第 26 卷第 9 期
2010 年 9 月

无 机 化 学 学 报
CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol.26 No.9
1617-1622

一维梯子型链状有机双膦酸铜 $Cu_3\{(C_5NH_{11})C(OH)(PO_3)_2\}_2(H_2O)_4\cdot 4H_2O$ 的合成和表征

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摘要：本文报道了一个新的有机双膦酸铜化合物 $Cu_3\{(C_5NH_{11})C(OH)(PO_3)_2\}_2(H_2O)_4\cdot 4H_2O$ (**1**)的合成及结构。该化合物呈梯子型双链结构,由 $Cu(1)O_5$ 四方锥体和 $Cu(2)O_6$ 八面体通过$\{PO_3C\}$四面体以共顶点方式连接而成。相邻的双链以几乎相互垂直的方式堆积,通过氢键作用形成了具有孔道的三维超分子网络结构,晶格水分子填充其中。磁性研究表明在铜离子间存在反铁磁相互作用。

关键词：铜；有机双膦酸；梯子双链结构；磁性

中图分类号：O614.121　　**文献标识码**：A　　**文章编号**：1001-4861(2010)09-1617-06

Synthesis and Characterization of One-Dimensional Ladder-Like Chain Copper Diphosphonate $Cu_3\{(C_5NH_{11})C(OH)(PO_3)_2\}_2(H_2O)_4\cdot 4H_2O$

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Abstract: This paper reports the synthesis and crystal structure of a new copper diphosphonate $Cu_3\{(C_5NH_{11})C(OH)(PO_3)_2\}_2(H_2O)_4\cdot 4H_2O$ (1) based on 1-hydroxy-1-(piperidin-4-yl)methylidenebisphosphonic acid ($hpdpH_4$). It shows an infinite ladder-like double chain structure in which the $Cu(1)O_5$ square pyramids and $Cu(2)O_6$ octahedra are linked by corner sharing $\{PO_3C\}$ tetrahedra. The double chains are packed in almost inter-perpendicular manner, forming a three-dimensional hydrogen-bonded supramolecular network. The lattice water molecules reside in the channels. The magnetic studies reveal that dominant antiferromagnetic interactions are mediated between the Cu(Ⅱ) ions. CCDC: 775855.

Key words: copper; diphosphonate; ladder-like chain structure; magnetic property

0 Introduction

Metal phosphonate chemistry has gained increasing attentions owing to their potential applications in catalysis, adsorption and separation, optics, and magnetism, etc[1-4]. Among the metal phosphonate compounds reported, copper phosphonates are of great interest because the Cu(Ⅱ) ion can exhibit different coordination geometries due to its Jahn-Teller distortion, and thus show various structures and properties[5]. For example, compound $Cu_3\{HO_2C(C_5H_3N)PO_3H)_2(H_2O)_2\}$ shows a chain structure with a long-range ferromagnetic ordering[6]. Compound $Cu_4(OH)(Ph_3CPO_3)_3(Ph_3CPO_3H)Py_4\cdot H_2O\cdot CH_3CN$ shows a tetranuclear cage structure

收稿日期:2010-02-25。收修改稿日期:2010-05-05。

国家自然科学基金(No.90922006)资助项目。

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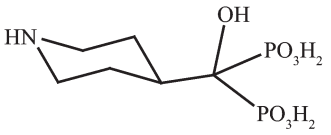
and weak antiferromagnetic interactions between the Cu(Ⅱ) centers[7]. In the case of layer compound $Cu_3(ImhedpH)_2 \cdot 2H_2O$ [$ImhedpH_4$ =(1-$C_3H_3N_2$)CH_2C (OH)(PO_3H_2)$_2$][8], ferrimagnetism is observed. In addition, Cu-Ln heterometallic phosphonates based on 2-pyridylphosphonate display open framework structures and weak ferromagnetic interactions between the Cu(Ⅱ) and Ln(Ⅲ) (Ln=Ce, Pr, Nd) ions[9]. Besides, some copper phosphonate clusters exhibit effective DNA-cleaving capacity as artificial nucleases in biological applications[10]. We have been interested in exploring metal phosphonates with new architectures by modulating the additional functional moieties of the phosphonate backbone. In this paper, we employ 1-hydroxy-1-(piperidin-4-yl)methylidenebisphosphonic acid ((3-$C_5H_{10}N$)$C(OH)(PO_3H_2)_2$, $hpdpH_4$, Scheme 1) to react with copper salt and obtain a new copper diphosphonate with formula $Cu_3\{(C_5NH_{11})C(OH)(PO_3)_2\}_2(H_2O)_4 \cdot 4H_2O$ (**1**). This compound shows a ladder-like double chain structure. Its electrochemical and magnetic properties are also investigated.



