

具有六重穿插非中心对称金刚石网络结构的 Cd(II)和 Zn(II)的配位高聚物

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摘要: 利用 1,4-二-(4-羧基吡啶基)丁烷(L)合成了两个新的三维配位聚合物 $\{(\text{CdL}_2) \cdot 4\text{H}_2\text{O} \cdot 2\text{ClO}_4\}_n$ **1** 和 $\{(\text{ZnL}_2) \cdot 4\text{H}_2\text{O} \cdot 2\text{ClO}_4\}_n$ **2**。单晶 X-射线结构分析表明, **1** 和 **2** 具有相同的计量式, 但其晶体属于不同的空间群(**1** 属于 $P\bar{4}n2$, **2** 属于 $P4_222$)。两种配合物中, 每个金属离子分别由配体与四个相邻的金属离子连接, 从而形成具有六重穿插的金刚石网络结构, 其网络中大的空腔被高氯酸根离子和 $(\text{H}_2\text{O})_4$ 分子簇所占据。

关键词: 非中心对称金刚石网络结构; 1,4-二-(4-羧基吡啶基)丁烷; Cd(II)配位化合物; Zn(II)配位化合物
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Cd(II) and Zn(II) Coordination Networks Involving 6-fold Acentric Diamondoid Structures

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Abstract: Two novel three-dimensional coordination polymers of Zn(II) and Cd(II) with 1,4-bis(4-carboxypyridinium)butane (L), namely $\{(\text{CdL}_2) \cdot 4\text{H}_2\text{O} \cdot 2\text{ClO}_4\}_n$ **1** and $\{(\text{ZnL}_2) \cdot 4\text{H}_2\text{O} \cdot 2\text{ClO}_4\}_n$ **2**, have been prepared by the reactions of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with L in aqueous solution, and structurally characterized. The results show that, although **1** and **2** have the same stoichiometric formula, they crystallize in different space groups with **1** in $P\bar{4}n2$ and **2** in $P4_222$. In both compounds, the metal atoms are each linked by L bridges to four adjacent metal centres, thus forming diamondoid networks with 6-fold penetration. The large void spaces formed in the network are filled with perchlorate anions and $(\text{H}_2\text{O})_4$ clusters. CCDC: **1**, 249252; **2**, 249251.

Key words: acentric diamondoid net; 1,4-bis(4-carboxypyridinium)butane; Cd(II) coordination polymer; Zn(II) coordination polymer

0 Introduction

The field of crystal engineering, especially the design and preparation of inorganic coordination supramolecules, has been subjected to extensive studies in the past decades for their potential use as functional materials^[1]. Supramolecules with various interpenetrating two-dimensional and three-dimensional networks have been synthesized and their structures determined. As for three-dimensional interpenetrating networks, structures involving diamond-related nets

make up of by far the largest class, including hydrogen bonded organic networks^[2] as well as coordination polymers^[3].

In recent years, by linking conjugated unsymmetrical, bifunctional ligands, such as isonicotinate, 4-[2-(4-pyridyl)ethenyl]benzoate, 4-(4-pyridyl)benzoate *etc.*, with transparent d^{10} metals, W. B. Lin and co-workers have successfully prepared coordination polymers involving acentric diamondoid net with various degree of interpenetration, in order to rationally synthesize materials of NLO properties^[4]. They demonstrated that di-

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amondoid coordination networks with an odd number-fold interpenetration are necessarily acentric, and emphasized the importance of unsymmetrical linkage groups in the synthesis of noncentrosymmetric metal-organic frameworks. Also, a relationship between the degree of interpenetration in neutral diamond-like nets and the length of the ligand was established^[5].

In previous studies we have employed 1,4-bis(4-carboxypyridinium)butane, a neutral compound with two naked carboxylate groups, as ligand to interact with Ag(I), Cu(II), and Mn(II) salts, and various three-dimensional coordination/hydrogen-bonded networks were obtained^[6]. The results showed that the carboxylate groups in this compound usually act in a monodentate fashion, and the pendent oxygen atoms of the carboxylate groups help constructing three-dimensional networks through their hydrogen bonding to aqua ligands or lattice water molecules. In order to construct coordination polymers with diamondoid structures, Cd(II) and Zn(II), which prefer to tetrahedral coordination sphere, were adopted to react with 1, 4-bis(4-carboxypyridinium)butane in present study. Two novel coordination polymers with diamondoid nets were obtained and their structures determined. The results showed that although both the compounds involve even number-fold (6-fold) interpenetrating diamondoid nets, they crystallize in chiral space groups and, respectively.

