

Synthesis, Structure and Physical Properties of A Novel 2D Cd(II) Coordination Polymer Involving 4-Thiopyridine Based on *in situ* Formation from 4,4'-Dithiodipyridine

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Exploratory synthesis of coordination polymer remains intensely active not only owing to their diverse topology and intriguing structures but also because of these materials' capabilities in industrially relevant applications such as ion-exchange, heterogeneous catalysts, optical devices, magnets, and gas storage.¹⁻⁶ It is well known that the organic ligand is the key factor that influences the construction of coordination polymer. Recently, the *in situ* ligand synthesis as a new approach to prepare coordination polymers are of great interest. *In situ* hydrothermal reactions usually not only provide products that are inaccessible or not easily obtainable by conventional methods, but also help discover the mechanism of some kinds of organic reactions.

Up to now, varieties of *in situ* ligand syntheses have been reported, including cleavage and formation of disulfide bonds, the formation of tetrazole rings, the formation of carbon-carbon bond by reductive or oxidative reaction, and the hydrolysis of carboxylate esters *etc.*⁷⁻¹¹ However, to our knowledge, the investigations on the cleavage of disulfide bonds are limited.¹²⁻¹⁴ Herein, we report the solvothermal cleavage of S-S bonds for 4,4'-dithiodipyridine (4-dtdp) and the formation of a new cadmium(II) coordination polymer [Cd₂(odpa)(4-pytH)₂·H₂O]_n (**1**) (4-pyt = 4-thiopyridine, H₄odpa = 4,4'-oxydiphthalic acid). In addition, the thermogravimetric analysis and photoluminescent property of the complex **1** have been investigated in detail.

As shown in Figure 1, complex **1** crystallizes in the centrosymmetric monoclinic space group *C2/c* with an asymmetric unit consisting of two crystallographically independent divalent cadmium ions (Cd1, Cd2), one-half of a fully deprotonated H₄odpa ligand situated across an inversion center and a intact 4-pytH ligand, along with half of an aqua ligand. Cd1 possesses a distorted {CdO₄S₂} octahedral coordination environment, with two S atoms from two different 4-pytH ligands and chelating carboxylate groups from two different odpa⁴⁻ ligands (Cd1-O1 = 2.444(3), Cd1-O1ⁱ = 2.444(3), Cd1-O2 = 2.368(2), Cd1-O2ⁱ = 2.368(2), Cd1-S1 = 2.5372(9), Cd1-S1ⁱ = 2.5372(9)) [symmetry codes: (i) -x, y, 0.5-z]. In contrast, Cd2 displays a distorted {CdO₇} pentagonal bipyramidal geometry, with the axial positions taken up by two oxygen donor atoms from monodentate carboxylate groups belonging to two different odpa⁴⁻ ligands

and the equatorial plane filled by an aqua ligand and four oxygen atom donors from four chelating carboxylate groups from four different odpa⁴⁻ ligands (Cd2-O2 = 2.418(2), Cd2-O2ⁱ = 2.418(2), Cd2-O3 = 2.507(2), Cd2-O3ⁱ = 2.507(2), Cd2-O4ⁱⁱ = 2.171(2), Cd2-O4ⁱⁱⁱ = 2.171(2), Cd2-O6 = 2.501(4)) [symmetry codes: (i) -x, y, 0.5-z; (ii) x, -y, z-1/2; (iii) -x, -y, -z+1].

As to the odpa⁴⁻ anion, the phenyl rings are not coplanar, with a dihedral angle of 75.1° and the carboxylate groups at the O1 and O3 positions make dihedral angles of 6.8° and 87.2°, respectively, relative to the plane of the linking phenyl ring. In complex **1**, the odpa⁴⁻ ligand adopts a μ₆-bridging mode with two of the four carboxylate groups in a μ₂-η²: η¹-

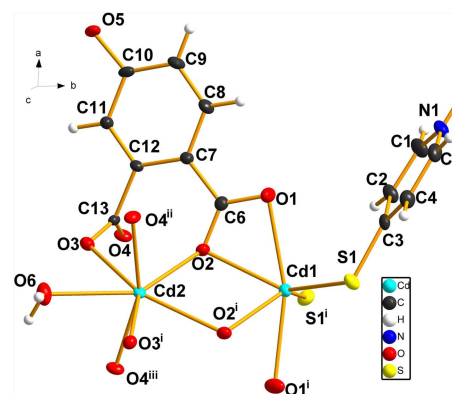
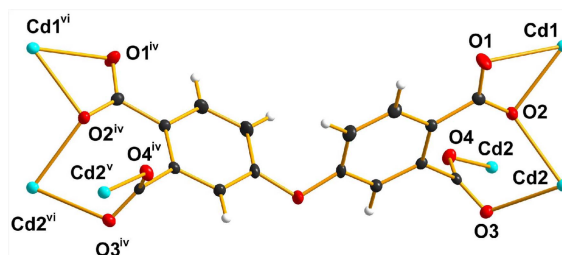