Scheme 1

1 Experimental

1.1 Materials and methods

1 - Hydroxy - 1-(piperidin-4-yl)methylidenebisphosphonic acid was prepared according to the literature method[11]. All the other starting materials were obtained commercially as reagent grade chemicals and used without further purification. The elemental analyses for C, H and N were performed in a PE240C elemental analyzer. The infrared spectrum was recorded on a VECTOR 22 spectrometer with KBr pellet. Thermal analyses were performed in nitrogen with a heating rate of 10 ℃·min^{-1} on a TGA-DTA V1.1b Inst 2100 instrument. The powder XRD pattern was recorded on a Shimadzu XD-3A X-ray diffracto-meter. The electrochemical experiments were carried out using a CHI 660C electrochemical analyzer (CHInstrume nts, Shanghai Chenghua Co.). A conventional three-electrode cell was used at room temperature (25 ℃). The modified glassy carbon electrode (1-GCE) was used as working electrode. A SCE and a platinum wire were used as reference and auxiliary electrodes, respectively. Magnetic susceptibility data of compound **1** were obtained on a polycrystalline sample 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[12].

1.2 Synthesis of $Cu_3\{(C_5NH_{11})C(OH)(PO_3)_2\}_2(H_2O)_4 \cdot 4H_2O$ (1)

A mixture of $CuSO_4$ (0.1 mmol, 0.016 g), $hpdpH_4$ (0.2 mmol, 0.055 g) and H_2O (8 mL) (pH=1.9) was briefly stirred and kept in a Teflon-lined autoclave (25 mL) at 120 ℃ for 72 h. After slow cooling to room temperature, the sky-blue block-like crystals were collected as a monophasic material, judged by powder X-ray diffraction pattern. Yield: 13 mg (45%) based on Cu. Anal. Calcd. for $C_{12}H_{40}Cu_3N_2O_{22}P_4$ (%): C, 16.38; H, 4.55; N, 2.73. Found(%): C, 16.21; H, 4.57; N, 3.34. IR (KBr, cm^{-1}): 3 471~3 043b, 2 757w, 2 537w, 2 493w, 1 619s, 1 469m, 1 384m, 1 126s, 1 066s, 1 029s, 964s, 889w, 865w, 713m, 634m, 588s.

1.3 Crystal structure determination

A single crystal with dimensions 0.18 mm×0.12 mm×0.08 mm for **1** was selected for indexing and intensity data collection 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 were collected in the θ range 1.92°~26.00° for **1** using a narrow-frame method with scan widths of 0.30° in ω and exposure time of 10 s/frame. Numbers of observed and unique reflections are 9 714 and 2 847 (R_{int}=0.030 1) for **1**. The data were integrated using the Siemens SAINT program[13], with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Absorption corrections were applied. The structure was solved by direct methods and refined on F^2 by full matrix least squares using SHELXTL[14]. All non-hydrogen atoms were located from the Fourier maps and refined anisotropically. All the hydrogen atoms were put on

calculated positions or located from the Fourier maps and refined isotropically with the isotropic vibration parameters related to the non-hydrogen atom to which they are bonded. Crystallographic data are listed in Table 1. The selected bond lengths and angles for compound **1** are given in Table 2.

CCDC: 775855.

Table 1　Crystallographic data for 1

Empirical formula	$C_{12}H_{40}Cu_3N_2O_{22}P_4$	V / nm^3	1.472(3)
Formula weight	878.96	Z	2
Crystal system	Monoclinic	D_c / (g·cm^{-3})	1.983
Space group	$P2_1/c$	F(000)	898
a / nm	0.625 23(7)	Goodness of fit on F^2	1.001
b / nm	1.307 42(14)	R_1, wR_2 [$I>2\sigma(I)$][a]	0.029 6, 0.078 4
c / nm	1.802 07(19)	R_1, wR_2 (All data)[a]	0.035 7, 0.081 7
β / (°)	92.193(10)	$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / (e·nm^{-3})	670, −465

