研究简报

二维配位聚合物$[K_2(5\text{-nbdc})_2Cd(Ⅱ)\cdot imH\cdot H_2O]_\infty$的合成和晶体结构

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Synthesis and crystal structure of Poly[Dipotassium bis(5-nitro-1,3-benzenedicarbonate) cadmium(Ⅱ)monoimidazolemonohydrate]

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Abstract: The crystal structure of the title complex, $[K_2(5\text{-nbdc})_2Cd(Ⅱ)\cdot imH\cdot H_2O]_\infty$ (5-nbdc=5-nitro-1,3-benzenedicarbonate, imH=imidazole) has been determined by X-ray diffraction analysis. The crystal data are: tetragonal, space group $P4_1$, M_r=694.93 for $CdC_{19}H_{12}N_4O_{13}K_2$, a=1.018 6(10) nm, b=1.018 6(10) nm, c=2.436 7(5) nm; Z=4, V=2.528 2(6) nm^3, F(000)=1 376, D_c=1.826 Mg·m^{-3}, μ=1.267 mm^{-1}. The title polymeric complex exhibits a two-dimensional framework, in which adjacent Cd(Ⅱ) ions are bridged by μ-O_4-5-nitro-1,3-benzenedicarbonate groups forming one-dimensional chains that are further linked by μ-O_3-5-nitro-1,3-benzenedicarbonate groups into two-dimensional anion rectangle sheets with large 32-membered rings. The strong π-π stacks of the benzene rings link these adjacent sheets into a three-dimensional van der Waals network. CCDC: 245527.

Key words: 5-nitro-1,3-benzenedicarbonic acid; cadmium(Ⅱ) complex; coordination polymer; crystal structure

In recent years, asymmetric organic ligands (such as m-pyridinecarboxylates) have been used as bi/tridentate bridges to build chiral coordination polymers of Cd(Ⅱ) or Zn(Ⅱ) for exploring non-linear optical materials[1]. In these reported coordination polymers, the generation of acentric polymeric coordination networks come mostly from the asymmetric organic ligands, especially, when the central ion is located at an inversion center or the geometry of the central ion is symmetric[2]. However, the acentricity of coordination polymer can be generated by the lack of a center of symmetry on center metals. Namely the symmetric organic ligand also has potentials to generate acentric polymeric coordination networks[3]. The research interests in the properties of coordination polymers, especially for non-linear optical and magnetic materials, had let us preparing a group of chiral coordination polymers constructed by symmetric organic ligand 4,4′-bipyridine[3-6]. In this work, we report a new two-dimensional chiral coordination polymer, viz. Poly[Dipotassium bis(5-nitro-1,3-benzenedicarbonate) cadmium(Ⅱ)monoimidazolemonohydrate], featuring the generation of acentric rectangle networks by the irregular acentric geometry of seven coordinate Cd(Ⅱ) ion.

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1 Experimental

1.1 Preparation

5-nitro-1,3-benzenedicarbolic acid was synthesized according to the published procedure[7]. A mixture containing of cadmium nitrate tetrahydrate (0.20 mmol), 5-nitro-1,3-benzenedicarbolic acid (0.40 mmol), imidazole (0.20 mmol), potassium hydroxide (0.40 mmol) and 5 mL of water in a 25 mL Teflon container was stirred and then was heated at 150 ℃ for three days. After decreasing the temperature to room temperature slowly, yellow crystals of suitable for X-ray analysis were obtained. The yield was 83% based on cadmium nitrate tetrahydrate. IR data (cm^{-1}): 3 083(m), 1 609(s), 1 560(s), 1 455(s), 1 405(s), 1 378(s), 1 197(m), 1 086(m), 931(w), 790(m), 729(s). Elemental analysis, found(%): C 32.73, H 1.98, N 8.00, O 30.03; calculated for $CdC_{19}H_{12}N_4O_{13}K_2$(%): C 32.84, H 1.74, N 8.06, O 29.93.