Figure 1. ORTEP view of asymmetric unit for complex **1**, displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Symmetry codes: i -x, y, 0.5-z; ii x, -y, z-1/2; iii -x, -y, -z+1.



Scheme 1. View of the coordination mode of odpa⁴⁻ ligand in complex **1**. Symmetry codes: iv 1-x, y, 1.5-z; v 1-x, -y, 1-z; vi 1+x, y, z+1.

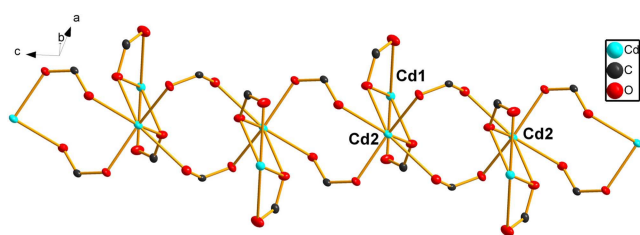


Figure 2. View of 1D infinite inorganic chain in complex 1.

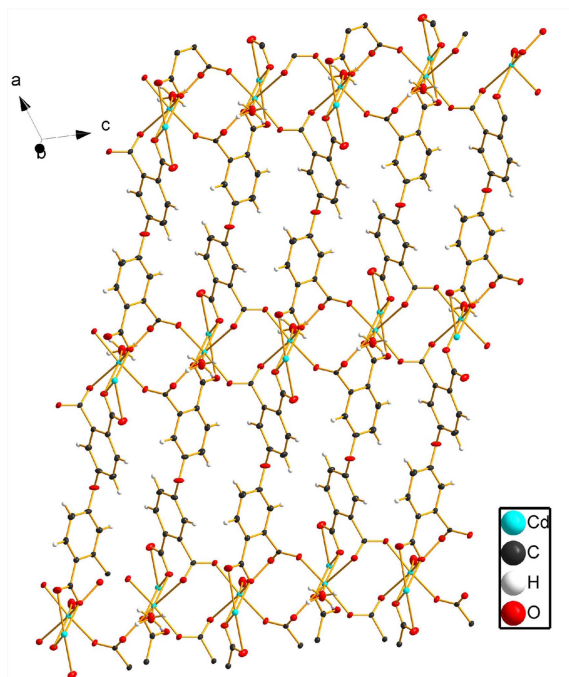
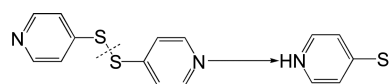


Figure 3. View of $[\text{Cd}_2(\text{odpa})]_n$ layer in complex 1.

bridging mode and the other in a $\mu_2\text{-}\eta^1$: η^1 bridging mode with a *syn-syn* conformation, respectively (Scheme 1). The Cd1 and Cd2 are connected by two different bridging carboxylate groups to give a $\text{Cd1}(\text{OCO})_2\text{Cd2}$ bimetallic subunit with a $\text{Cd1}\cdots\text{Cd2}$ distance of 3.8206(7) Å. Furthermore, Cd2 atoms in such subunits are bridged through $\mu_2\text{-}\eta^1$: η^1 -bridging carboxylate groups to generate a 1D infinite inorganic chain along the *c* axis with a $\text{Cd2}\cdots\text{Cd2}$ distance of 4.7156(9) Å (Figure 2). These rod-shaped chains are further connected together by the odpa ligands, giving rise to the final 2D framework (Figure 3).

The 4-pyH ligand, generated from the S-S cleavage of the 4-dtdp ligand and then protonated in an acidic environment, links one Cd1 ion through its S atom (Scheme 2). The 4-pyH ligands are arranged up and down the layers (Figure 4) and link the adjacent layers to a 3D supermolecular framework by hydrogen bonds ($\text{N1}\cdots\text{O3} = 2.845(5)$ Å, $\text{N1-H}\cdots\text{O3} = 150(6)^\circ$ and $\text{N1}\cdots\text{O6} = 3.229(4)$ Å, $\text{N1-H}\cdots\text{O6} = 133(5)^\circ$).

