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Structure and magnetic properties of a novel copper diphosphonate with pillared layered structure: $Cu_2(H_2O)_2\{O_3PCH_2N(C_2H_4)_2NCH_2PO_3\}$

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Abstract

Compound $Cu_2(H_2O)_2\{O_3PCH_2N(C_2H_4)_2NCH_2PO_3\}$ (**1**) has a pillared layered structure in which the organic groups of N,N'-piperazinebis(methylenephosphonate) are sandwiched between the inorganic layers. Compared with other copper phosphonates with layered or pillared layered structures, the inorganic layer in **1** is unique in that each $\{CPO_3\}$ tetrahedron is corner-shared with three $\{CuO_4N\}$ square pyramids through three oxygen donors. Ferromagnetic interactions are mediated between the metal centers. Crystal data: *Pbca*, $a = 10.0830(16)$ Å, $b = 9.4517(15)$ Å, $c = 13.218(2)$ Å, $V = 1259.7(3)$ Å^3, $Z = 4$.

Keywords: Copper diphosphonate; N,N'-piperazinebis(methylenephosphonate); Ferromagnetic coupling

1. Introduction

In recent years, the exploration of new transition metal phosphonate compounds has gained an increased attention due to their potential application in ion exchange, catalysts, protonic conductor, and sensors [1]. In many cases, metal phosphonates adopt layered or pillared layered structures. Antiferromagnetic interactions are frequently found to be dominant in these systems. Compounds such as $Fe(RPO_3)\cdot H_2O$ ($R = CH_3$, C_2H_5, C_6H_5) [2–4], $Cr(CH_3PO_3)\cdot H_2O$ [5] and $Mn(C_nH_{2n+1}PO_3)\cdot H_2O$ [6] are of particular interest because they exhibit weak ferromagnetism due to spin canting.

In this paper, we report the synthesis of a new Cu(II) diphosphonate $Cu_2(H_2O)_2\{O_3PCH_2N(C_2H_4)_2NCH_2PO_3\}$ (**1**). Its structure is quite different from compounds $(VO)(H_2O)\{O_3PCH_2NH(C_2H_4)_2NHCH_2PO_3\}$ [7] and $M\{O_3PCH_2NH(C_2H_4)_2NHCH_2PO_3\}\cdot H_2O$ (M = Mn, Co) [8], where the same diphosphonic acid is employed. More interestingly, ferromagnetic exchange couplings are propagated between the copper(II) ions in compound **1**, although no long-range ordering is observed above 1.8 K.

2. Experimental

2.1. Material and methods

The N,N'-piperazinebis(methylenephosphonic acid) was synthesized by Mannich-type reaction according to the literature [9]. Other starting materials were reagent grade used as purchased. Elemental analyses were performed on a PE 240C elemental analyzer. Infrared spectra were recorded on a VECTOR 22 spectrometer with pressed KBr pellets. Thermal analyses were performed in nitrogen with a heating rate of 10°C/min on a Perkin Elmer Pyris 1 TGA instrument. The magnetic susceptibility data were obtained on polycrystalline samples (21.4 mg) using a Quantum Design SQUID magnetometer (dc measurements) and a MagLab System 2000 magnetometer (ac measurements).

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Diamagnetic corrections were obtained from Pascal's constants [10].

2.2. Synthesis of *$Cu_2(H_2O)_2\{O_3PCH_2N(C_2H_4)_2NCH_2PO_3\}$ (**1**)*

A mixture of $Cu(en)_2(NO_3)_2$ (1.125 mmol, 0.3456 g), and $H_2O_3PCH_2N(C_2H_4)_2NCH_2PO_3H_2$ (0.75 mmol, 0.2055 g) were thoroughly mixed with water (10 cm^3) in a Teflon-lined autoclave (pH = 4.34). The autoclave was placed inside an oven at 140°C for 48 h. The final pH of the reaction mixture is 5.00. On cooling down to the room temperature, pale-blue needlelike crystals of compound **1** were collected, washed with water and dried in air. Yield: 40% based on Cu. Found (calcd.) for $Cu_2C_6H_{16}N_2P_2O_8$: C, 16.64 (16.63); H, 3.63 (3.72); N, 6.50 (6.47)%. IR (KBr, cm^{-1}): 3301m, 3094m, 2935w, 2860 w, 1724w, 1630w, 1467m, 1309m, 1206m, 1116m, 1070s, 1011s, 991s, 850m, 820m, 795m, 643w, 584m, 468m, 419w. Thermal analysis revealed that the compound started to decompose at ca. 220°C. The weight loss between 220°C and 265°C is 9.3%, slightly larger than the calculated value of 8.3% for the release of two coordinated water molecules. Above 265°C, compound **1** loses weight continuously with the collapse of the structure.