1 Experiments

1.1 Synthesis

The ligand 1,4-bis(4-carboxypyridinium)butane (**L**) was synthesized by the method described previously^[6a]. Cd(ClO₄)₂·6H₂O and Zn(ClO₄)₂·6H₂O were prepared by reactions of freshly deposited CdCO₃ and ZnCO₃ with HClO₄ aqueous solution, respectively, and recrystallized in distilled water. The IR spectra were recorded from KBr pallet in the range of 4 000~400 cm⁻¹ on a Bio-Rad Exalibur FTS3000 spectrometer.

The synthesis routings of coordination compounds **1** and **2** were similar: the mixture of **L** and the corresponding metal perchlorates in H₂O (*c.a.* 8 cm³) was heated at about 60 °C for *c.a.* 15 min and filtered. The crystals of the complexes available to single crystal X-ray structure analysis were obtained after standing of the filtration at ambient temperature for several days.

For **1**, **L** (1 mmol) and Cd(ClO₄)₂·6H₂O (1 mmol), colorless prismatic crystals, yield 88%, IR: 1 629 cm⁻¹ [carboxylate ν_{asym}], 1 367 cm⁻¹ [carboxylate ν_{sym}]; for **2**, **L** (1 mmol) and Zn(ClO₄)₂·6H₂O (1 mmol), pale yellow prismatic crystals, yield 82%, IR: 1 623 cm⁻¹ [carboxylate ν_{asym}], 1 372 cm⁻¹ [carboxylate ν_{sym}].

1.2 X-ray data collection and structure refinement

The diffraction data for both **1** (colorless prism, 0.25 mm × 0.20 mm × 0.15 mm) and **2** (pale yellow prism, 0.25 mm × 0.23 mm × 0.13 mm) were collected at 298(2) K on a Bruker SMART-CCD diffractometer (graphite-monochromated Mo *K*α radiation, λ = 0.071 073 nm). Both structures were solved by the direct method, and the non-hydrogen atoms were refined anisotropically by full-matrix least squares method using the SHELXTL program package^[7]. All hydrogen atoms were located on the difference Fourier map and allowed to ride on their respective parent atoms. The hydrogen atoms were included in the structure factor calculations, whereas their positions were not refined. Crystallographic data, and the selected bond lengths and angles for **1** and **2** are listed in Table 1 and 2, respectively. Final atomic coordinates and equivalent isotropic thermal parameters along with their estimated standard deviation, a listing of observed and calculated structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with CCDC as supplementary material, and copies are available on request.

CCDC: **1**, 249252; **2**, 249251.

2 Results and discussion

2.1 Crystal structure of {(CdL₂)·4H₂O·2ClO₄}_n (**1**)

Compound **1** crystallizes in the chiral space group $P\bar{4}n2$ (No.118) with the Cd atoms lying on the $\bar{4}$ axes and the ligand **L** adopting a crystallographic *C*_{2v} symmetry. The distorted tetrahedral coordination geometry of Cd atom [Cd-O: 0.225 1(2) nm; O-Cd-O: 88.9°~120.6°] is furnished by its coordinating to four carboxylate groups in a monodentate fashion from four different **L** molecules (Fig.1).

The Cd1 centre is connected to four adjacent Cd centres through the **L** bridges to result in a three-dimensional polymeric network with a diamondoid struc-

Table 1 Crystal data and structure refinement for 1 and 2

	1	2
Formula	C ₆₄ H ₈₀ Cd ₂ Cl ₄ N ₈ O ₄₀	C ₆₄ H ₈₀ Zn ₂ Cl ₄ N ₈ O ₄₀
<i>M</i>	1 967.96	1 873.90
Crystal system	Tetragonal	Tetragonal
Space group	<i>P</i> $\bar{4}$ <i>n</i> 2 (No.118)	<i>P</i> 4 ₂ 22 (No.93)
Crystal size/ mm	0.25 × 0.20 × 0.15	0.25 × 0.23 × 0.13
<i>a</i> / nm	1.277 3(2)	1.310 6(2)
<i>b</i> / nm	1.277 3(2)	1.310 6(2)
<i>c</i> / nm	1.164 5(2)	1.126 9(2)
<i>V</i> / nm ³	1.899 9(5)	1.935 7(6)
<i>Z</i>	1	1
<i>D_c</i> / (Mg·m ⁻³)	1.720	1.608
<i>F</i> (000)	1 004	968
<i>μ</i> / cm ⁻¹	8.06	8.61
<i>θ</i> range / (°)	2.25 to 26.35	1.55 to 25.02
Reflections collected	8 518	8 099
Independent reflections	1 937 [<i>R</i> (int)=0.030 7]	1 721 [<i>R</i> (int)=0.051 2]
Final <i>R</i> indices	0.024 4 [<i>I</i> >2σ(<i>I</i>)]	0.037 8 [<i>I</i> >2σ(<i>I</i>)]
<i>wR</i>	0.065 1	0.092 1
Goodness of fit on <i>F</i> ²	1.073	0.987
Data / restraints / parameters	1937 / 0 / 135	1721 / 0 / 136
Largest diff. peak and hole / (e·nm ⁻³)	347 and -352	718 and -545
Flack parameter	0.02(3)	0.14(3)