[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 (°) for 1

Cu(1)-O(6B)	0.193 3(2)	Cu(1)-O(5)	0.195 6(2)	Cu(1)-O(2)	0.196 8(2)
Cu(1)-O(2W)	0.198 4(2)	Cu(1)-O(1W)	0.222 5(2)	Cu(2)-O(1)	0.194 0(2)
Cu(2)-O(4)	0.198 8(2)	Cu(2)-O(7)	0.253 5(2)	P(1)-O(1)	0.153 9(2)
P(1)-O(3)	0.150 7(2)	P(1)-O(2)	0.153 6(2)	P(2)-O(5)	0.152 9(2)
P(2)-O(4)	0.153 6(2)	P(2)-O(6)	0.151 6(2)		
O(6B)-Cu(1)-O(5)	153.46(9)	O(6B)-Cu(1)-O(2)	92.51(8)	O(5)-Cu(1)-O(2)	93.59(8)
O(6B)-Cu(1)-O(2W)	86.08(9)	O(5)-Cu(1)-O(2W)	86.27(8)	O(2)-Cu(1)-O(2W)	176.43(9)
O(6B)-Cu(1)-O(1W)	109.53(8)	O(5)-Cu(1)-O(1W)	96.10(8)	O(2)-Cu(1)-O(1W)	91.55(8)
O(2W)-Cu(1)-O(1W)	92.02(9)	O(1)-Cu(2)-O(4C)	88.93(8)	O(1)-Cu(2)-O(4)	91.07(8)

Symmetry codes: A: $x-1$, y, z; B: $x+1$, y, z; C: $-x$, $-y+1$, $-z+1$.

2　Results and discussion

2.1　Syntheses and preliminary characterization

Compound **1** has been synthesized by reaction of copper sulfate and $hpdpH_4$ under hydrothermal condition. It is found that the M/ligand ratio, pH value of the reaction mixture and reaction temperature play crucial roles in yielding compound **1**. The pure crystalline phase of compound **1** can be obtained only at 120 ℃ with the M/L molar ratio of 2:1 and without adjusting the pH value of the mixture. Any change to the above conditions resulted in floccule-like materials.

The powder X-ray diffraction pattern for compound **1** is shown in Fig.1. The experimental pattern (**1**) is in good agreement with that simulated from the crystal data (**1**-simulated), indicating the high phase purity of as-synthesized **1**. The IR spectrum of **1** displays a sharp absorption peak at 1 619 cm^{-1}, indicating the presence of ν(C-N) stretching vibration. The strong peaks appeared in the range of 964~1 126 cm^{-1} are attributed to the characteristic stretching vibrations of the phosphonate groups in compound **1**.

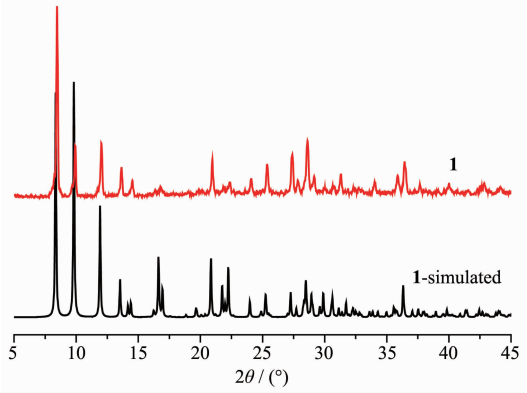
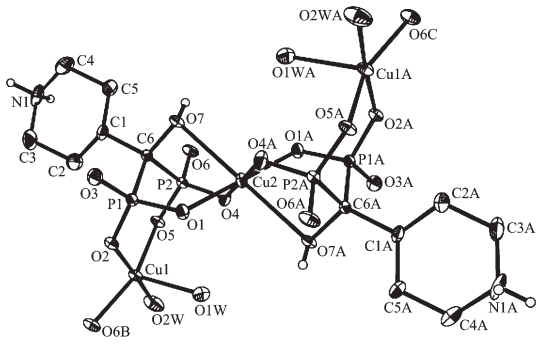


Fig.1　Powder X-ray diffraction patterns for **1** and **1**-simulated

2.2 Crystal structure

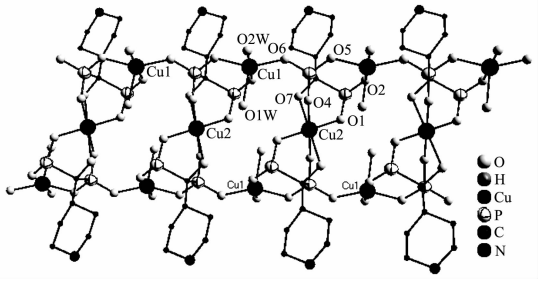
Compound **1** crystallizes in monoclinic space group $P2_1/c$. As shown in Fig.2, the asymmetric unit of the structure contains 1.5 Cu atoms, one $hpdpH^{3-}$, two coordinated and two lattice water molecules. The Cu2 atom locates at a special position in the mirror plane while the Cu1 at a general position. The Cu1 has a distorted square pyramidal environment. The basal four binding sites are provided by three phosphonate oxygens (O2, O5, O6B) from two $hpdpH^{3-}$ ligands and one water molecule (O2W). The axial site is occupied by another water molecule (O1W). The Cu2 atom is six-coordinated by two pair of phosphonate oxygens (O1, O4 and O1A, O4A) and two hydroxyl oxygens (O7 and O7A) from two equivalent $hpdpH^{3-}$ ligands forming an octahedral geometry. The Cu-O(P) distances fall in the range of 0.193 3(2)~0.222 5(2) nm, in agreement with those in the other reported copper phosphonate compounds[3a,4c]. The Cu-O7 distance [0.253 5(2) nm] is much longer due to the Jahn-Teller effect[15].

