第 26 卷第 9 期 无 机 化 学 学 报 Vol.26 No.9
2010 年 9 月 CHINESE JOURNAL OF INORGANIC CHEMISTRY 1703-1706

研究简报

一维双链镉(Ⅱ)配合物$[Cd(C_5H_5N)CH_2C(OH)(PO_3)(PO_3H)\cdot 3H_2O]_n$的合成与晶体结构

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关键词:镉配合物;吡啶基二膦酸;晶体结构
中图分类号:O614.24+2 **文献标识码**:A **文章编号**:1001-4861(2010)09-1703-04

Synthesis and Crystal Structure of a Double Chain Complex $[Cd(C_5H_5N)CH_2C(OH)(PO_3)(PO_3H)\cdot 3H_2O]_n$

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Abstract: A new cadmium complex $[Cd(C_5H_5N)CH_2C(OH)(PO_3)(PO_3H)\cdot 3H_2O]_n$ ($(C_5H_4N)CH_2C(OH)(PO_3H_2)_2$=1-hydroxy-2-(2-pyridyl)ethylidene-1,1-diphosphonate acid) has been synthesized under hydrothermal conditions. Single crystal structure determination reveals that the compound has a ladder-like chain structure in which the edge-shared $\{CdO_6\}$ octahedra are linked by $\{CPO_3\}$ tetrahedra through corner-sharing. The chains of $\{Cd(C_5H_5N)CH_2C(OH)(PO_3)(PO_3H)\}_n$ are linked by inter-chain hydrogen bonds, forming a supramolecular layer. CCDC: 722396.

Key words: cadmium complex; pyridyl-diphosphonate; crystal structure

Metal phosphonates have attracted much attention due to their potential applications in areas of catalysis, ion exchange, intercalation chemistry and material chemistry[1-6]. It has been well known that the monophosphonic acids RPO_3H_2, where R represents an alkyl or aryl group, prefer to form zero-dimensional cages and layered structures with transition metal ions[1-4,7]. By introducing other functional groups such as amino[8], carboxylate[9], macrocyles[10] and a second phosphonate groups,[6] compounds with new structures and properties can be obtained.

Based on the diphosphonic acid (1-hydroxy-2-ethylidene-1,1-diphosphonate acid, $hedpH_4$), compounds with 1D, 2D and 3D structures have been prepared[6]. To further investigate the effect of substituted groups on the structure of the corresponding metal diphosphonate compounds, recently Zheng have constructed a systematic study on the metal coordination chemistry of 4-amino-1-hydroxybutane-1,1-diphosphonic acid[11], 1-hydroxy-2-(1-imidazole)-1, 1-ethylidenediphosphonic acid[12] and 1-hydroxy-2-(3-pyridyl)ethylidene-1,1-diphosphonic acid[13]. In the present work, we use 1-hydroxy-2-(2-pyridyl)ethylidene-1,1-diphosphonic acid to react with $3CdSO_4\cdot 8H_2O$ and afford a cadmium(Ⅱ) diphosphonate with 1D coordination array, which has a formula of $[Cd(C_5H_5N)CH_2C(OH)(PO_3)(PO_3H)\cdot 3H_2O]_n$.

收稿日期:2010-04-26。收修改稿日期:2010-05-22。
江苏省教育厅自然科学基金(No.08KJB150001)和国家自然科学基金(No.20971017)资助项目。
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1 Experimental

1.1 Materials and methods

All the starting materials were reagent grade used as purchased. 1-hydroxy-2-(2-pyridyl)ethylidene-1,1-diphosphonate acid ($hpedpH_4 \cdot H_2O$) was synthesized according to the literature[14]. Elemental analyses were performed on a PE 240C elemental analyzer. The infrared spectra were recorded on a VECTOR 22 spectrometer with pressed KBr pellets. Powder X-ray diffraction pattern was recorded using Cu $K\alpha$ radiation on a Rigaku D/max-2200/pc diffractometer.