2.3. *Crystallographic studies*

A single crystal with dimension $0.3 \times 0.1 \times 0.05\,mm^3$ for compound **1** was used for structural determination on a Bruker SMART APEX CCD diffractometer using graphite monochromatized Mo-$K\alpha$ radiation ($\lambda = 0.071073$ Å) at room temperature. A hemisphere of data was collected using a narrow-frame method with scan widths of 0.30° in ω and an exposure time of 10 s/frame. The data were integrated using the Siemens SAINT program [11] with the intensities corrected for Lorentz factor, polarization, air absorption due to variation in the path length through the detector faceplate. Number of measured, unique, and observed reflections [$I > 2\sigma(I)$] are 7660, 1750, 1057 ($R_{int} = 0.0771$). Empirical absorption corrections were applied for the compound. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL [12]. The nonhydrogen atoms were refined with anisotropic displacement parameter. All H atoms, except those attached to O1W, were placed in calculated positions. The H atoms of the water molecule were located from the difference Fourier maps and were refined isotropically. Crystallographic data are summarized in Table 1, atomic coordinates in Table 2, selected bond lengths and angles in Table 3.

Table 1
Crystallographic data for **1**

Formula	$Cu_2C_6H_{16}N_2P_2O_8$
M	433.23
Crystal system	orthorhombic
Space group	*Pbca*
a (Å)	10.0830(16)
b (Å)	9.4517(15)
c (Å)	13.218(2)
V (Å^3)	1259.7(3)
Z	4
Dc (g/cm^3)	2.186
F(000)	872
Goodness-of-fit on F^2	0.896
R_1, wR_2 [$I > 2\sigma(I)$]^a	0.0417, 0.0617
(all data)	0.0698, 0.0660
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	0.730, −0.643

$^a R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\right]^{1/2}$.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **1**

Atom	x	y	z	$U(eq)$
Cu(1)	0.9277(1)	0.1444(1)	0.7192(1)	0.014(1)
P(1)	0.8203(1)	0.4668(1)	0.6908(1)	0.013(1)
O(1)	0.8101(2)	0.3070(3)	0.6964(2)	0.018(1)
O(2)	0.7269(2)	0.5389(3)	0.7654(2)	0.015(1)
O(3)	0.9633(2)	0.5141(3)	0.7021(2)	0.015(1)
O(1W)	0.10817(3)	0.2597(3)	0.6796(2)	0.019(1)
N(1)	0.6188(3)	0.5327(4)	0.5598(2)	0.013(1)
C(1)	0.7649(4)	0.5254(5)	0.5676(3)	0.016(1)
C(2)	0.5830(4)	0.6108(4)	0.4683(3)	0.019(1)
C(3)	0.5647(4)	0.3878(4)	0.5495(3)	0.016(1)

$U(eq)$ is defined as one-third of the trace of the orthogonalized, U_{ij} tensor.

3. Results and discussion

3.1. *Description of crystal structure*

Compound **1** has a pillared layered structure. Fig. 1 shows the building unit of the structure with atomic labeling scheme. Clearly, the Cu atom has a square pyramidal environment. The basal plane is defined by three phosphonate oxygens [O1, O2A and O3B] from three equivalent phosphonate ligands and O1W from water molecule. The Cu–O distances range from 1.949 to 1.967 Å. The axial site is occupied by N1A from the phosphonate ligand with a much longer Cu–N bond length (2.402 Å). The N,N'-piperazinebis(methylenephosphonate) acts as a multi-dentate ligand using both its phosphonate oxygen and piperazine nitrogen atoms. Each $\{CPO_3\}$ of the ligand coordinates to three Cu sites through its three oxygen donors. Each $\{CuO_4N\}$ square pyramid is in turn corner-shared by three $\{CPO_3\}$ tetrahedra from three equivalent diphosphonate ligands, hence forming an inorganic layer containing 12-mem-