Each $hpdpH^{3-}$ behaves as a hexa-dentate ligand, chelates and bridges the Cu1 and Cu2 atoms through phosphonate oxygens O2, O5, O6 and O1, O4, O7, respectively. The trimer units of $Cu_3(hpdpH)_2(H_2O)_4$ are further linked together through corner-sharing of $\{PO_3C\}$ tetrahedra, forming a ladder-like double chain structure (Fig.3), which is analogous to the anionic copper-hedp chain in compound $(NH_4)_2Cu_3\{CH_3C(OH)(PO_3)_2\}_2(H_2O)_4$[16]. Within the chain, the Cu1 … Cu2 and Cu1 … Cu1 distances across the O-P-O bridges are 0.470 4 and 0.625 2 nm, respectively. Extensive network of intra- and inter-chain hydrogen bonds are observed among the phosphonate groups, piperidine groups and water molecules (Table 3). The neighboring chains are packed in the inter-perpendicular manner, generating channels along the *a*-axis where the lattice



50% probability, all hydrogen atoms except those attached to N are omitted for clarity

Fig.2 Trimer unit in **1** with labeling scheme



Uncoordinated phosphonate oxygen (O3) atoms are omitted for clarity

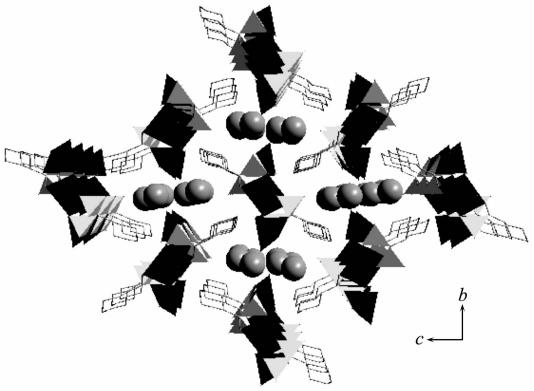
Fig.3 A fragment of the double-chain in structure **1**

Table 3 Hydrogen bonds for 1

D–H…A	*d*(D-H) / nm	*d*(H…A) / nm	*d*(D…A) / nm	∠(DHA) / (°)
O(3W)–H(3WA)…O(5)	0.087	0.192	0.276 3(3)	161.2
O(3W)–H(3WB)…O(4WD)	0.062	0.233	0.293 3(5)	164.5
O(4W)–H(4WB)…O(3WE)	0.085	0.272	0.293 3(5)	96.1
O(7)–H(7)…O(2A)	0.082	0.200	0.280 8(3)	169.3
O(1W)–H(1WA)…O(4)	0.082	0.226	0.295 3(3)	143.1
O(1W)–H(1WA)…O(1)	0.082	0.260	0.308 9(3)	119.2
O(1W)–H(1WB)…O(1F)	0.082	0.192	0.272 9(3)	167.2
N(1)–H(1B)…O(4G)	0.090	0.195	0.282 8(3)	163.1
N(1)–H(1B)…O(1H)	0.090	0.260	0.314 7(3)	119.9
N(1)–H(1A)…O(3H)	0.090	0.192	0.278 6(3)	160.6
O(2W)–H(2WA)…O(3WI)	0.082	0.201	0.274 7(4)	149.9

Symmetry codes: A: *x*−1, *y*, *z*; B: *x*+1, *y*, *z*; C: −*x*, −*y*+1, −*z*+1; D: *x*−1, *y*+1, *z*; E: *x*+1, *y*−1, *z*; F: −*x*+1, −*y*+1, −*z*+1; G: *x*,−*y*+3/2, *z*−1/2; H: −*x*, *y*+1/2, −*z*+1/2; I: −*x*+1, −*y*+2, −*z*+1.

water molecules reside (Fig.4). The stacking fashion of compound **1** is significantly different from that in compound $(NH_4)_2Cu_3\{CH_3C(OH)(PO_3)_2\}_2(H_2O)_4$. In the latter case, the ladder-like chains are linked by moderately strong inter-chain hydrogen bonds, forming a supramolecular layer[16].



