

КРАТКИЕ СООБЩЕНИЯ

UDC 548.73:547.13:546.48

CRYSTAL STRUCTURE OF A NOVEL CADMIUM SULFATE COORDINATION POLYMER BASED ON THE MULTIDENTATE 2-(3-(4-(PYRIDIN-4-YL)PHENYL)-1H-1,2,4-TRIAZOL-5-YL) PYRIDINE LIGAND

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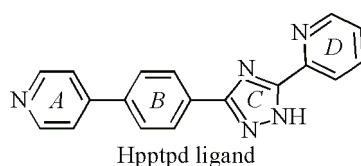
Received May, 6, 2012

A novel metal-organic coordination polymer, namely $[\text{Cd}_2(\text{Hpptpd})_2(\text{SO}_4)_2(\text{H}_2\text{O})]_n$ (**I**) (Hpptpd = 2-(3-(4-(pyridin-4-yl)phenyl)-1H-1,2,4-triazol-5-yl)pyridine), is hydrothermally synthesized and characterized by elemental analysis, IR and X-ray single crystal diffraction. The X-ray diffraction analysis reveals that **I** crystallizes in the triclinic system, space group *P*-1 with $a = 8.593(6) \text{ \AA}$, $b = 9.832(6) \text{ \AA}$, $c = 11.845(7) \text{ \AA}$, $\alpha = 68.172(10)^\circ$, $\beta = 88.002(12)^\circ$, $\gamma = 84.916(11)^\circ$, $V = 925.3(10) \text{ \AA}^3$, $Z = 2$. In **I**, the Cd(II) atom is heptacoordinated and displays a CdN_3O_4 pentagonal bipyramidal geometry. A pair of head-to-tail arranged Hpptpd ligands with a chelating + bridging mode binds two Cd(II) ions to form a centrosymmetric $[\text{Cd}_2(\text{Hpptpd})_2]$ subunit which is bridged by two centrosymmetric sulfate anions to form a zig-zag chain. The interchain $\text{O}_{\text{water}}\cdots\text{H}\cdots\text{O}_{\text{sulfate}}$ hydrogen bond extend the one-dimensional (1D) chain into a two-dimensional (2D) supramolecular sheet incorporating centrosymmetric twelve-membered R_4^4 (12) hydrogen-bonding rings. The adjacent sheets further interdigitate with each other to form the resultant three-dimensional (3D) supramolecular framework by $\text{N}_{\text{Hpptpd}}\cdots\text{H}\cdots\text{O}_{\text{sulfate}}$ hydrogen bonds and $\pi\cdots\pi$ stacking interactions.

Keywords: coordination polymer, cadmium complex, sulfate, 2-(3-(4-(pyridin-4-yl)phenyl)-1H-1,2,4-triazol-5-yl)pyridine.

The design and synthesis of metal-organic coordination polymer, often referred to as metal-organic frameworks (MOFs), have attracted more attention not only because of their appealing structural and topological novelty but also owing to their tremendous potential applications in gas storage and separations [1, 2], heterogeneous catalysis [3], ion exchange [4], nonlinear optics [5], magnetism [6, 7], and molecular recognition [8–10]. To the best of our knowledge, in the assembly process of MOFs, many factors can affect the final crystal structure, such as the structure of the organic ligand [11], the coordination geometry of the metal ion [12], the metal-ligand ratio, and so on. Secondary interactions such as hydrogen bonding, $\pi\cdots\pi$ stacking and host-guest interactions must also be considered. Recently less attention was given to the supramolecular architectures based on N-donor ligands, especially multidentate N-donor ligands [13]. Unlike the common bipyridine or biimidazole ligands [14], the multidentate N-donor ligands such as 3-(2-pyridyl)-5-(4-pyridyl)-1,2,4-triazole are rarely studied and especially attractive due to (i) it can act not only as bridging but also chelating ligands; (ii) it can adopt *cis* or *trans* transformations based on the rotation of the $\text{C}_{\text{triazole}}\text{—}\text{C}_{\text{pyridine}}$ bond; (iii) triazole can be a neutral or anionic unit depending on whether the H atom on it is deprotonated or not. Thus, this kind of ligands deserves to be further investigated in the crystal engineering field. In this paper, we chose the multidentate N-donor ligand 2-(3-(4-(pyridin-4-yl)phenyl)-1H-1,2,4-triazol-5-

yl)pyridine (Hpptpd, Scheme 1) and CdSO_4 to build the first cadmium sulfate complex of the novel Hpptpd ligand $[\text{Cd}_2(\text{Hpptpd})_2(\text{SO}_4)_2(\text{H}_2\text{O})]_n$ (**I**).