Table 3
Selected bond lengths (Å) and angles (deg) for **1**

Cu(1)–O(1)	1.964(3)	P(1)–O(2)	1.524(3)
Cu(1)–O(2A)	1.949(3)	P(1)–O(3)	1.517(3)
Cu(1)–O(3B)	1.951(3)	N(1)–C(1)	1.479(4)
Cu(1)–O(1W)	1.967(3)	N(1)–C(2)	1.462(5)
Cu(1)–N(1A)	2.402(3)	N(1)–C(3)	1.481(5)
P(1)–O(1)	1.516(3)	C(3)–C(2E)	1.507(5)
O(2A)–Cu(1)–O(3B)	87.75(11)	O(1)–P(1)–C(1)	109.18(19)
O(2A)–Cu(1)–O(1)	88.00(11)	O(3)–P(1)–C(1)	106.99(17)
O(3B)–Cu(1)–O(1)	156.25(11)	O(2)–P(1)–C(1)	104.74(17)
O(2A)–Cu(1)–O(1W)	176.28(12)	P(1)–O(1)–Cu(1)	138.27(17)
O(3B)–Cu(1)–O(1W)	92.69(12)	P(1)–O(2)–Cu(1C)	121.36(16)
O(1)–Cu(1)–O(1W)	90.13(13)	P(1)–O(3)–Cu(1D)	140.72(17)
O(2A)–Cu(1)–N(1A)	83.91(11)	C(2)–N(1)–C(1)	109.1(3)
O(3B)–Cu(1)–N(1A)	107.49(11)	C(2)–N(1)–C(3)	107.4(3)
O(1)–Cu(1)–N(1A)	95.27(11)	C(1)–N(1)–C(3)	109.3(3)
O(1W)–Cu(1)–N(1A)	99.47(12)	C(2)–N(1)–Cu(1C)	117.1(3)
O(1)–P(1)–O(3)	110.70(16)	C(1)–N(1)–Cu(1C)	98.9(2)
O(1)–P(1)–O(2)	111.83(17)	C(3)–N(1)–Cu(1C)	114.6(2)
O(3)–P(1)–O(2)	113.05(16)	N(1)–C(1)–P(1)	112.6(3)

Symmetry transformations used to generate equivalent atoms: A: $-x+3/2, y-1/2, z$; B: $-x+2, y-1/2, -z+3/2$; C: $-x+3/2, y+1/2, z$; D: $-x+2, y+1/2, -z+3/2$; E: $-x+1, -y+1, -z+1$.

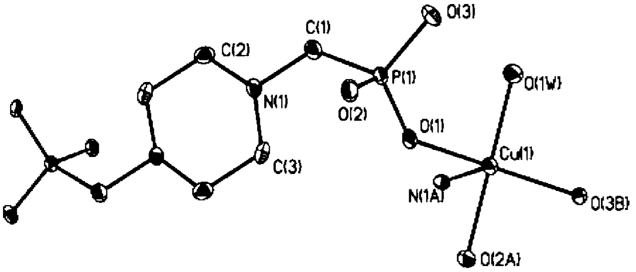

Fig. 1. Building unit of compound **1** with atomic labeling scheme (50% probability).

bered $\{–Cu–O–P–O\}_3$ rings (Fig. 2). The Cu⋯Cu distances over the O–P–O bridges are 5.931, 5.012 and 5.107 Å for Cu1⋯Cu1H, Cu1⋯Cu1I and Cu1H⋯Cu1I, respectively. These layers are pillared by the organic backbone $\{CH_2N(C_2H_4)_2NCH_2\}$ of the *N*,*N*′-piperazinebis(methylenephosphonate) ligand, generating a 3D structure with channels. The shortest separation within the channel is ca. 3.6 Å between O2 and C2. The coordinated water molecules point toward the channels (Fig. 3).

The structure of compound **1** is different from those of $[(VO)(H_2O)\{O_3PCH_2NH(C_2H_4)_2NHCH_2PO_3\}]$ and $[M\{O_3PCH_2NH(C_2H_4)_2NH\ CH_2PO_3\}]\cdot H_2O$ (M = Mn, Co) where the same phosphonate ligand is employed. In the latter compounds, one of the three phosphonate oxygens of each $\{RPO_3\}$ terminus is pendant and both nitrogen atoms are protonated. Consequently, the inorganic layer of compound $[(VO)(H_2O)\{O_3PCH_2NH(C_2H_4)_2NHCH_2PO_3\}]$ contains 16-membered $\{–V–O–P–O\}_4$ rings in which each $\{VO_6\}$ octahedron is corner-shared with four $\{CPO_3\}$ tetrahedral [7]. In the structures of $[M\{O_3PCH_2NH(C_2H_4)_2NHCH_2PO_3\}]\cdot H_2O$ (M = Mn, Co), binuclear units of corner-sharing metal and phosphorus tetrahedra are connected by organic moieties of the diphosphonate ligand, forming a three-dimensional structure with large 44-membered rings [8].