1.2 X-ray single crystal structure determination

A yellow crystal with a size 0.47 mm × 0.32 mm × 0.26 mm was selected for X-ray diffraction analysis. The reflection data were collected on a Siemens R3m diffractometer using Mo $K\alpha$ radiation (λ=0.071 073 nm) from a rotating anode generator operating at 50 kV and 25 mA. A total of 12 970 independent reflections were collected within the limit $2.18° \leqslant \theta \leqslant 26.02°$ using the ω-2θ mode, in which 4 541 reflections with $I>2\sigma(I)$ were considered as observed. The corrections for Lp factors were applied[8]. The structure was solved by patterson method[9]. Hydrogen atoms of the 5-nitro-1,3-benzenedicarbolic acid ligand, imidazole and water molecules were placed at calculated positions and allowed to ride on their respective parent atoms, assigned fixed isotropic thermal parameters. All calculations and refinements were carried out on a PC-586 computer using the SHELX-97 Program Package [10]. The Crystal structure refinement parameters of the compound are given in Table 1.

Table 1 Crystal structure refinement parameters of the title compound

Empirical formula	$CdC_{19}H_{12}N_4O_{13}K_2$	β / (°)	90.00
F_w	694.93	γ / (°)	90.00
Crystal size/ mm	0.47 × 0.32 × 0.24	V / nm^3	2.528 2(6)
Crystal system	Tetragonal	Z	4
Space group	$P4_1$	ρ_{calc} / ($g \cdot cm^{-3}$)	1.826
a / nm	1.018 60(10)	μ(Mo $K\alpha$) / mm^{-1}	1.267
b / nm	1.018 60(10)	R_1 [$I>2\sigma(I)$]	0.051 9
c / nm	2.436 7(5)	wR_2 (all data)	0.162 4
α / (°)	90.00	F(000)	1 376

CCDC: 245527.

2 Results and discussion

The IR and elemental analysis for the product are in good agreement with the title complex. The selected bond lengths and bond angles are given in Table 2. The molecular structure of the title complex with atom numbering scheme is shown in Fig.1. Fig.2 and Fig.3 depict the packing diagram of title compound.

The title compound crystallizes in the acentric space group $P4_1$. Usually the geometry of seven coordinate Cd(Ⅱ) ion are either distorted pentagonal bipyramidal [11,12] or pseudo-octahedral [13]. However, in the title compound the seven coordinate Cd(Ⅱ) ion shows a irregular coordination geometry [14]. The metal ion Cd1,

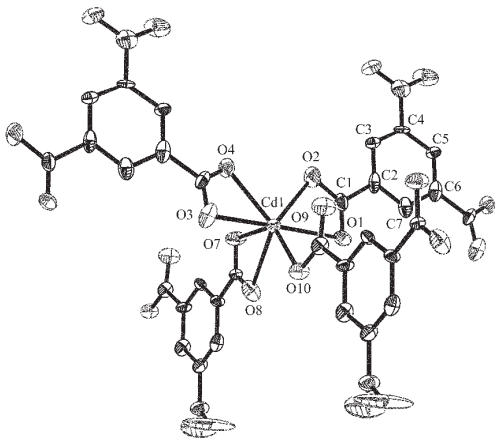

Fig.1 ORTEP plot of the title complex, and the displacement ellipsoids are shown at the 35% probability level
The lattice imidazole, water molecules and potassium ions were omitted for clarity.

Table 2　Selected bond lengths (nm) and bond angles (°) of the title compound

Cd(1)-O(1)	0.256 1(5)	Cd(1)-O(4)	0.233 2(6)	Cd(1)-O(8)	0.239 0(7)
Cd(1)-O(2)	0.231 1(7)	Cd(1)-O(7)	0.249 6(5)	Cd(1)-O(10)	0.229 6(5)
Cd(1)-O(3)	0.258 0(6)				
O(1)-Cd(1)-O(2)	52.7(3)	O(2)-Cd(1)-O(4)	81.5(2)	O(3)-Cd(1)-O(10)	83.8(2)
O(1)-Cd(1)-O(3)	170.5(2)	O(2)-Cd(1)-O(7)	86.7(3)	O(4)-Cd(1)-O(7)	82.0(2)
O(1)-Cd(1)-O(4)	133.7(3)	O(2)-Cd(1)-O(8)	124.2(2)	O(4)-Cd(1)-O(8)	120.9(2)
O(1)-Cd(1)-O(7)	89.4(2)	O(2)-Cd(1)-O(10)	126.3(2)	O(4)-Cd(1)-O(10)	129.8(2)
O(1)-Cd(1)-O(8)	86.6(2)	O(3)-Cd(1)-O(4)	51.3(3)	O(7)-Cd(1)-O(8)	52.7(3)
O(1)-Cd(1)-O(10)	88.0(2)	O(3)-Cd(1)-O(7)	99.7(2)	O(7)-Cd(1)-O(10)	133.1(3)
O(2)-Cd(1)-O(3)	130.1(3)	O(3)-Cd(1)-O(8)	96.7(3)	O(8)-Cd(1)-O(10)	80.4(2)

