

КРАТКИЕ СООБЩЕНИЯ

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A NEW Cd(II) COORDINATION POLYMER CONSTRUCTED BY A FLEXIBLE CARBOXYLATE LIGAND

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A new two-dimensional Cd(II) coordination polymer, [Cd(dtb)(CH₃OH)]_n (**H₂DTNB** = 5,5'-dithiobis(2-nitrobenzoic acid)), has been synthesized by solvothermal method, and characterized by elemental analysis, IR and single-crystal X-ray diffraction analysis. The complex crystallizes in the orthorhombic *Pbca* space group, with *a* = 15.1365(19), *b* = 7.6198(10), *c* = 31.761(4) Å, β = 90°, *V* = 3663.2(8) Å³, *Z* = 8, *Mr* = 538.77, *D_c* = 1.954 g/cm³ and *F*(000) = 2128. The final *R* = 0.040 and *wR* = 0.0866 for 3603 observed reflections with *I* > 2σ(*I*). In the complex, the Cd(II) ion is coordinated with six oxygen atoms from four carboxylate groups of distinct **DTNB** ligands and one methanol molecule. The adjacent Cd centers are interconnected by the flexible carboxylate ligand to form a two-dimensional (2D) structure.

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The design and synthesis of metal coordination polymers have attracted considerable attention not only because of their intriguing molecular architectures [1—5] but also owing to their wide potential applications in the fields of catalysis, molecular-based magnets, electrical conductivity, separation, gas storage, molecular recognition and zeolite-like materials [6—11]. During the past few decades, aromatic polycarboxylate ligands have been extensively employed to construct novel coordination polymers due to the versatile coordination modes, such as terminal monodentate, chelating, bridging tridentate, etc. [12—14], and strong coordinating capability of the carboxylate groups. In addition, flexible multicarboxylate ligands would be a kind of favorable precursors for the construction of coordination polymer with diverse structures and intriguing properties. Commonly, such ligands have diverse coordination modes, adjustable ligand-length, unique helical system and specific positional orientation [15]. Up to now, great contributions of helical coordination polymers with fascinating properties have been obtained by utilizing flexible multicarboxylate ligands [16]. With the above consideration, 5,5'-dithiobis (2-nitrobenzoic acid) (**H₂DTNB**) is selected to construct coordination polymer because of its high flexibility as well as multicarboxylic groups attached to the aromatic ring. However, only a few examples of coordination polymers based on **H₂DTNB** ligand have been reported [17—20]. As a continuation of our investigation of this ligand, herein we report the synthesis and structure of a novel 2D coordination polymer, [Cd(**DTNB**)(CH₃OH)]_n.

Experimental. General materials and instruments. All the reagents were obtained from commercial sources and used without further purification. The FT-IR spectra were recorded from KBr pellets in the range of 400—4000 cm⁻¹ on a vector 22 Bruker spectrophotometer. Elemental analyses of C, H, and N were performed on a Perkin-Elmer 240C analyzer. Crystal structure determination was carried out on a Bruker SMART APEX II CCD diffractometer.

Synthesis of complex [Cd(DTNB)(CH₃OH)]_n (1). A mixture of 5,5'-dithiobis(2-nitrobenzoic acid) (0.0396 g, 0.1 mmol), Cd(NO₃)₂·4H₂O (0.0308 g, 0.1 mol), isobutanol (0.7 mL), and methanol (0.8 mL) was sealed in a glass tube and heated at 85 °C for several days. Pure colorless crystals were collected, washed with methanol, and dried in air. Yield: 30 % based on Cd(NO₃)₂·4H₂O. Anal. Calcd. for CdC₁₅H₁₀N₂O₉S₂ (%): C 33.44, H 1.87, N 5.20. Found (%): C 33.45, H 1.89, N 5.20. IR: (KBr, cm⁻¹) 3423(s), 1607(s), 1564(m), 1436(s), 1408(m), 1358(m), 1332(m), 1217(w), 805(m), 620(w).

Crystal structure determination. Suitable single crystals of complex **1** were carefully selected for X-ray structure analysis with a linear dimensions of 0.15×0.20×0.15 mm. The data were collected on a Bruker SMART APEX II CCD diffractometer using a graphite-monochromatized MoK_α radiation (λ = 0.071073 nm) at 293(2) K. A total of 18241 reflections were collected in the range of 2.57 ≤ θ ≤ 26° by using a ω-2θ scan mode, of which 3603 were unique with R_{int} = 0.0866. The crystal is orthorhombic, space group *Pbca*, *a* = 15.1365(19) Å, *b* = 7.6198(10) Å, *c* = 31.761(4) Å, α = β = γ = 90°, *V* = 3663.2(8) Å³, *Z* = 8, ρ(calc) = 1.954 g/cm³, the absorption coefficient μ is 1.475 mm⁻¹.