CuO_6 octahedra and PO_3C tetrahedra are presented as black and grey polyhedron, Lattice water molecules are shown as red balls

Fig.4　Structure **1** packed along the *a*-axis

2.3　Thermal stability

Thermal analysis of **1** shows several steps of weight losses in the range of 30~700 ℃. The first step weight loss (7.9%) between 30 and 85 ℃ is close to that calculated for the removal of four lattice water molecules (8.2%). The second step weight loss between 90 and 184 ℃ is 5.9%, in agreement with the removal of three coordinated water molecules (6.1%). The fourth coordination water is released above 200 ℃, which is accompanied with the collapse of the framework.

2.4　Electrochemical and magnetic properties

For copper complexes, the abilities to undergo reversible one-electron redox process have attracted more attention in electrochemical research[17]. Compound **1** is insoluble in common solvents, so compound **1**-modified glassy carbon electrode (1-GCE) was fabricated as the working electrode to study its electrochemical behavior. The electrochemical study of 1-GCE was carried out in 1 mol·L^{-1} KNO_3 aqueous solution. Fig.5 shows the cyclic voltammogram at 1-GCE. It can be seen that compound **1** undergoes one-electron reversible reduction in the potential range of 600 to −800 mV, attributed to the characteristic redox couple of Cu(Ⅱ)/Cu(Ⅰ)[18]. The mean peak potential $E_{1/2}=(E_{pa}+E_{pc})/2$ is approximately −108 mV.

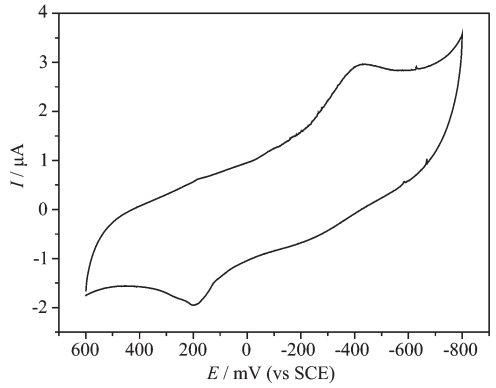


Fig.5　Cyclic voltammogram of 1-GCE in 1 mol·L^{-1} KNO_3 solution in the potential range of 600 to −800 mV, scan rate: 20 mV·s^{-1}

Fig.6 shows the $\chi_M T$ and χ_M^{-1} vs T plots for compound **1**. The effective magnetic moment per Cu_3 unit at 300 K is 3.12μ_B, which is close to the value expected for an isolated system of S=1/2 (3.15μ_B for g=2.1). In the temperature of 30~300 K, the magnetic behavior follows the Curie-Weiss law with a Weiss constant of θ=−27.4 K. Upon cooling, the $\chi_M T$ value decreases gradually, indicating the dominant antiferromagnetic interactions between Cu (Ⅱ) centers through O-P-O pathways.

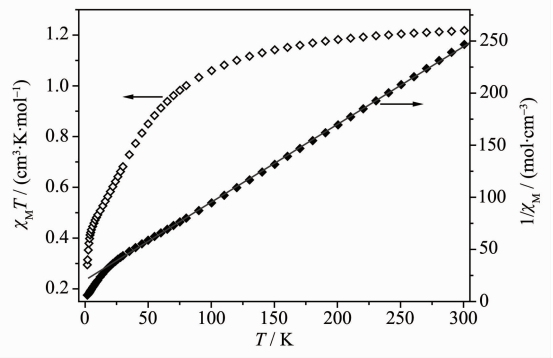


Fig.6　$\chi_M T$ and χ_M^{-1} vs T plots for compound **1**

3　Conclusions

In this paper, a new copper diphosphonate compound $Cu_3\{(C_5NH_{11})C(OH)(PO_3)_2\}_2(H_2O)_4\cdot 4H_2O$ (**1**) has been synthesized by hydrothermal reaction of copper sulfate and 1-hydroxy-1-(piperidin-4-yl)methylidenebisphosphonic acid. It features a ladder-like double chain structure in which the $Cu1O_5$ square pyramids and $Cu2O_6$ octahedra are connected through the corner sharing PO_3C tetrahedra. These chains are

connected through extensive hydrogen bonds forming a supramolecular network structure containing one-dimensional channels where the lattice water molecules reside. A quasi-reversible electrochemical reaction is observed for compound **1**, corresponding to the redox couple of Cu^{2+}/Cu^{+}. Antiferromagnetic interactions are dominant between the magnetic centers in compound **1**.

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