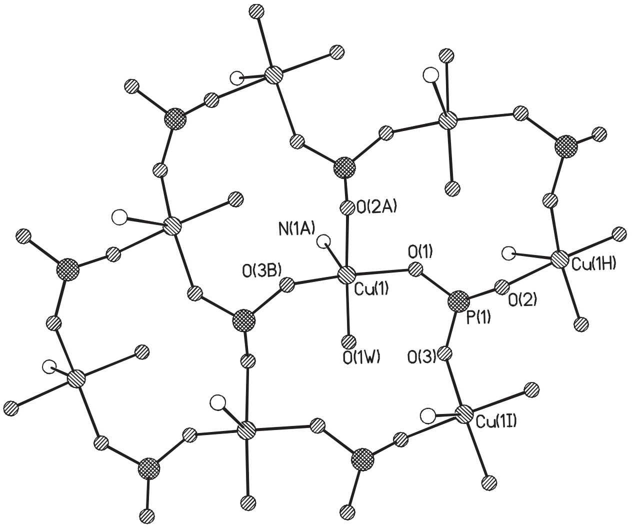

Fig. 2. One layer of compound **1** viewed along *c*-axis.

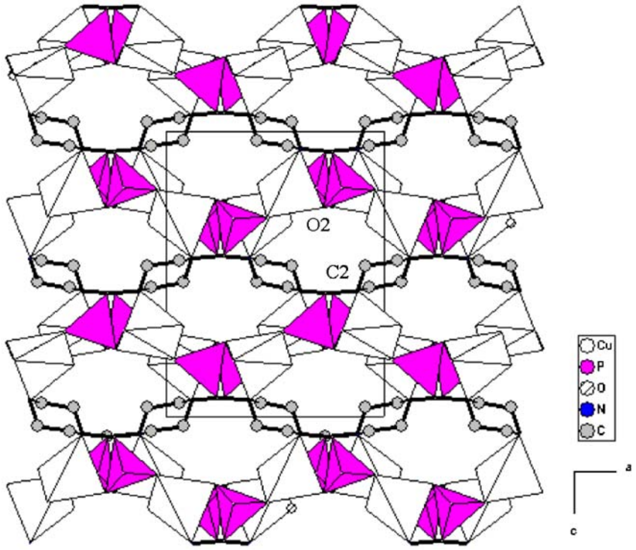

Fig. 3. Structure of compound **1** packed along the [010] direction. All the H atoms are omitted for clarity. The $\{CuO_4N\}$ and $\{CPO_3\}$ are presented as light and shaded polyhedra.

Compound **1** is also unique compared with the other copper phosphonates with layered or pillared layered structures such as, for example, $Cu(C_2H_3PO_3)\cdot H_2O$ [13], $Cu_2(O_3PC_2H_4PO_3)(H_2O)_2$, $Cu_2(O_3PC_3H_6PO_3)(H_2O)_2$ [14] and $Cu_2(O_3PCH_2C_6H_4CH_2PO_3)(H_2O)_2$ [15]. Although the inorganic layers of these compounds are again made up of $\{CuO_5\}$ square pyramids and $\{CPO_3\}$ tetrahedral, each $\{CPO_3\}$ tetrahedron is corner-shared with four $\{CuO_5\}$ square pyramids and, therefore, forming layers containing 4- and 8-membered rings. While in compound **1**, each $\{CPO_3\}$ tetrahedron is corner-shared with three $\{CuO_4N\}$ square pyramids, resulting in layers containing 12-membered rings. The unique arrangement of structure **1** could be responsible for the ferromagnetic behavior of the title compound.