The structure was solved by direct methods and refined on *F*² by full-matrix least-squares techniques using the SHELXL-97 crystallographic soft package [21]. Hydrogen atoms bonded to the carbon atoms were generated geometrically and refined isotropically with the riding mode. All of the non-hydrogen atoms were refined by anisotropic thermal parameters. The final R factors for reflections with *I* > 2σ(*I*) are as follows: *R*₁ = 0.040, *wR*₂ = 0.0866. Selected bond lengths and bond angles are given in Table 1. CIF file containing complete information on the studied structure was deposited with CCDC, deposition No. 996741, and is freely available upon request from the following web site: www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion. Crystal structure of the complex. Single crystal X-ray analysis revealed that the complex **1** crystallizes in orthorhombic space group *Pbca*. The hydrogen bond interactions of **1** are shown in Table 2. As exhibited in Fig. 1, the asymmetric unit of **1** consists of one Cd(II)

Table 1

Selected bond lengths (Å) and bond angles (deg.) for the complex **1**

Bond		Angle		Angle	
Cd1—O1	2.261(3)	O2b—Cd1—O7a	107.12(12)	O7c—Cd1—O9	93.99(10)
Cd1—O7a	2.358(3)	O1—Cd1—O7a	95.92(11)	O7c—Cd1—O1	81.68(11)
Cd1—O9	2.337(3)	O2b—Cd1—O7c	110.86(13)	O2b—Cd1—O9	95.20(12)
Cd1—O8a	2.455(3)	O9—Cd1—O7a	87.67(10)	O1—Cd1—O8a	83.00(11)
Cd1—O2b	2.166(3)	O7a—Cd1—O8a	53.75(8)	O9—Cd1—O8a	97.24(10)
Cd1—O7c	2.237(3)	O2b—Cd1—O1	86.09(13)	O7a—Cd1—O7c	141.65(11)
		O1—Cd1—O9	175.66(11)	O7c—Cd1—O8a	88.12(9)
		O2b—Cd1—O8a	156.49(12)		

Symmetry transformation: a = -x+2, y-1/2, -z+3/2; b = -x+3/2, y-1/2, z; c = x-1/2, y, -z+3/2.

Table 2

Hydrogen-bonding geometry parameters (Å, deg.) for the complex **1**

D—H···A	D—H	H···A	D—A	D—H···A
O9—H9···O8	0.842	1.954(19)	2.750(4)	157(4)
C12—H12···O6(i)	0.930	2.686(6)	3.507(4)	177.18(2)
C15—H15···O5(j)	0.959	2.586(8)	3.644(5)	170.51(3)

(i) x-1/2, -y+1/2, -z+1; (j) -x+3/2, -y, -z+1/2.

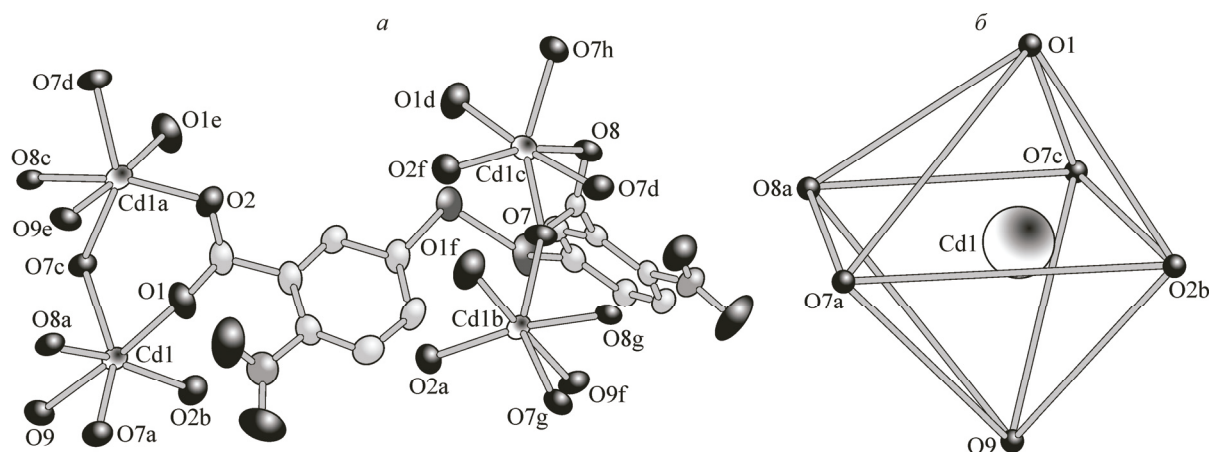


Fig. 1. Coordination environment of the Cd(II) ions in complex **1** with the hydrogen atoms omitted for clarity (30 % probability displacement ellipsoids) (a). Distorted octahedral geometry of the Cd(II) ion in the title complex (b).