1.2 Synthesis of $[Cd(C_5H_5N)CH_2C(OH)(PO_3)(PO_3H)\cdot 3H_2O]_n$ (1)

A mixture of $3CdSO_4\cdot 8H_2O$ (0.077 g, 0.1 mmol), $hpedpH_4\cdot H_2O$ (0.030 g, 0.1 mmol), NaN_3 (0.026 g, 0.4 mmol) and H_2O (8 mL), was heated at 110 ℃ for 7 days in a Teflon-lined stainless autoclave (25 mL). Colorless needle-like crystals of **1** were obtained with 55% yield based on Cd. Anal. Calcd. for **1** $C_7H_{15}CdNO_{10}P_2$: C, 18.79; H, 3.38; N, 3.13%. Found: C, 18.55; H, 3.05; N, 3.34%. IR (KBr): The broad bands around 3 412 cm^{-1} are attributed to ν(O-H) of water. Weak absorption at 1 649 cm^{-1} is due to the HOH bending vibration. The moderate absorptions at 1 547, 1 476 and 1 395 cm^{-1} are attributed to ν(C-C) and ν(C-N) of pyridyl group. The strong absorptions at 1 151, 1 073, 998 and 958 cm^{-1} are attributed to ν(P-O) of phosphonate group[15].

1.3 Crystallographic studies

Single crystal with dimensions 0.30 mm×0.10 mm×0.10 mm was selected for indexing and intensity data collection on a Rigaku SCX mini 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 3.23°~27.47° by using a narrow frame method with scan widths of 0.30° in ω and an exposure time of 5 s/frame. Numbers of observed and unique reflections are 7 336 and 3 179 (R_{int}=0.019). The data were integrated using the Siemens SAINT program[16], 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 structures were solved by direct methods and refined on F^2 by full matrix least squares using SHELXTL[17]. All the non-hydrogen atoms were located from the Fourier maps, and were refined anisotropically. The H atoms of the pyridyl group were placed in calculated positions (C-H=0.093 nm) and allowed to ride on their respective parent atoms. H atoms bound to O and N atoms were located in a difference Fourier map. Crystallographic refinement details are listed in Table 1. Selected bond lengths and angles are given in Table 2.

CCDC: 722396.

Table 1 Crystallographic data for 1

Empirical formula	$C_7H_{15}CdNO_{10}P_2$	V / nm^3	0.694 1(3)
Formula weight	447.54	Z	2
Crystal system	Triclinic	D_c / ($g\cdot cm^{-3}$)	2.141
Space group	$P\bar{1}$	F(000)	444
a / nm	0.569 32(11)	μ / mm^{-1}	1.854
b / nm	1.053 7(2)	GOF on F^2	1.079
c / nm	1.289 8(3)	R_1, wR_2 [$I>2\sigma(I)$]	0.021 0, 0.048 7
α / (°)	66.23(3)	all data	0.023 7, 0.049 6
β / (°)	78.72(3)	$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ / ($e\cdot nm^{-3}$)	409, –487
γ / (°)	83.80(3)		

Table 2 Selected bond lengths (nm) and angles (°) for 1

Cd1-O1	0.225 1(2)	Cd1-O7A	0.251 3(2)	P1-O3	0.151 4(2)
Cd1-O4	0.220 6(2)	Cd1-O3C	0.222 8(2)	P2-O4	0.152 3(2)
Cd1-O3A	0.240 3(2)	P1-O1	0.150 8(2)	P2-O5	0.152 2(2)
Cd1-O6A	0.223 2(2)	P1-O2	0.155 9(2)	P2-O6	0.152 0(2)