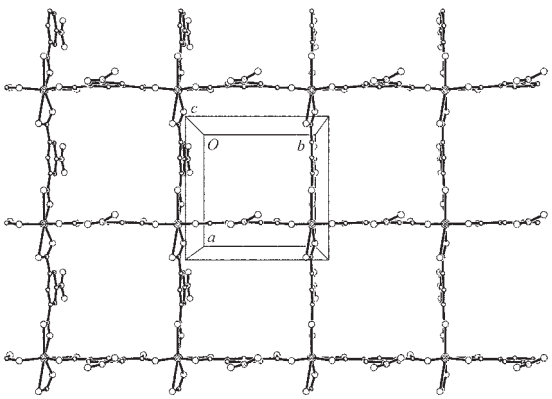

Fig.2　View of the two-dimensional anion sheet of the compound along *c* axis, showing the rectangle large 32-member ring in the lattice

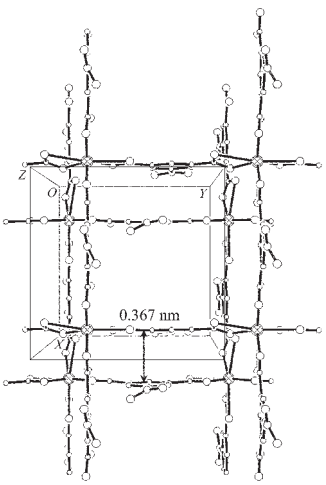

Fig.3　Side view of the π-π stacks between two dimensional anion sheets of the compound along *b* axis

being located at acentric coordination envirement, is coordinated by seven oxygen atoms: four of them from two bidentate chelating carboxylates of two 5-nitro-1, 3-benzenedicarbonate groups are bonded to the Cd1 ion [Cd1-O1 =0.256 1(5) nm; Cd1-O2=0.231 1(7) nm; Cd1-O3= 0.258 0(6) nm; Cd1-O4=0.233 2(6) nm] on the bc plane, and three of them from other two chelating carboxylates of two 5-nitro-1,3-benzenedicarbonate groups (one is monodentate and another is bidentate) [Cd1-O7=0.249 6(5) nm; Cd1-O8=0.239 0(7) nm; Cd1-O10=0.229 6 (5) nm;] are bonded to Cd1 on the *ac* plane (Fig.1).

As expected, the adjacent Cd1 ions are firstly linked by μ-O_4-5-nitro-1,3-benzenedicarbonate bridges, thus forming infinite one-dimemsional chains, and then these chains are further linked by μ-O_3-5-nitro-1, 3-benzenedicarbonate bridges into two dimensional rectangle sheets (the Cd-Cd separations are 0.713 5 and 0.921 2 nm and all of the Cd-Cd-Cd angle is 90°), showing large 32-member rings in the *c* axis (Fig.2). The absence of a center of symmetry on the metal center ensures the acentricity of the rectangle network. Finally the inerdigitated benzene rings form strong π-π sticks[2], in which the centroid-to-centroid distance is 0.367 nm and the shortest distance between inerdigitated benzene rings is 0.322 nm, extend these sheets into a three-dimensional van der Waals network (Fig. 3). The void space of network from the inerdigitation of benzene rings of adjacent rectangle sheets is efficiently filed by one imidazole molecule, one water molecule and two potassium cations enclathrated and no meaningful hydrogen bonds are found in the lattice of the title compound.

3　Conclusion

In summary, we have found a rational synthesis approach toward acentric solid materials based on

two-dimensional rectangle coordination networks by using symmetric organic ligand and seven coordinate Cd(Ⅱ) metal ion in the absence of center of symmetry. We will extend this strategy by using other symmetric organic ligands (especially these with push-pull effects) and seven coordinate Cd(Ⅱ) metal ion to synthesize new chiral coordination polymers.

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