Symmetry code: a = $-x+2, -1/2+y, -z+3/2$; b = $-x+3/2, -1/2+y, z$; c = $x-1/2, y, -z+3/2$; d = $-x+2, y+1/2, -z+3/2$; e = $-x+3/2, y+1/2, z$; f = $x+1/2, y, -z+3/2$; g = $-x+5/2, -1/2+y, z$; h = $-x+5/2, 1/2+y, z$

center, one **DTNB** Ligand and one coordinated methanol molecule. In complex, each Cd(II) center is coordinated to six O atoms from four carboxylate groups of distinct **DTNB** ligands (O1, O7a, O8a, O2b, O7c) and one methanol molecule (O9), forming a distorted octahedral geometry. The coordination environment of Cd(II) center of complex **1** is similar to that of previous reported complex $[\text{Cd}(\text{dtb})(\text{H}_2\text{O})]_n$ [20]. In the distorted octahedral geometry, four carboxylate oxygen atoms (O7a, O8a, O2b, O7c) occupy the equatorial plane, while one carboxylate oxygen atom (O1) and one oxygen from methanol molecule (O9) hold the axial positions. The total bond angles of O7a—Cd1—O8a, O7a—Cd1—O2b, O2b—Cd1—O7c, O7c—Cd1—O8a is 358.85° (close to 360°). The O1—Cd1—O9 angle is 175.66° and deviates from the ideal value of 180° for a normal octahedron, which indicates the octahedral geometry of Cd(II) center is distorted. The Cd—O distances range from 2.166(3) to 2.455(3) Å (average 2.302 Å), which are comparable to the values of the reported Cd(II) complex [20]. The torsion angles of C6—S2—S1—C13 and the dihedral angle between two phenyl rings in DTNB ligand are $85.93(19)$ and $77.00(0.13)^\circ$, respectively. In complex, the carboxylate groups of **DTNB** ligand show two different coordination modes: bridging and chelating/bridging tridentate fashions. The Cd1...Cd1A distance is 3.914 Å, which is comparable to the value of the Cd(II) complex [22].

As shown in Fig. 1, the adjacent Cd1 and Cd1a ions are bridged by the carboxylate groups through the O1, O2, O7c atoms to construct binuclear unit. The binuclear Cd(II) units are further linked together by the rest carboxylate groups of **DTNB** ligands to construct a double pseudo-helical chain along *b* axis (Fig. 2). Then, the neighboring pseudo-helical chains are interconnected through the

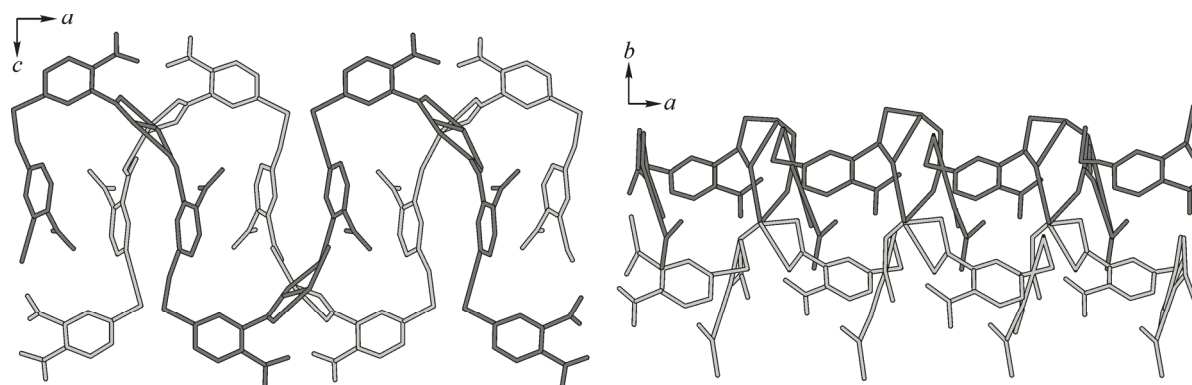


Fig. 2. The double helical chain viewed along the *b* axis (left) and *c* axis (right)