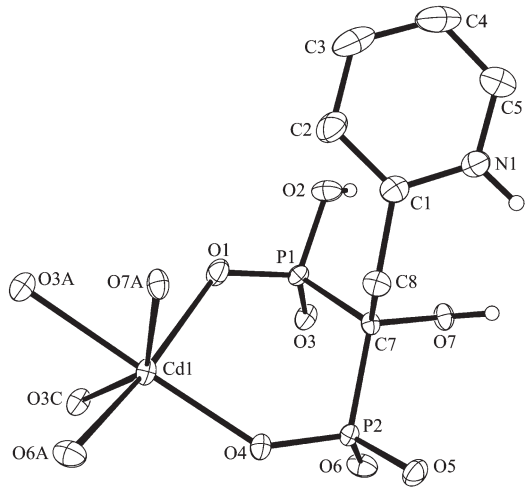
Continued Table 1

O1-Cd1-O4	89.92(7)	O3A-Cd1-O6A	80.83(7)	O6A-Cd1-O7A	76.14(7)
O1-Cd1-O3A	92.88(7)	O3A-Cd1-O7A	72.51(7)	O6A-Cd1-O3C	98.32(7)
O1-Cd1-O6A	162.26(7)	O3A-Cd1-O3C	76.59(7)	O7A-Cd1-O3C	149.09(7)
O1-Cd1-O7A	86.16(7)	O4-Cd1-O6A	93.86(7)	Cd1B-O3-Cd1C	103.41(7)
O1-Cd1-O3C	96.29(7)	O4-Cd1-O7A	98.76(7)		
O3A-Cd1-O4	170.61(7)	O4-Cd1-O3C	112.03(7)		

Symmetry codes: A: −1+x, y, z; B: 1+x, y, z; C: −x, 2−y, −z; D: −1−x, 2−y, −z.

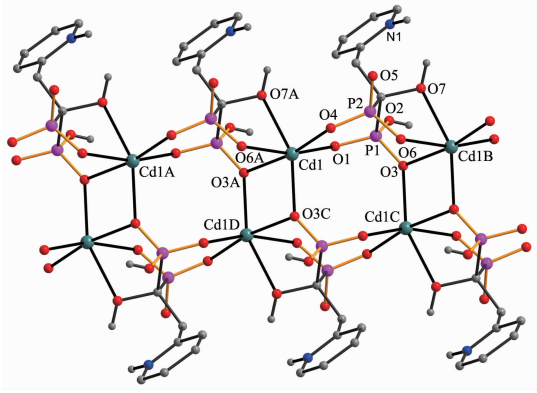
2　Results and discussion

Compound **1** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit consists of one cadmium atom, one [(C_5H_5N)CH_2C(OH)(PO_3)(PO_3H)]$^{2-}$ ligand and three lattice water molecules (Fig.1). The Cd atom has a distorted-octahedral geometry with six positions are occupied by five phosphonate oxygen atoms [O1, O4, O3A, O6A, O3C] and one hydroxyl oxygen atom (O7A) from three equivalent ligands. The Cd-O bond distances are in the range of 0.220 6(2)~0.251 3(2) nm, which are close to those values in $Cd_2(H_2O)_2$[(C_5H_5NH)CH_2C(OH)(PO_3)(PO_3H)]$_2$ [0.223 4(6)~0.242 7(7) nm][18] and in Cd(FA)(pyim)(H_2O) [0.227 5(3)~0.245 4(3) nm][19]. The [(C_5H_5N)CH_2C(OH)(PO_3)(PO_3H)]$^{2-}$ behaves as a pentadentate ligand, using four phosphoante oxygens (O1, O3, O4, O6) and one hydroxyl oxygen (O7). The pyridyl nitrogen (N1) atom and one phosphoante oxygen (O2) and hydroxyl oxygen (O7) are protonated. The remaining phosphoante oxygen [O5] is pendent [P-O5 0.152 2(2) nm]. The phosphonate oxygen [O3] acts as a μ_2-O bridge and links the two equivalent cadmium atoms into a {Cd_2O_2} dimer. The Cd1B-O3-Cd1C bond angle is 103.41(7)°, and the Cd1B⋯Cd1C distance is 0.363 6(1) nm. These dimers are linked by O-P-O groups into a ladder-like double chain along a-axis (Fig.2). The Cd ⋯ Cd distances across the O-P-O bridges are 0.494 0(1) nm and 0.569 3(1) nm for Cd1⋯Cd1C and Cd1⋯Cd1A, respectively.



