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研究简报

一个新的具有梯子型链状结构的有机二膦酸铜化合物的合成和结构

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关键词:　二膦酸铜化合物　晶体结构　1-羟亚乙基二膦酸

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Synthesis and Structure of a New Copper Diphosphonate with a Ladder-Like Chain Structure

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In this paper we describe a new copper diphosphonate compound $[NH_2(C_2H_4)_2NH_2]Cu_3(hedp)_2(H_2O)_4$ (hedp = 1-hydroxyethylidenediphosphonate, $CH_3C(OH)(PO_3)_2$) synthesized under hydrothermal conditions. Single crystal structure determination reveals that the compound contains anionic ladder-like chains of $\{Cu_3(hedp)_2(H_2O)_4\}_n$ which are linked by moderately strong inter-chain hydrogen bonds, forming a supramolecular layer. The protonated piperazine fill the spaces between the layers.

Keywords:　**copper diphosphonate**　**crystal structure**　**1-hydroxyethylidenediphosphonate**

0 Introduction

The metal phosphonate chemistry has been of increasing interest in the past decade due to their potential applications in ion exchanges, adsorptions and sensors[1~4]. A number of phosphonate compounds have been prepared, among which the copper compounds are unique because of the versatile coordination capabilities of Cu ions[5~7]. Based on 1-hydroxyethylidenediphosphonate [hedp, $CH_3C(OH)(PO_3)_2$], several copper phosphonates have been obtained in our laboratory including $[NH_3(CH_2)_2NH_3]Cu_2(hedp)_2 \cdot H_2O$, $[NH_3CH(CH_3)CH_2NH_3]Cu_2(hedp)_2$[8], $(NH_4)_2Cu_3(hedp)_2(H_2O)_4$, $[NH_2(CH_2)_4NH_2]Cu_3(hedp)_2 \cdot 2H_2O$, $[NH_2(C_2H_4)_2NH_2]Cu_3(hedp)_2$[9], $Na_2Cu_{15}(hedp)_6(OH)_2(H_2O)$[10] and $Cu_4(hedp)_2(pz)(H_2O)_2$[11]. Their structures range from one-dimensional chain, two-dimensional layer to three-dimensional open framework. In this paper we report the synthesis and characterization of $[NH_2(C_2H_4)_2NH_2]Cu_3(hedp)_2(H_2O)_4$ which shows a new structure type.

1 Experimental Section

1.1 Materials and Methods

All the starting materials were reagent grade used as purchased. Elemental analyses were performed on a PE 240C elemental analyzer. Infrared spectrum was recorded on a IFS66V spectrometer with pressed KBr pellet.

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1.2 Synthesis of $[NH_2(C_2H_4)_2NH_2]Cu_3(hedp)_2(H_2O)_4$ (1)

A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (2mmol, 0.4835 g), 50% aqueous solution of $hedpH_4$ (1cm³), piperazine (2mmol, 0.3327g) and H_2O (8cm³) was heated in a Teflon lined autoclave at 140℃ for 72h. After slow cooling, light blue needle-like crystals appeared as a monophasic material. Anal. Calcd. for $C_8H_{28}Cu_3N_2O_{18}P_4$: C, 12.72% ; H, 3.71% ; N, 3.71%. Found: C, 13.51% ; H, 3.44% ; N, 4.05%. IR (KBr, cm^{-1}): 3125s(br), 1597(m), 1487(m), 1461(m), 1439(m), 1376(m), 1325(m), 1202(m), 1134(s), 1094(vs), 1031(s), 999(s), 974(s), 953(s), 893(m), 873(m), 821(m), 760(m), 720(m), 670(m), 582(s), 536(m), 500(m).

1.3 Crystallographic Studies

A single crystal with dimensions 0.40×0.20×0.20mm³ was used for structural determination on a Bruker Smart Apex CCD diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$Å) at room temperature. 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 correction was applied.

The structure was solved by direct method and refined on F^2 by full-matrix least squares using SHELXTL[13]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were either put in calculated positions or located in difference electron density maps, and were treated as riding atoms having isotropic displacement parameters related to the atoms to which they are bonded. Crystallographic data are summarized in Table 1, and selected bond lengths and angles in Table 2.

