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层状有机膦酸铜配合物 $Cu(O_3PC_6H_4COOH)$

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摘要:本文报道了一个新的有机膦酸铜化合物:$Cu(O_3PC_6H_4COOH)$ (**1**)。该化合物具有新型层状结构,由扭曲平面结构的$\{CuO_4\}$共边形成的二核单元通过$\{CPO_3\}$四面体连接起来,形成一个含有 4-,8-,和 14-元环的无机层。苯甲酸基团通过中等强度的氢键连接起来,并填充在层与层之间。磁性表征显示铜离子之间存在反铁磁性相互作用。化合物 **1** 的晶体属单斜晶系,*C*2/*c* 空间群。

关键词:铜;有机膦酸;层状结构;磁性
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Copper Phosphonate Complex $Cu(O_3PC_6H_4COOH)$ Showing a New Type of Layered Structure

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Abstract: A new copper phosphonate complex $Cu(O_3PC_6H_4COOH)$ (**1**) is reported in this paper. It shows a novel type of layered structure, where dimers of distorted $\{CuO_4\}$ planes are connected by $\{CPO_3\}$ tetrahedra, forming an inorganic layer containing 4-, 8- and 14-member rings. The phenylcarboxylate groups fill in the interlayer spaces with moderate strong hydrogen bond interactions. Magnetic analysis shows antiferromagnetic interaction between Cu(Ⅱ) ions. Crystallographic data for **1**: monoclinic, space group *C*2/*c*, a=3.813 5(7) nm, b=0.811 85(14) nm, c=0.522 49(9) nm, β=92.816(4)°, V=1.615 7(5) nm^3, Z=8. CCDC: 703675.

Key words: copper; phosphonate; layered structure; magnetic property

Metal phosphonate chemistry is developing very quickly because of their potential for applications in exchange, sorption, catalysis and magnetism etc[1]. Many efforts have been made to prepare new materials with novel structures, to understand their structural-property relationships and, eventually, to design and synthesize related materials with targeted properties. Copper phosphonates are a class of interesting hybrid materials with rich structural and magnetic properties[2]. Usually, copper monophosphonates with formula $Cu(RPO_3)(H_2O)$ (R=alkyl, phenyl, vinyl)[3] exhibit conventional layered structures in which the inorganic layers made up of $\{CuO_5\}$ square pyramids and $\{CPO_3\}$ tetrahedra are separated by organic groups. Other structure types may be obtained by introducing additional functional groups such as hydroxyl[4], amino[5], carboxylate[6], pyridyl[7,8] and a second phosphonate group[9].

In this paper, we use 4-carboxyphenylphosphonic acid ($HOOCC_6H_4PO_3H_2$, 4-cppH$_3$) to react with copper salts. A new copper phosphonate with formula

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$Cu(O_3PC_6H_4COOH)$ (**1**) is obtained, which shows a novel type of layered structures. The magnetic property is also investigated.

1 Experimental section

1.1 Materials and methods

All starting materials were of reagent quality and were obtained from commercial sources without further purification. The 4-carboxyphenylphosphonic acid was synthesized by an Arbuzov-type reaction using methyl 4-bromobenzoate as the precursor and anhydrous nickel chloride as catalyst[10]. Elemental analyses were performed on a Perkin Elmer 240C elemental analyzer. The IR spectra were obtained as KBr disks on a VECTOR 22 spectrometer. XRD patterns were recorded on an XRD-6000 X-ray diffractometer. Magnetic susceptibility data were obtained on microcrystalline samples using a Quantum Design MPMS-XL7 SQUID magnetometer. Diamagnetic corrections were made for both the sample holder and the compound estimated from Pascal′s constants[11].

1.2 Synthesis of $Cu(O_3PC_6H_4COOH)$ (1)

A mixture of $CuSO_4 \cdot 5H_2O$ (0.2 mmol, 0.05 g), 4-$cppH_3$ (0.2 mmol, 0.040 4 g) in 8 mL H_2O, with the pH adjusted from 1.91 to 3.22 by 1 mol·L^{-1} NaOH, was stirred for 10 minutes at room temperature. Then the mixture was transferred to a Teflon-lined autoclave and heated at 140 ℃ for 2 days. After the autoclave is slowly cooled to room temperature, blue blocky crystals were obtained as a monophasic product, judged by the XRD measurements. Yield: 0.046 g (88% based on Cu). Anal. found (calcd) for $C_7H_5O_5PCu$: C 31.87(31.89), H 1.95 (1.91)%. IR (KBr, cm^{-1}): 3 428(w), 2 921(w), 2 670 (w), 2 549(w), 1 695(vs), 1 563(w), 1 500(w), 1 430(m), 1 396(w), 1 317(w), 1 281(m), 1 147(m), 1 116(m), 1 069 (vs), 1 032(vs), 1 009(vs), 945(vs), 861(m), 766(m), 716 (m), 695(w), 766(w), 716(w), 694(w), 584(s), 559(m), 466(w).