Lattice water and all H attached to carbon atoms are omitted for clarity

Fig.1　Building unit of structure **1** with the atomic labeling scheme (thermal ellipsoids at 50% probability)



All H attached to carbon atoms are omitted for clarity, Symmetry codes are the same as those in Table 2

Fig.2　A fragment of chain of compound **1** with atomic labeling scheme

The ladder-like chain observed in the title compound is similar to that in other metal diphosphoantes[20]. Compound **1** may be compared with compound $Cd_2(H_2O)_2$[(C_5H_5NH)CH_2C(OH)(PO_3)(PO_3H)]$_2$, where the 1-hydroxy-2-(3-pyridyl)ethylidene-1, 1-diphosphonate acid is employed. In the latter compound, however, a {$Cd_2(\mu$-O)} dimer is found. The dimers are bridged together by O-P-O groups into a new type of double chain structure[18]. Clearly, the formation of a particular structure is dependent on the substitution positions of pyridyl groups.

Between the chains, there are extensive hydrogen-bonding interactions, which are formed among the protonated pyridyl nitrogen atom [N1], phosphonate oxygen atoms [O2, O5 and O6] and the lattice water molecules (O1W, O2W and O3W) (Table 3). A supramolecular layer is therefore constructed parallel to the ab plane. The planes are packed into a three-dimensional network through van der Waals forces.

Table 3 Hydrogen-bond geometry for 1

D–H···A	D-H / nm	H···A / nm	D···A / nm	D–H···A / (°)
N1–H1···O5^{i}	0.091(3)	0.175(3)	0.264 6(3)	168(3)
O7–H7···O5^{i}	0.094(3)	0.165(3)	0.258 0(3)	172(3)
O1W–H1WA···O1^{ii}	0.087(4)	0.190(4)	0.2766(3)	172(4)
O3W–H3WA···O2W^{ii}	0.077(5)	0.216(5)	0.286 0(5)	152(5)
O1W–H1WB···O3W^{iii}	0.082(4)	0.192(4)	0.273 3(5)	180(5)
O2W–H2WB···O4^{iv}	0.092(6)	0.196(6)	0.287 6(4)	174(6)
O3W–H3WB···O6^{iv}	0.086(5)	0.187(5)	0.271 8(3)	169(5)
O2–H6···O1W	0.072(4)	0.184(3)	0.255 2(3)	170(4)
O2W–H2WA···O3W	0.089(6)	0.226(6)	0.306 3(5)	150(5)

Symmetry codes: ^{i} 1–x, 1–y, –z; ^{ii} 1+x, y, z; ^{iii} 1–x, 2–y, 1–z; ^{iv} x, y, 1+z.

The XRD powder pattern of compound **1** was collected at 2θ from 5° to 80° (Fig.3). The powder pattern matches with the ones simulated from the single crystal diffraction data, thus the compound exists as a single phase.

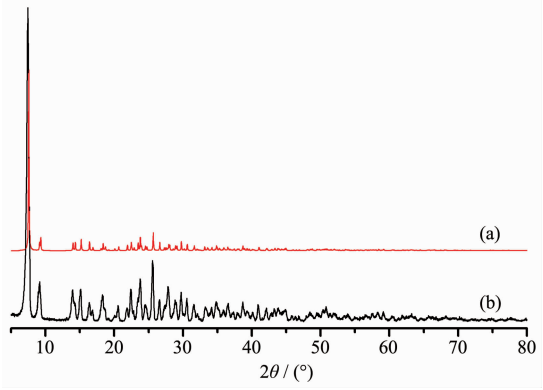


Fig.3 Simulated (a) and observed (b) powder X-ray diffraction patterns of compound **1**

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