$R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$, $w = 1/[\sigma^2 F_o^2 + (aP)^2 + bP]$, $P = [2F_c^2 + \max(F_o^2, 0)]/3$, **1**: $a=0.041$ 6, $b=0.310$ 8; **2**: $a=0.063$ 5, $b=0$.

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

1					
Cd(1)-O(1)	0.225 1(2)	Cd(1)-O(1A)	0.225 1(2)	Cd(1)-O(1B)	0.225 1(2)
Cd(1)-O(1A)	0.225 1(2)	O(1)-C(1)	0.124 8(4)	O(2)-C(1)	0.124 2(4)
O(1A)-Cd(1)-O(1B)	120.6(1)	O(1A)-Cd(1)-O(1)	120.6(1)	O(1B)-Cd(1)-O(1)	88.9(1)
O(1A)-Cd(1)-O(1C)	88.9(1)	O(1B)-Cd(1)-O(1C)	120.6(1)	O(1)-Cd(1)-O(1C)	120.6(1)
O(1)-C(1)-O(2)	125.1(3)	O(4)-C(1)-O(3)	127.7(5)		
2					
Zn(1)-O(1)	0.197 0(2)	Zn(1)-O(1A)	0.197 0(2)	Zn(1)-O(1B)	0.197 0(2)
Zn(1)-O(1C)	0.197 0(2)	O(1)-C(1)	0.125 7(5)	O(2)-C(1)	0.123 2(5)
C(4)-N(1)	0.132 9(5)	N(1)-C(5)	0.133 6(5)	N(1)-C(7)	0.148 9(4)
O(1A)-Zn(1)-O(1)	101.0(2)	O(1A)-Zn(1)-O(1B)	130.1(2)	O(1)-Zn(1)-O(1B)	99.5(2)
O(1A)-Zn(1)-O(1C)	99.5(2)	O(1)-Zn(1)-O(1C)	130.1(2)	O(1B)-Zn(1)-O(1C)	101.0(2)
O(2)-C(1)-O(1)	127.3(4)	O(2)-C(1)-C(2)	117.9(4)	C(1)-O(1)-Zn(1)	117.8(3)

Symmetry transformations used to generate equivalent atoms: **1**: A: y , $1-x$, $2-z$; B: $1-x$, $1-y$, z ; C: $1-y$, x , $2-z$;

2: A: x , $1-y$, $2-z$; B: $-x$, y , $z+2$; C: $-x$, $1-y$, z .

ture (Fig.2), which is extremely elongated in the *c* direction with a distance between the top-most and bot-

tom-most extremities of an adamantane unit as large as 6.98 70 nm. The very large void space of one net-

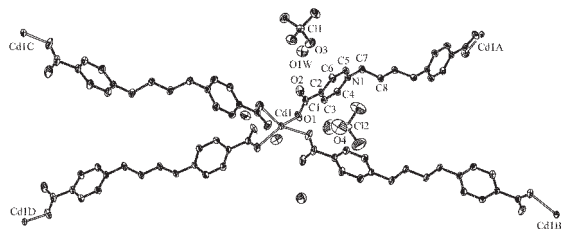


Fig.1 Perspective view (thermal ellipsoids at the 35% probability level) of the motif of **1** with atomic numbering scheme.

Hydrogen atoms are omitted for clarity.

Symmetry code: A: $-1/2+x, 3/2-y, -3/2+z$; B: $1/2+x, 1/2-y, -3/2+z$; C: $1/2+x, 3/2-y, 3/2+z$; D: $-1/2+x, 1/2-y, 3/2+z$.