Experimental. Materials and methods. All reagents and solvents employed were commercially available and used as received without further purification. The C, N, and H analysis was performed on an EA1110 CHNS-0 CE 65 elemental analyzer. IR (KBr pellet) spectrum was recorded on a Nicolet Magna 750FT-IR spectrometer.

Synthesis of complex I. A mixture of $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ (51 mg, 0.067 mmol), Hpptpd (60 mg, 0.20 mmol), NaOH (4.0 mg, 0.10 mmol), and 14 ml of H_2O were sealed in a 25 ml Teflon-lined stainless steel autoclave ($\text{pH} \approx 6$) and heated at 170°C for 3 days, and then slowly cooled to room temperature. Light yellow crystals of **I** were obtained by filtration, washed with distilled water, and dried at ambient temperature (the yield was $\sim 82\%$). Anal. Calc. for $\text{C}_{18}\text{H}_{15}\text{CdN}_5\text{O}_5\text{S}$: C, 41.12; H, 2.88; N, 13.32; found: C, 41.45; H, 3.02; N, 13.15%. IR spectrum (KBr, ν , cm^{-1}): 3415 (vs), 1725 (vs), 1624 (vs), 1533 (vs), 1409 (s), 1367 (s), 1121 (m), 991 (w), 610 (m).

Table 1

Crystallographic data for **I**

Empirical formula	$\text{C}_{18}\text{H}_{15}\text{CdN}_5\text{O}_5\text{S}$
Formula weight	525.81
Wavelength, \AA	0.71073
Crystal system	Triclinic
Space group	$P-1$
Unit cell dimensions: $a, b, c, \text{\AA}$	8.593(6), 9.832(6), 11.845(7)
$\alpha, \beta, \gamma, \text{deg.}$	68.172(10), 88.002(12), 84.916(11)
Volume, \AA^3	925.3(10)
Z	2
$D(\text{called}), \text{g/cm}^3$	1.887
μ, mm	1.338
$F(000)$	524.0
Crystal size, nm	0.15×0.10×0.10
θ Range, deg.	3.7—49.98
Reflections collected	4742
Independent reflections (R_{int})	3232 (0.0340)
Max., min. transmission	0.8779, 0.8246
T, K	293(2)
Goodness-of-fit on F^2	1.011
Final R indices ($I > 2\sigma(I)$) ^a	$R1 = 0.0450, wR2 = 0.0959$
R indices (all data)	$R1 = 0.0618, wR2 = 0.1040$
Largest diff. peak and hole, $\text{e}/\text{\AA}^3$	0.62 and -0.56

^a $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|$; $wR_2 = \sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]^{1/2}$.

Selected bond lengths (Å) and angles (deg.) in **I**

Bond	<i>d</i> , Å	Angle	ω , deg.	Angle	ω , deg.
Cd1—N5 ⁱ	2.273(5)	N5 ⁱ —Cd1—N1	158.39(16)	N1—Cd1—N2	72.09(15)
Cd1—N1	2.308(5)	N5 ⁱ —Cd1—O1W	102.82(16)	O1W—Cd1—N2	79.28(14)
Cd1—O1W	2.346(4)	N1—Cd1—O1W	89.15(16)	O1 ⁱⁱ —Cd1—N2	157.27(15)
Cd1—O1 ⁱⁱ	2.387(4)	N5 ⁱ —Cd1—O1 ⁱⁱ	90.19(15)	O1—Cd1—N2	135.56(14)
Cd1—O1	2.447(4)	N1—Cd1—O1 ⁱⁱ	110.04(15)	N5 ⁱ —Cd1—O2	82.35(15)
Cd1—N2	2.503(4)	O1W—Cd1—O1 ⁱⁱ	78.14(13)	N1—Cd1—O2	81.36(15)
Cd1—O2	2.647(4)	N5 ⁱ —Cd1—O1	98.77(15)	O1W—Cd1—O2	163.03(13)
		N1—Cd1—O1	83.36(15)	O1 ⁱⁱ —Cd1—O2	118.30(13)
		O1W—Cd1—O1	137.94(14)	O1—Cd1—O2	55.08(13)
		O1 ⁱⁱ —Cd1—O1	66.05(16)	N2—Cd1—O2	84.41(14)
		N5 ⁱ —Cd1—N2	92.29(15)		

Symmetry codes: (i) $-x+2, -y+1, -z+2$; (ii) $-x+1, -y+2, -z+1$.