1.3 Crystal structure determination

A single crystal of dimensions 0.24 mm×0.20 mm ×0.18 mm for **1** was used for structural determinations on a Bruker SMART APEX CCD diffractometer using graphite-monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) at room temperature. A hemisphere of data was collected in the θ range 2.1°~26.00° using a narrow-frame method with scan width of 0.30° in ω and an exposure time of 5 s/frame. Total number of reflections are 4 151 while numbers of observed $[I>2\sigma(I)]$ and unique reflections are 1 582 and 960 (R_{int}=0.042) for **1**. The data were integrated using the Siemens SAINT program[12] with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Empirical absorption corrections were applied. The structure was solved by direct methods and were refined on F^2 by full matrix least squares using SHELXTL[13]. All the non-hydrogen atoms were located from the Fourier maps, and were refined anisotropically. All H atoms were refined isotropically, with the isotropic thermal vibration parameters related to the non-H atom to which they are bonded. The H atoms at carboxyl groups are found from the difference Fourier maps. Crystallographic and refinement details are listed in Table 1, and selected bond lengths and angles in Table 2.

CCDC: 703675.

Table 1 Crystallographic data

Empirical formula	$C_7H_5O_5PCu$	β / (°)	92.816(4)
Formula weight	263.62	Z	8
Crystal system	Monoclinic	D_c / (g·cm^{-3})	2.168
Space group	$C2/c$	F(000)	1 048
a / nm	3.813 5(7)	Goodness-of-fit on F^2	1.08
b / nm	0.811 85(14)	R_1, wR_2 $[I>2\sigma(I)]$[a]	0.0548, 0.1240
c / nm	0.522 49(9)	$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·nm^{-3})	−570, 430
V / nm^3	1.615 7(5)		

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

Table 2　Selected bond lengths (nm) and angles (°)

Cu(1)-O(1A)	0.193 3(4)	Cu(2)-O(3D)	0.196 6(4)	O(3)-P(1)	0.156 8(4)
Cu(1)-O(3)	0.197 4(4)	O(1)-P(1)	0.152 1(4)		
Cu(2)-O(2)	0.192 5(4)	O(2)-P(1)	0.152 0(4)		
O(1A)-Cu(1)-O(1B)	92.7(2)	O(3C)-Cu(1)-O(3)	84.1(2)	O(2)-Cu(2)-O(3D)	164.2(2)
O(1A) -Cu(1)-O(3C)	163.8(1)	Cu(1)-O(3)-Cu(1D)	95.7(2)	O(2)-Cu(2)-O(3F)	93.6(2)
O(1A)-Cu(1)-O(3)	93.7(2)	O(2)-Cu(2)-O(2E)	92.2(2)	O(3D)-Cu(2)-O(3F)	84.5(2)

Symmetry codes: A: x, $-y$, $z+1/2$; B: $-x+2$, $-y$, $-z+2$; C: $-x+2$, y, $-z+5/2$; D: $-x+2$, $-y+1$, $-z+2$; E: $-x+2$, y, $-z+3/2$; F: x, $-y+1$, $z-1/2$.

2　Results and discussion

2.1　Structure of $Cu(O_3PC_6H_4COOH)$ (1)

Compound **1** crystalizes in monoclinic space group *C*2/*c*. The asymmetric unit consists of two independent Cu atoms, each with 1/2 occupancy, and one 4-cppH^{2-}. Both Cu atoms reside at special positions with coordinates (0, 0.931 1, 1.75) for Cu(1) and (0, 0.571 4, 1.75) for Cu(2), respectively. Both are four-coordinated, with the four binding sites provided by phosphonate oxygen atoms from four equivalent phosphonate ligands (Fig.1). The Cu-O bond lengths fall in the range of 0.192 5(4)~0.197 4(4) nm, in agreement with those in $Cu_3(OOCC_5H_3NPO_3)_2(H_2O)_2$ [Cu-O 0.193 4(3)~0.199 8(3) nm][14]. The O-Cu-O bond angles are 92.7(2)°, 93.7(2)°, 84.1 (2)° and 163.8 (1)° around the Cu(1) atom, and 92.2(2)°, 93.6(2)°, 84.5(2)° and 164.2(2)° around the Cu (2) atom, respectively. Therefore, the coordination environments around the Cu atoms can be best described by distorted planar geometries.