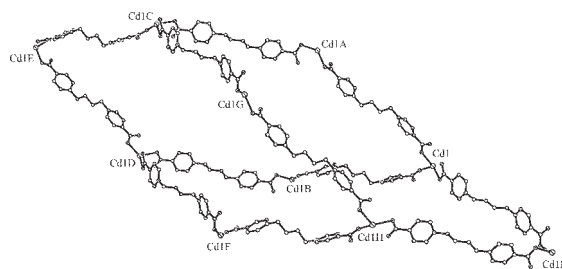


Fig.2 Perspective view of the diamondoid unit in **1**

work thus formed is partially avoided by 6-fold interpenetrations with the nodes of other five nets arranged equally spaced along c axes.

Although the positively charged networks are highly interpenetrated, large void spaces still exist. These void spaces are further filled with perchlorate anions and water molecules. Interestingly, some perchlorate anions, which lie on the axes, are included in the distorted tetrahedral cages formed by four pyridyl rings from the adjacent diamondoid networks, thus filling some void spaces. Other void spaces, i.e. the large channels which are aligning along c direction, are occupied by perchlorate anions and clusters (Fig. 3) which interact with the diamondoid networks through the hydrogen bonds between each water molecule and the pendent oxygen atoms of the carboxylate groups [$O2 \cdots O1W$: 0.284 3 nm].

2.2 Crystal structure of $\{(ZnL_2) \cdot 4H_2O \cdot 2ClO_4\}_n$ (**2**)

Compound **2** has the same stoichiometric formula with **1**, but crystallizes in the chiral space group $P4_222$ (No.93). At beginning, we thought it was an isostructure of **1**, thus trying to solve its structure in

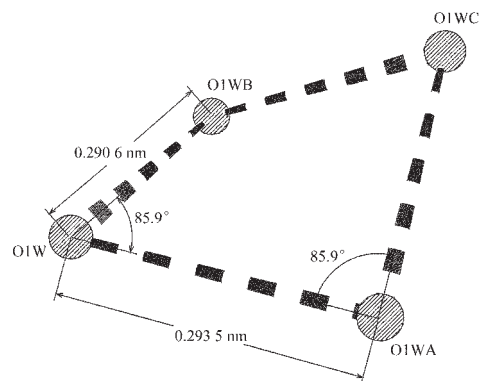


Fig.3 Perspective view of the $(H_2O)_4$ cluster in **1**
Symmetry code: A: $1-x, 2-y, z$; B: $3/2-y, 3/2-x, 3/2-z$; C: $-1/2+y, 1/2+x, 3/2-z$.

space group $P\bar{4}n2$ (No.118), but failed either by using the direct method or the Patterson method. In addition, the attempt to refine the structure by substituting the Cd atom in **1** with Zn atom led to the divergence of the structure.

As depicted in Fig.4, the Zn atoms lying on the axes are ligated by four carboxylate groups in a monodentate fashion from four different **L** ligands, leading to a distorted tetrahedral ZnO_4 coordination sphere [$Zn-O$: 0.197 0(2) nm; $O-Zn-O$: $99.5^\circ \sim 130.1^\circ$]. The $M-O$ distance in **2** is much shorter than that in **1** due to the smaller radius of Zn atom compared with that of Cd atom.

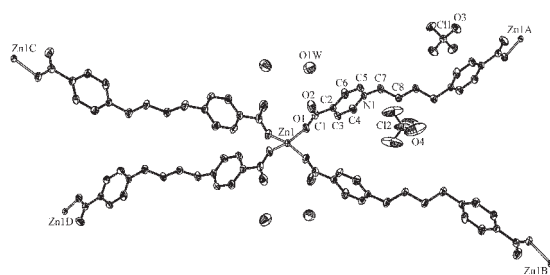


Fig.4 Perspective view (thermal ellipsoids at the 35% probability level) of the motif of **2** with atomic numbering scheme

Hydrogen atoms are omitted for clarity.

Symmetry code: A: $1-y, x, -3/2+z$; B: $-y, 1+x, -3/2+z$; C: $-y, x, 3/2+z$; D: $1-y, 1+x, 3/2+z$.

Similar to **1**, the Zn1 atom in **2** is linked to four adjacent Zn centres by **L** linkages thus forming a positively charged diamondoid structure (Fig.5). Also, the network is elongated in the c direction with a separation of 6.761 4 nm between the top-most and bottom-