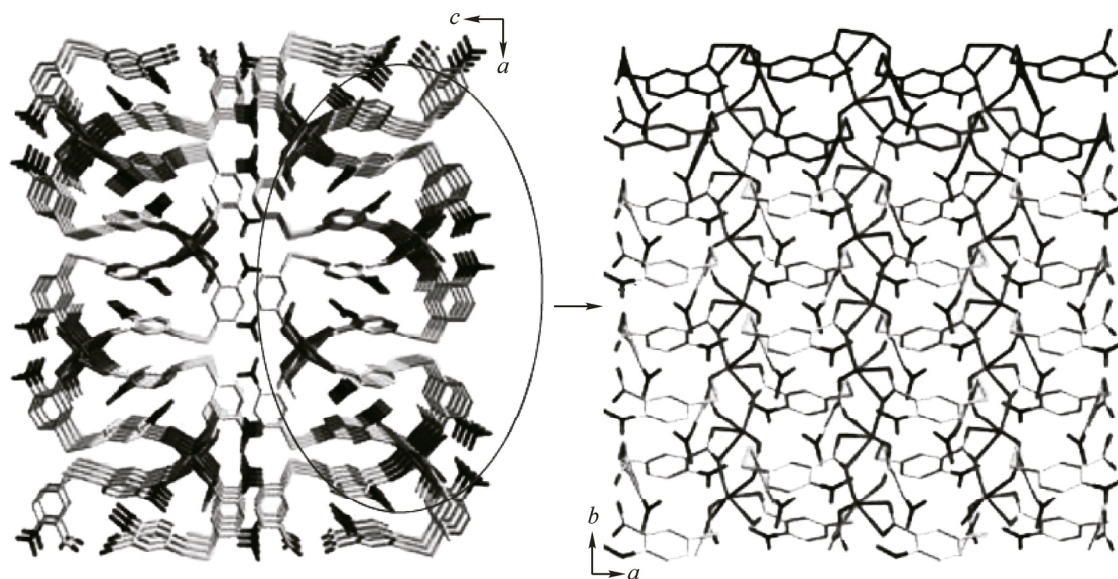
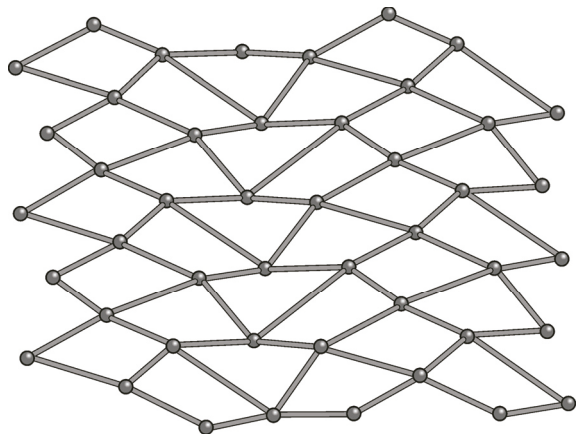


Fig. 3. Crystal packing view from the *b*-axial of complex **1** with the hydrogen atoms and coordinated methanol molecules omitted for clarity (left). The two dimensional framework constructed by double helical chains in *ab*-plane (right)

chelating/bridging tridentate carboxylate groups of **DTNB** ligand to form a two dimensional (2D) framework along the *ab*-plane (Fig. 3). In the 2D framework of **1**, the Cd(II) center and **DTNB** ligand can be reviewed as four-connected nodes. On the basis of this simplification and according to topological analysis by the TOPOS 4.0 program package [23], the network of **1** is a 4^4 -*sql* topology (Fig. 4).

Notably, there are abundant hydrogen bonding interactions among/within the 2D networks, which leads to the formation of a three dimensional supermolecular structure. For instance, there are typical intermolecular hydrogen bonds among the OH groups of coordinated methanol molecules and carboxylate oxygen atoms of **DTNB** ligand (Table 2). The $d(D\cdots A)$ distance of intermolecular hydrogen bond is 2.750 Å. In addition, atypical hydrogen bonding interactions, such as C—H \cdots O, are also observed in the complex with long $d(D\cdots A)$ distance as 3.507—3.644 Å. Undoubtedly, such weak intramolecular interactions are beneficial to the stabilization of the complex.

IR analyses. In the infrared spectrum, the broad band centered at ca. 3423 cm^{-1} is assigned to the O—H stretching vibration, which indicates the presence of the methanol molecules involved in hydrogen-bonding interactions. The absorptions for the antisymmetric stretching vibrations $\nu_{\text{as}}(\text{CO}_2^-)$ of the carboxyl appear at 1607 cm^{-1} , and symmetric stretching vibrations $\nu_{\text{s}}(\text{CO}_2^-)$ are observed with three



signals at 1436, 1408, and 1332 cm^{-1} , respectively. The absence of any strong absorption bands around 1700 cm^{-1} confirms the complete deprotonation of **H₂DTNB** ligand during the solvothermal reactions [20]. The strong band at 1564 and 1358 cm^{-1} are characteristic of the stretching vibration of NO_2 , which indicates that the nitro groups don't coordinate with the metal center. In conclusion, the IR spectrum of complex **1** is in agreement with the X-ray crystal structural analysis.

Fig. 4. Schematic description of the 2D topology of **1**

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