A novel copper organophosphonate with a pore-like 3D framework and Cu–Cu magnetic ordering†

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$H_2O_3PCH_2NH_2^+CH_2PO_3H^-$ was hydrothermally reacted with Cu(II) in aqueous solution at a 1 : 1 ratio, forming $Cu_3[NH_2(CH_2PO_3)_2]_2$ (1). Two kinds of coordination environments exist around the central copper ions: a distorted square planar Cu(1) ion and an octahedral Cu(2) ion. They are bridged with one terminal oxygen atom forming a 3D-coordination framework of layers sharing corners. Novel antiferromagnetic coupling between the two kinds of Cu units was observed at 15 K, followed by ferromagnetic ordering at 9 K.

Metal phosphonates have potential applications in the areas of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry and materials chemistry.[1] Many of the metal phosphonates are layered species in which the metal octahedra are bridged by phosphonic acid tetrahedra to form two-dimensional layers that are separated by hydrophobic regions of the organic moieties. The hydrothermal method has proved to be a promising technique in the preparation of highly stable, infinite metal–ligand frameworks exhibiting many interesting properties.[2] Using ligands with two phosphonic acid groups attached to a diamine group such as $(HO_3PCH_2NHRNHCH_2PO_3H_2)$, several groups have produced a variety of metal phosphonates, such as mononuclear chelate complexes, complexes with a 1D chain structure and a 3D network structure based on dimeric units and pillared layered compounds.[3] The crystal structure of a copper complex with $C_2H_5N(CH_2PO_3H_2)_2$ was reported by Makaranets et al.[4] And very recently, N-methyliminobis(methylenephosphonic acid) (H_4L) together with $Mn(H_3L)_2·H_2O$, $Cd(H_3L)_2·H_2O$, $Zn_3(HL)_2$ and $Zn(H_2L)(H_2O)$ complexes were reported by our group.[5] The first two are isostructural compounds with a layer structure. $Zn_3(HL)_2$ features a 3D network, and its 1 : 1 complex $Zn(H_2L)(H_2O)$ forms a double chain. The 1D structure of $Co[NH_2(CH_2PO_3H)_2]_2(H_2O)_2$ was reported by Jankovics et al.[6a] and the powder structure of $Cu_3[NH_2(CH_2PO_3)_2]_2$ was elucidated by Cabeza and co-workers.[6b]

The hydrothermal reaction of Cu(II) with $H_2O_3PCH_2NH_2^+CH_2PO_3H^-$ in a 1 : 1 molar ratio, at 150 °C led to the formation of deep blue cubic 1.‡ A small amount of methanol was layered onto the surface of a mixed solution to increase the pressure in the vessel. The IR spectrum of 1 clearly shows the presence of a strong peak at 1627 cm⁻¹, suggesting the formation of NH_2^+ during the reaction. Also, two kinds of v_{as} of PO_3 were observed at 1097 and 1056 cm⁻¹, respectively. The peak that occurs at 982 cm⁻¹ is assigned to $v_s(PO_3)$. The characteristic vibration absorption peak of Cu–O is located around 542 cm⁻¹.[7]

Single crystal X-ray analysis§ ¶ has revealed that there are two crystallographically independent metal atom centers bridged by μ-phosphonic oxygen atoms in the crystal structure (Fig. 1). Cu(1) is coordinated to four oxygen atoms from one ligand in a distorted square planar geometry. Cu(2) is in a distorted octahedral geometry coordinated with six oxygen

atoms from two different ligands, showing a typical octahedral coordination environment. The Cu–O distances range from 2.389(3) to 1.910(3) Å. The most striking features of 1 are: firstly, a localized complex ring system containing one octahedrally coordinated Cu and two distorted square planar Cu ions connected by single oxygen bridges. Both phosphonate groups of the ligand are completely deprotonated and act as hexadentate ligands. The amine group is still protonated. Each ligand carries three negative charges, requiring a metal–ligand ratio of 3 : 2. The protonated nitrogen atoms form hydrogen bonds with phosphonate oxygen atoms (N(1)–H(1D)···O(5) 2.720(5) Å, 173(4)°). The Cu_2O_9 polyhedron is interconnected by phosphonate groups, resulting in the formation of the 3D framework with various voids as shown in Fig. S1.† There are 16-membered rings formed by three copper ions and two ligands as shown in Fig. 1. One octahedrally coordinated copper ion (Cu2) is located in the center of the 16-membered ring with (2Cu1, 2P1, 2P2, 2O2, 2O3, 2N1, 2C1, 2C2), and is connected with the other two distorted square planar copper atoms through two equivalent bridged phosphate oxygen atoms (O1). The adjacent 16-membered rings are tilted from each other and share corners through the O1 and O4 oxygen atoms to form a 3D framework as shown in Fig. 2. A center of symmetry exists in such 16-membered rings with the octahedral copper atoms located in the inversion center. The bond distances between the bridging O(1) atom and the two different coordination environments, Cu(1) and Cu(2) ions, are different [Cu(1)–O(1) 1.929(3) Å, Cu(2)–O(1) 2.389(3) Å].

