Cu^{2+} appears at first sight to have a simple Curie–Weiss form (Fig. 4), but when the effective moment is calculated from these data as a function of temperature, the value at relatively high temperatures is found to be significantly lower than would be expected for paramagnetic Cu^{2+} with $g \approx 2.0$ (Fig. 4). One interpretation of these data is that the central copper ions, Cu(1), bound through bridging phenolic oxygen atoms, O(11), have strong antiferromagnetic coupling such that by 350 K they effectively form a singlet pair, and the Cu^{2+} ions Cu(1) and Cu(2) bonded through a phosphonate linkage O(21)–P(2)–O(22) are more weakly coupled. The data were least-squares fitted to an expression for the susceptibility of a linear tetrameric cluster of Cu^{2+} ions in which the exchange interaction between the central pair of ions is J_2, and between these ions and the nearest-neighbour terminal ions is J_1;[26,27] the expression also included a TIP term, and the possibility of paramagnetic impurities, for

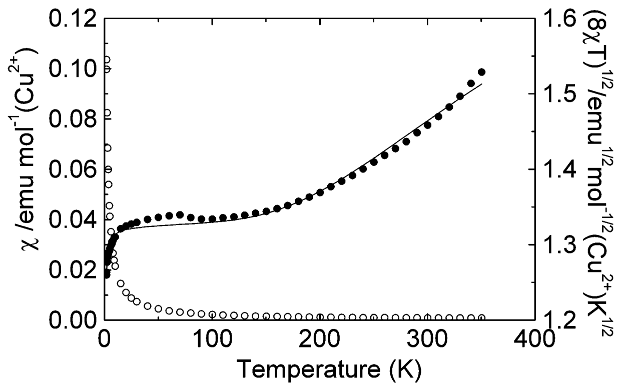

Fig. 4 Magnetic susceptibility, χ (○) and $(8\chi T)^{1/2}$ (●) of **1**; the solid line represents a least-squares fit of the copper tetramer expression to values of $(8\chi T)^{1/2}$, as discussed in the text.

instance arising from monomeric Cu^{2+} species. All Cu^{2+} ions were assumed to have the same value of $g = 2.12$, chosen to be consistent with the EPR data. The result of this procedure is displayed in Fig. 4 for $|J_1| = 17.3$ (0.4) K, $J_2 = -432$ (12) K, $\chi_{TIP} = 60$ (20) emu mol^{-1} and 3 mol% paramagnetic ($S = ½$) impurity. We have chosen to represent the optimised form of the expression in Fig. 4 as the variation of $(8\chi T)^{1/2}$ (which is approximately the magnetisation of each copper ion) with temperature because it is more sensitive to the optimised parameters.

Conclusions

In the context of our original intention to develop H_5mbpp as a surface modifying ligand, we have shown that it can function in a trinucleating mode, with the possibility of further complex stabilisation through hydrogen bonding of the protonated phosphonate arm to surface oxides. Further deprotonation would allow the coordination of additional surface metal ions. The central phenolic oxygen can address metal oxide surfaces with an M ··· M separation of *ca* 3.1 Å which compares with the Cu ··· Cu distances found[28] in the CuO mineral tenorite of 2.9005(3), 3.0830(4) and 3.1734(4) Å.

Acknowledgements

The authors would like to thank the national EPR service in Manchester for the Q-band EPR spectrum of **1** and the EPSRC (UK) for support (D. K. H. and P. A. L.).

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