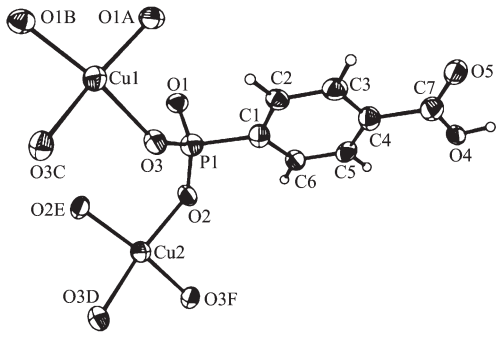


Fig.1　Building unit of **1** with atomic labeling scheme (50% probability)

The 4-cppH^{2-} serves as a tetra-dentate ligand by using its three phosphonate oxygens. The phosphonate oxygens O(1) and O(2) each binds to Cu(1) and Cu(2) atoms, respectively. While O(3) acts as a μ_3-O bridge and links Cu(1) and Cu(2) atoms into a dimer. The Cu(1)⋯Cu(2) distance and Cu(1)-O(3)-Cu(2D) angle within the dimer are 0.292 1(1) nm and 95.7(2)°, respectively. Each {CPO_3} tetrahedron is corner-shared with four {CuO_4} and vice versa, thus forming a two-dimensional inorganic layer in the bc plane which contains 4-, 8- and 14-member rings (Fig.2). The inorganic layers are linked by 4-cppH^{2-} through hydrogen bonds between carboxylate oxygens O(4) and O(5) [O(4)⋯O(5^{i}): 0.262 8(5) nm, symmetry code: ^{i} $3/2-x$, $1/2-y$, $2-z$]. Consequently, a supramolecular pillared layered structure is built up with extremely long interlayer distance 1.937 2 nm (Fig.3).

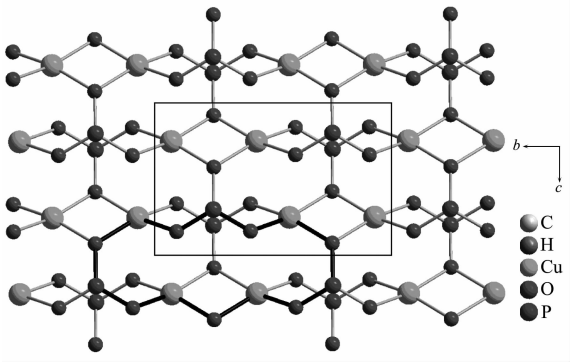
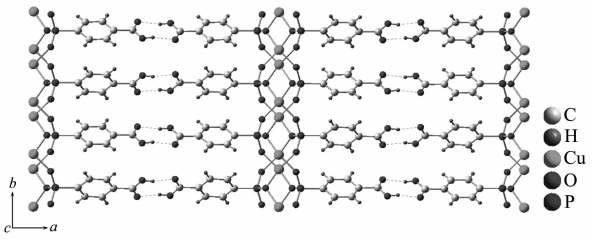


Fig.2　One inorganic layer of structure **1** viewed along a-axis



Hydrogen bonds are shown as dotted lines

Fig.3　Packing of structure **1** viewed along the *c*-axis

It is of interest to compare structure **1** with those of $Cu(RPO_3)(H_2O)$[3]. In the latter cases, each Cu atom has a distorted square pyramidal coordination environment.

The basal positions are filled with three phosphonate oxygen atoms and one water molecule. The apical position is occupied by the fourth phosphonate oxygen. Since compound **1** does not contain coordination water, the basal positions around the Cu atom have to be completed by four phosphonate oxygen atoms. This leads to the formation of a novel inorganic layer that contains 4-, 8- and 14-member rings instead of 4- and 8-member rings as observed in $Cu(RPO_3)(H_2O)$.

2.2 Infrared spectra and magnetic property

The IR spectrum of **1** displays a sharp absorption peak at 1 694.73 cm^{-1}, indicating the presence of ν(C=O) stretching vibration of the carboxyl group. The absorption peaks from 860 cm^{-1} to 1 430 cm^{-1} are assigned to the stretching vibrations of the phosphonate group in the ligand (Fig.4).