Fig. 3 shows the temperature dependent magnetic moment of 1 over the whole temperature region from 2 to 300 K. In the high temperature region, the moment $m(T)$ reciprocally decreases with increasing temperature. The moments are fit to the Curie law as shown in the dashed line in Fig. S2,† which is indicative of typical paramagnetic behavior. Since 1 contains two different coordination modes of Cu ions (hexa- and tetracoordinate), it would be expected that different local magnetic moments would exist for these two sites. The average effective number of Bohr magnetons is ~ 1.8 μ_B per Cu ion in the high temperature range, and this value is retained until 100 K. The value of the effective number of Bohr magnetons at room temperature is significantly
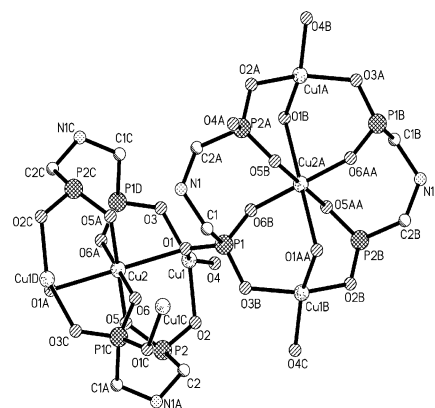

Fig. 1 The coordination environment of copper atoms in 1.

† Electronic supplementary information (ESI) available: crystal structure of compound 1; plot of $1/\chi_m$ vs. T for 1; magnetic hysteresis loop of 1 at 2 K. See http://www.rsc.org/suppdata/cc/b3/b304610a/
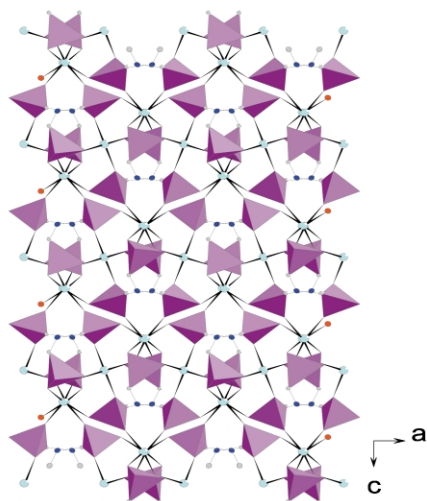
Fig. 2 View of crystal structure of compound **1** along the *b* axis. The phosphonate groups C–PO$_3$ are represented by tetrahedra (purple). Cu, N, C, O atoms are shown as cyan, blue and grey and red solid circles, respectively.

close to Cu(II) independent spins of $S = \frac{1}{2}$. This is due to the absence of an orbital contribution to the magnetic moment for a distorted geometry around the Cu atoms.

With temperature decreasing further, the moment diverges from the Curie law below 100 K (Fig. 3). The magnetic moment decreases continuously from the Curie law. It points to an overall antiferromagnetic coupling of the intra-molecular Cu(II)–O chain in the 3D lattice, which favors a long-range antiferromagnetic ordering. According to the *M–T* curve, the Neel temperature is about 15 K as labeled by an arrow in Fig. 3. As the temperature drops further, the onset of ferromagnetic ordering occurs at about 9 K. As shown in the insert of Fig. 3, the susceptibility is observed to increase sharply as *T* drops to T_c, following the power law: $m(T) \sim (T - T_c)^{-\gamma}$, where T_c is 7.65 K and γ is 4/3. In **1**, the ferromagnetic interaction comes from the exchange network which comprises the two kinds of interactions, coupling between CuO$_4$ and CuO$_6$ (Cu1···Cu2 3.344 Å) units and the coupling between CuO$_4$ and CuO$_4$ (Cu1···Cu1 6.689 Å) units within the molecule.

In addition, magnetization hysteresis measurements were done under a cyclic field up to ±40 kOe. A magnetic hysteresis is also observed at 2 K as shown in Fig. S3.† Magnetic field dependencies of the moment *m*(H) with field decreasing and increasing are labeled here as "∇" and "∆", respectively. The

insert shows hysteresis loops with coercivity of 500 Oe. The hysteresis further confirms the ferromagnetic ordering at low temperature. To elucidate the nature of this magnetic transition, *a.c.* susceptibility measurements were performed. The *a.c.* susceptibility shows a peak in both the in-phase and out-of-phase signals at about 8.5 K. This confirms the existence of a long-range magnetic ordering in which there is a net magnetic moment.

Notes and references

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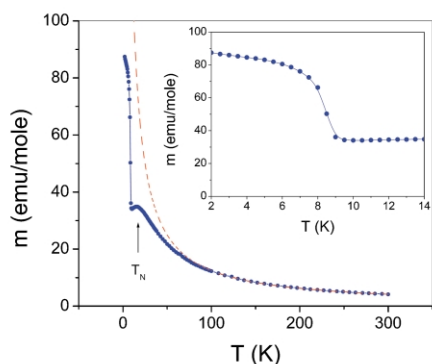

Fig. 3 Thermal variation of $\chi_m T$ for **1** at an applied field of 1 kOe. (Insert: a detailed view of the ferromagnetic transition at low temperature.)