X-ray crystallography. The crystallographic data for **I** were collected at room temperature with a Bruker Apex II CCD diffractometer with a graphite-monochromated MoK α radiation source ($\lambda = 0.71073$ Å). The structure was solved by direct methods using SHELXS-97 [15] and refined on F^2 by full matrix least squares using SHELXL-97 [16]. All of the nonhydrogen atoms were refined anisotropically. All other hydrogen atoms were placed in geometrically ideal positions and constrained to ride on their parent atoms. Crystallographic data and experimental details for the structural analyses are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2. The atomic coordinates and other parameters of structure **I** have been deposited with the Cambridge Crystallographic Data Center (no. 925570; deposit@ccdc.cam.ac.uk).

Results and discussion. Structure of [Cd₂(Hpptpd)₂(SO₄)₂(H₂O)]_n (I**).** The X-ray single-crystal diffraction analysis reveals that the asymmetric unit of (**I**) contains one Cd(II) atom, one Hpptpd ligand, one SO₄²⁻ anion, and one coordinated water molecule. As shown in Fig. 1, Cd1 is seven-coordinated by three O atoms from two sulfates, three N atoms from two Hpptpd ligands, and one O atom from a water molecule, giving a pentagonal bipyramidal coordination environment. The Cd—N and Cd—O bond lengths are in the range of 2.273(5)—2.503(4) Å and 2.387(4)—2.647(4) Å respectively, which are well-matched to those observed in similar complexes [17—21]. For the Hpptpd ligand, the aromatic rings can freely rotate along the C—C bonds to adjust themselves to match with the coordination preferences. Considering the conformation of Hpptpd, we define six important geometric parameters, α , β , γ , δ , ϵ , which represent the dihedral angles between the A/B, B/C, C/D, A/C, and B/D aromatic rings respectively (Scheme 1). The respective six values are 33.7(3)°, 16.3(3)°, 10.8(3)°, 49.7(3)°, and 26.2(3)°. A pair of head-to-tail arranged Hpptpd ligands with a [chelating +

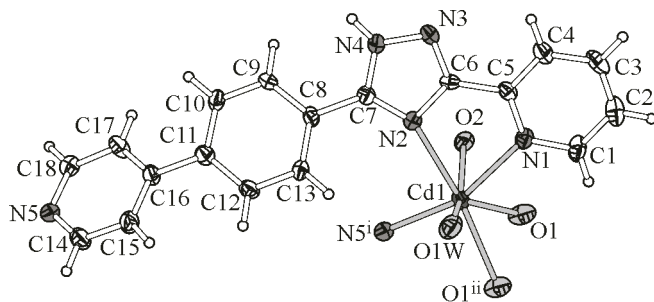


Fig. 1. Structure of **I**, showing the atom numbering scheme and the coordination environment around the Cd(II) centre. Displacement ellipsoids are drawn at 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Symmetry codes: (i) $-x+2, -y+1, -z+2$; (ii) $-x+1, -y+2, -z+1$