Table 1 Crystallographic Data

compound	1
formula	$C_8H_{28}Cu_3N_2O_{18}P_4$
M	754.82
crystal system	triclinic
space group	$P\bar{1}$
a/Å	6.2379(9)
b/Å	8.8896(12)
c/Å	11.0494(15)
α/(°)	102.296(2)
β/(°)	99.38(2)
γ/(°)	104.353(2)
V/Å³	548.40(13)
Z	1
D_c/(g·cm^{-3})	2.286
$F(000)$	381
μ(Mo $K\alpha$)/cm^{-1}	32.67
goodness of fit on F^2	1.085
R_1, wR_2[$I > 2\sigma(I)$]	0.0326, 0.0883
(all data)	0.0352, 0.0993
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$/(e·Å^{-3})	0.883, −0.603

a: $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$

$wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

CCDC: 184369

2 Results and Discussions

Compound **1** consists of anionic ladder-like chains of $\{Cu_3(hedp)_2(H_2O)_4\}_n^{2n-}$ and protonated piperazine cations. Fig. 1 shows part of the chain with atomic labeling scheme. Two Cu atoms, Cu(1) and Cu(2) are crystallographically distinguished. The Cu(1) atom,

Table 2 Selected Bond Lengths(Å) and Angles (°) for 1

Cu(1)-O(4)	1.956(2)	Cu(1)-O(1)	2.020(2)	Cu(2)-O(2)	1.924(3)
Cu(2)-O(3B)	1.931(3)	Cu(2)-O(5)	1.934(3)	Cu(2)-O(2W)	1.961(3)
Cu(2)-O(1W)	2.357(3)	P(1)-O(3)	1.520(3)	P(1)-O(2)	1.526(3)
P(1)-O(1)	1.537(3)	P(2)-O(6)	1.498(3)	P(2)-O(4)	1.534(3)
P(2)-O(5)	1.541(3)				
O(4)-Cu(1)-O(1A)	90.04(11)	O(4)-Cu(1)-O(1)	89.96(10)	O(2)-Cu(2)-O(3B)	161.08(11)
O(2)-Cu(2)-O(5)	95.73(11)	O(3B)-Cu(2)-O(5)	93.13(11)	O(2)-Cu(2)-O(2W)	85.55(11)
O(3B)-Cu(2)-O(2W)	82.61(11)	O(5)-Cu(2)-O(2W)	168.79(12)	O(2)-Cu(2)-O(1W)	94.14(11)
O(3B)-Cu(2)-O(1W)	102.28(11)	O(5)-Cu(2)-O(1W)	91.79(11)	O(2W)-Cu(2)-O(1W)	99.23(11)
P(1)-O(1)-Cu(1)	116.60(15)	P(1)-O(2)-Cu(2)	124.64(15)	P(1)-O(3)-Cu(2C)	144.74(17)
P(2)-O(4)-Cu(1)	120.19(15)	P(2)-O(5)-Cu(2)	132.53(16)		

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

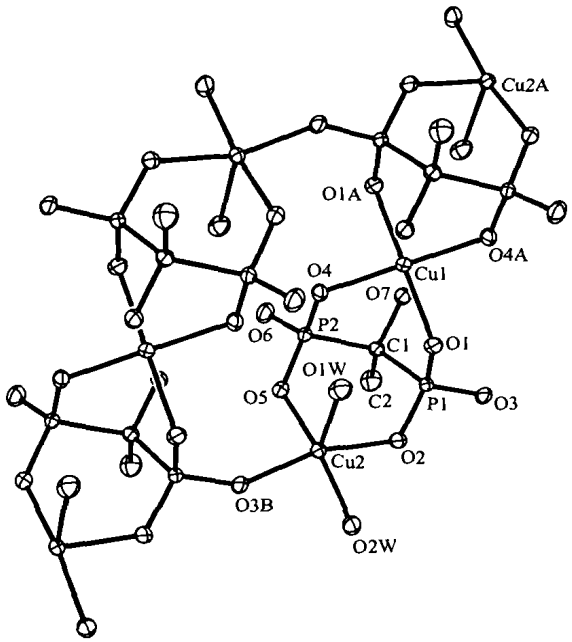

Fig. 1　A fragment of the double chain in **1** with atomic labeling scheme (50% probability)
All H atoms are omitted for clarity

sitting in an inversion center, has an approximately square planar coordination environment. The four biting sites are provided by two pairs of phosphonate oxygens [O(1), O(4)] from two equivalent hedp ligands. The Cu(2) atom has a distorted square pyramidal geometry. Three of its four equatorial positions are filled with phosphonate oxygens [O(2), O(5), O(3B)]. The remaining two positions are occupied by water molecules. The Cu-O distances (Table 2) are in agreement with those found in the other Cu-hedp compounds[8-11]. The Cu(2)-O(1W) bond length [2.357 (3) Å] is relatively longer because of John-Teller effect.