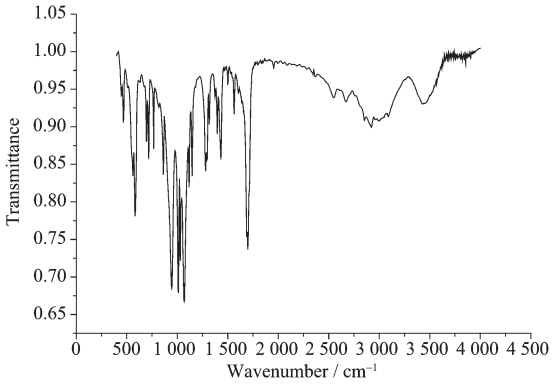


Fig.4 IR spectrum of the complex **1**

The temperature dependent molar magnetic susceptibility of compound **1** was measured at 100 Oe in the temperature range 2~300 K. The χ_M and $\chi_M T$ versus T plots for compound **1** is shown in Fig.4. The room temperature magnetic moment per Cu is 1.91μ_B, which is slightly higher than the theoretical value (1.73μ_B) for spin only value S=1/2. On cooling from 300 K, the gradual decreasing of $\chi_M T$ indicates a dominant antiferromagnetic interaction, which is also confirmed by a negative Weiss constant (C=0.547 $cm^3 \cdot K \cdot mol^{-1}$ and θ=−54.022 K) determined by Curie-Weiss law $\chi_M = C/(T-\theta)$ in the temperature range 50~300 K. As already described, the inorganic layers of compound **1** can be viewed as $\{Cu_2O_2\}$ dimers linked by O-P-O bridges (Fig. 2). The Cu(1)⋯Cu(2) distance and Cu(1)-O(3)-Cu(2D) angle within the dimer are 0.292 1(1) nm and 95.7(2), respectively, which are comparable to those in $[NH_3(CH_2)_2NH_3]_2[Cu_2(hedp)_2]\cdot H_2O$ and $[NH_3CH(CH_3)CH_2NH_3]_2[Cu_2(hedp)_2]$ [15]. Thus direct overlap of the magnetic orbitals is possible within the dimer. The magnetic data were analyzed by the Bleaney-Bowers expression based on a Heisenberg Hamiltonian $H = -2JS_1S_2$ [11]:

$$\chi_M = \frac{Ng^2\beta^2}{kT}\frac{1}{3+\exp[-2J/(kT)]}(1-\rho)+\frac{Ng^2\beta^2}{4kT}\rho$$

where $|2J|$ is the singlet-triplet energy gap and N, g, β and k have their usual meanings. ρ is a variable fraction of paramagnetic impurities. A good fit, shown as the solid lines in Fig.5, was obtained in the temperature range 8~300 K with parameters g=2.21, $2J$=−55.2 cm^{-1} and ρ=0.013%. The $2J$ value is comparable to those in $[NH_3(CH_2)_2NH_3]_2[Cu_2(hedp)_2]\cdot H_2O$ (−61.8 cm^{-1}) and $[NH_3CH(CH_3)CH_2NH_3]_2[Cu_2(hedp)_2]$ (−57.3 cm^{-1})[15].

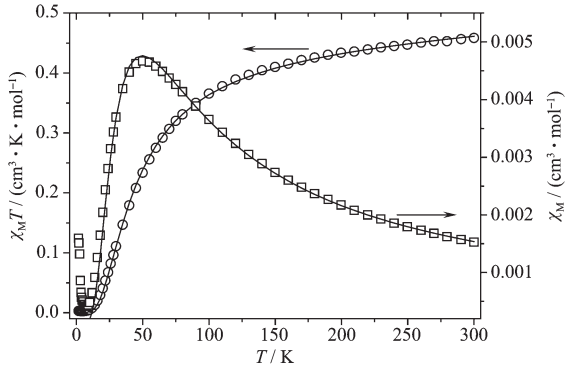


Fig.5 χ_M and $\chi_M T$ vs T plots for the complex **1**

3 Conclusion

In this paper we report the hydrothermal synthesis of $Cu(O_3PC_6H_4COOH)$ (**1**) which shows a new type of pillared layered structure. Moderately strong antiferromagnetic interactions are mediated between the Cu(Ⅱ) ions.

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