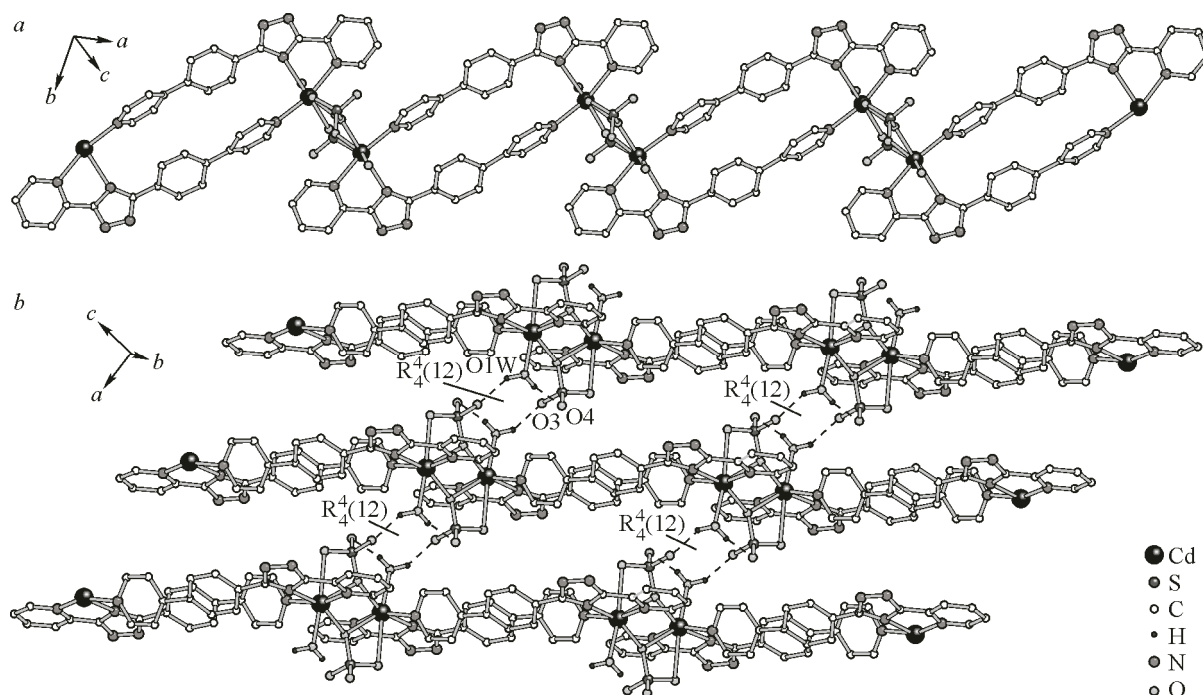


Fig. 2. Ball-and-stick view of the 1D zigzag chain (a), Ball-and-stick view of the 2D supramolecular sheet incorporating twelve-membered $R_4^4(12)$ hydrogen-bonding rings (b)

+ bridging] mode bind two Cd(II) ions to form a centrosymmetric $[\text{Cd}_2(\text{Hpptpd})_2]$ subunit. The $\kappa^2\text{-O:O,O'}\text{-SO}_4^{2-}$ anion plays the role of a bridge to connect the $[\text{Cd}_2(\text{Hpptpd})_2]$ subunits to form a 1D zigzag chain (Fig. 2, a). A survey of the 2012 Version of the Cambridge Structural Database (CSD; Version 5.33, August 2012 update; Allen, 2002) shows that no structures have been published containing both CdSO_4 and Hpptpd ligand, and only six examples incorporating the SO_4^{2-} anion of the $\kappa^2\text{-O:O,O'}$ binding mode have been published previously.

The hydrogen bonds between SO_4^{2-} and a coordinated water molecule form a twelve-membered $R_4^4(12)$ hydrogen-bonding motif [22] and play two important roles in the crystal packing. The intrachain hydrogen bond ($\text{O1W}\cdots\text{O4}^{\text{ii}} = 2.758(6) \text{ \AA}$) consolidates the 1D chain, whereas the interchain hydrogen bond ($\text{O1W}\cdots\text{O3}^{\text{iv}} = 2.711(6) \text{ \AA}$) extends the 1D chain into a 2D supramolecular sheet (Fig. 2, b). The adjacent 2D sheets are interdigitated with each other to form the resultant 3D supramolecular framework (Fig. 3) via the $\text{N}_{\text{Hpptpd}}\text{-H}\cdots\text{O}_{\text{sulfate}}$ hydrogen bond ($\text{N4-H4A}\cdots\text{O2}^{\text{iii}} = 2.677(6) \text{ \AA}$) and $\pi\cdots\pi$ stacking interactions ($\text{Cg1}\cdots\text{Cg1}^{\text{v}} = 3.625(4) \text{ \AA}$; $\text{Cg2}\cdots\text{Cg2}^{\text{iii}} = 3.668(4) \text{ \AA}$ and $\text{Cg2}\cdots\text{Cg3}^{\text{iii}} = 3.844(4) \text{ \AA}$; Cg1, Cg2, and Cg3 are the centroids of N1/C1—C5, N2/C6/N3/N4/C7, and C8—C13 rings respectively). (Symmetry codes: (iii) $-x+1, -y+2, -z+2$; (v) $-x+1, -y+3, -z+1$).

In summary, a new mononuclear Cd(II) complex based on the Hpptpd ligand has been hydrothermally prepared and structurally characterized by the single crystal X-ray diffraction analysis. Each Cd(II) ion in the complex displays a CdN_3O_4 pentagonal bipyramidal geometry. The molecule of I is stabilized by the hydrogen bonding and $\pi\cdots\pi$ stacking interactions.

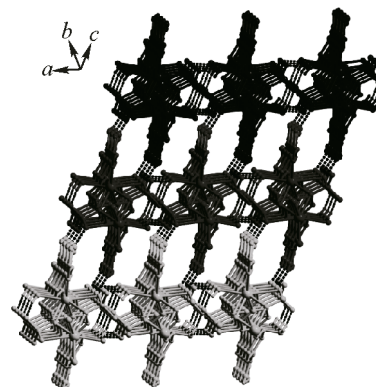


Fig. 3. Ball-and-stick view of the 3D supramolecular framework built from interdigitated supramolecular 2D sheets ($\text{N}_{\text{Hpptpd}}\text{-H}\cdots\text{O}_{\text{sulfate}}$ hydrogen bonds shown in black dashed lines)

Acknowledgements. This work was supported by the NSFC (Grant No. 21201110), Independent Innovation Foundation of Shandong University (2011GN030), the Special Fund for Postdoctoral Innovation Program of Shandong Province (201101007), and the China Postdoctoral Science Foundation (2012M511492).

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