Each $hedp^{4-}$ acts as a bis(chelating) ligand and bridges the Cu(1) and Cu(2) atoms. A trimer unit of $Cu_3(hedp)_2$ is thus formed (Fig. 1). The neighboring trimers are further connected through the coordination of the phosphonate oxygen [O(3)] of one trimer to the Cu(2) atom of the other trimer, resulting in infinite ladder-like chains along the *a*-axis (Figs. 1 and 2). The remaining phosphonate oxygen [O(6)] is pendent [P(2)-O(6) 1.498(3) Å]. Between the chains, there exist moderately strong hydrogen bonds, leading to the formation of a two-dimensional supramolecular layer (Fig. 2). The O(1W) ···O(4), O(1W) ···O(1), O(2W) ···O(1) and O(7) ···O(5) contacts between the chains are 2.728(4) Å, 2.858(4) Å, 2.717(4) Å and 2.776(4) Å, respectively. The protonated piperazine cations fill the inter-layer spaces (Fig. 3).

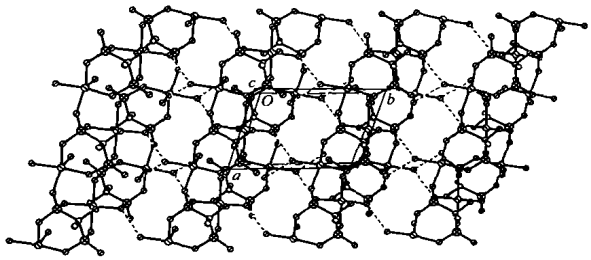

Fig. 2　One layer of copper phosphonate in **1** viewed along *c*-axis
All H atoms are omitted for clarity

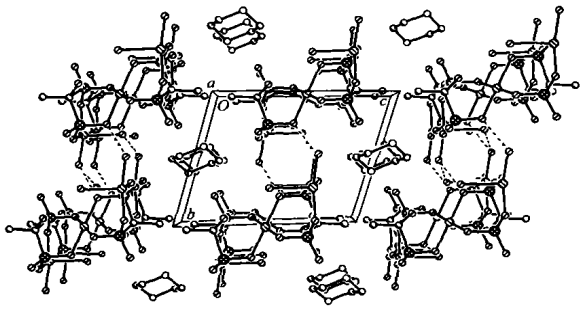

Fig. 3　Crystal packing of **1** viewed along *a*-axis
All H atoms are omitted for clarity

The anionic ladder-like chain observed in the title compound is very similar to that in $(NH_4)_2Cu_3(hedp)_2(H_2O)_4$[9]. In the latter, however, the inter-chain hydrogen bonding interactions result in a three-dimensional network with channels filled by NH_4^+ cations. The different packing arrangement of the two compounds could originate from the different templates. Clearly, the $[NH_2(C_2H_4)_2NH_2]^{2+}$ cation is distinguished from NH_4^+ in such aspects as size, charge, H-bonding abilities and directions. Consequently, compound **1** with a supramolecular layer structure is resulted, although its composition is closely related to that of $(NH_4)_2Cu_3(hedp)_2(H_2O)_4$.

Compound **1** may also be compared with the dehydrated compound $[NH_2(C_2H_4)_2NH_2]Cu_3(hedp)_2$[9], where the same template (piperazine) is employed. In the latter compound, however, a covalently linked

layer structure is found. It is worth noted that in the chain compound **1**, each Cu(2) atom is terminated by two water molecules. These coordinated waters are further involved in the extensive inter-chain hydrogen bonding network. The removal of these water molecules could cause the rearrangement of the structure, and hence the formation of a dehydrated compound with higher dimensionalities.

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