3.2. Magnetic studies

The temperature-dependent molar magnetic susceptibilities of compound **1** were measured in a magnetic field of 5 kOe in the temperature range 2–300 K (Fig. 4). The effective magnetic moment at 300 K, calculated from $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, is $2.45\,\mu_B$ per Cu_2, in agreement with the theoretical value ($2.45\,\mu_B$) for two isolated Cu(II) ions ($S = 1/2$, $g = 2.0$). The susceptibility data above 50 K can be fitted by Curie–Weiss law, $\chi_M = Ng^2\beta^2/[2k(T-\theta)]$, resulting in parameters $g = 2.1$ and $\theta = +6.3$ K. The positive Weiss constant indicates a ferromagnetic interaction between Cu(II) centers. This is confirmed by the continuous increasing of $\chi_M T$ value upon cooling. The ac susceptibility measurements performed in the range 1.8–10 K, at $H_{ac} = 5$ Oe and frequencies of 111, 199, 355, 633 and 1111 Hz, show both in-phase (χ') and out-of-phase (χ'') signals at low temperature. No frequency dependence was observed. The lack of peaks in both χ' and χ'' versus T curves suggests that long-range ferromagnetic ordering is absent above 1.8 K. The field-dependent magnetization of compound **1** measured at 2.0 K shows no hysteresis loop as would be expected (Fig. 5). The saturation magnetization at 49.2 kOe is 2.20 N β per Cu_2 unit, close to the value of 2.1 N β anticipated for a spin value of $S = 1/2$ with $g = 2.1$.

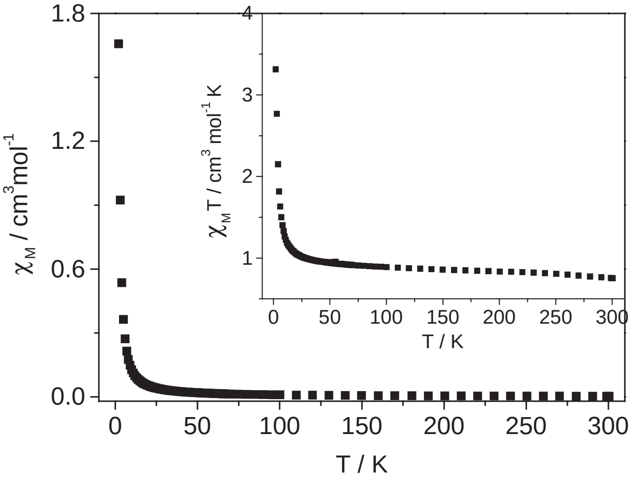

Fig. 4. χ_M and $\chi_M T$ (inset) versus T plots for compound **1**.

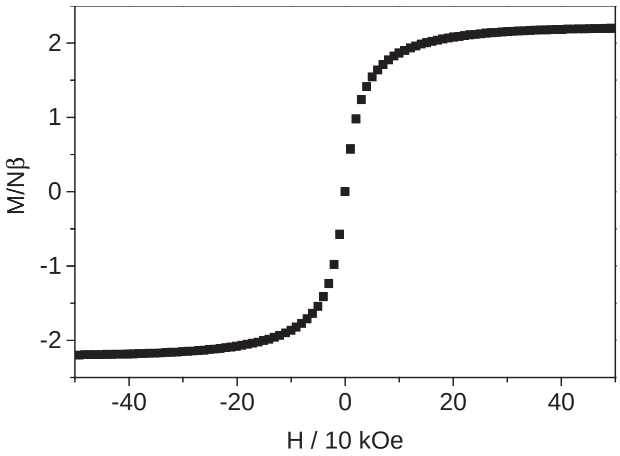

Fig. 5. Field-dependent magnetization of compound **1**.

The observed magnetic behavior of compound **1** has to be related to its structure. In the other layer or pillared layered copper phosphonates such as $Cu(C_2H_3PO_3)\cdot H_2O$, $Cu_2(O_3PC_2H_4PO_3)(H_2O)_2$, $Cu_2(O_3PC_3H_6PO_3)(H_2O)_2$ and $Cu_2(O_3PCH_2C_6H_4CH_2PO_3)(H_2O)_2$, each $\{CPO_3\}$ tetrahedron is corner-shared with four $\{CuO_5\}$ square pyramids. Thus, one of the three phosphonate oxygens must share two CuO_5 units. Consequently, antiferromagnetic interactions between the magnetic centers can be mediated through the μ–O as well as O–P–O bridges. In compound **1**, however, each $\{CPO_3\}$ is corner-shared with three $\{CuO_4N\}$ units through its three phosphonate oxygens, forming a layer containing triangular units of $\{PO_3Cu_3\}$. The neighboring Cu(II) ions are purely bridged by O–P–O units. This triangular arrangement must be responsible for the ferromagnetic behavior of compound **1**, although the reason is still not clear to us. Ferromagnetic exchange was also observed in a carbonato-bridged complex $(\mu\text{-}CO_3)[Cu_3(Medpt)_3(ClO_4)_3](ClO_4)$ which has a similar triangular array of $\{CO_3Cu_3\}$ [16].

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