A further insight into the nature of this intricate framework can be acquired by using topological analysis. A topological analysis of this net was performed with TOPOS software.¹⁵ From the topological point of view, if the bi-



Scheme 2. Schematic representation of *in situ* ligand synthesis from the 4,4'-dithiodipyridine under hydrothermal conditions.

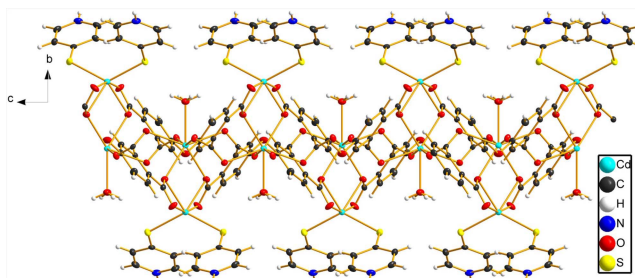


Figure 4. View of $[\text{Cd}_2(\text{odpa})(4\text{-pyH})_2\cdot\text{H}_2\text{O}]_n$ layer in complex 1.

nuclear motifs and odpa ligands are considered as 4-connected nodes, the whole 2D framework can be simplified as a 4-connected net with the (4, 4) topology.

Thermogravimetric analysis of **1** (Figure 5) demonstrates that a weight loss of 2.40% in 120–190 °C corresponds to the release of half of an aqua ligand (calculated 2.23%) for complex **1**. The organic ligands began to decompose at 280 °C, with the 31.70% mass remnant at 840 °C consistent with production of CdO (31.81% calcd).

The photoluminescent property of complex **1** have been studied in the solid state at room temperature. The free ligands show the emission maximum at 406 nm for H_2odpa (excitation at 354 nm), which may be caused by the $\pi^*\text{-n}$ or $\pi^*\text{-}\pi$ transition.¹⁶ Irradiation of complex **1** with ultraviolet light ($\lambda_{\text{ex}} = 310$ nm) in the solid state resulted in a relatively broad emission band centered on ~ 360 nm (Figure 6). According to a recent review of d^{10} metal coordination polymer luminescence, the Cd(II) ions are difficult to oxidize and reduce. As a result, the emissive behavior of **1** can be attributed to ligand-centered electronic transitions.¹⁷

In conclusion, we have successfully synthesized a new cadmium(II) coordination polymer based on *in situ* formed

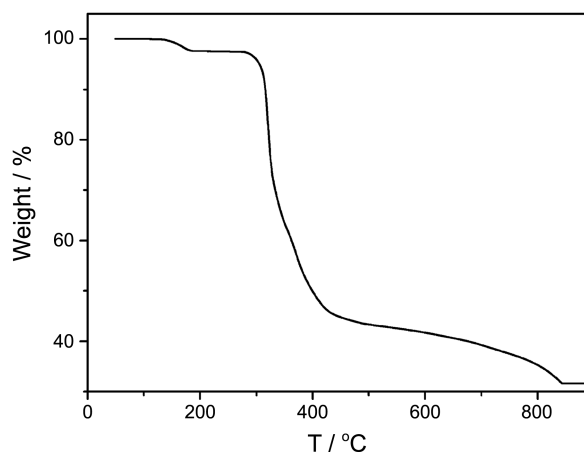


Figure 5. Thermogravimetric curve of complex **1**.

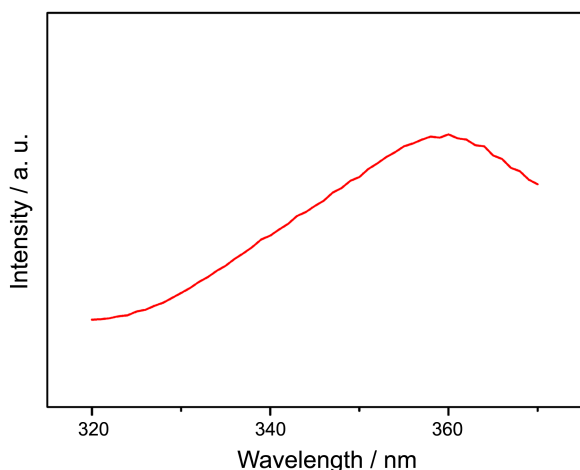


Figure 6. The solid-state emission spectrum of complex **1** recorded at room temperature.

Table 1. Crystal and experimental data of **1**

Empirical formula	$C_{26}H_{18}Cd_2N_{10}O_{10}S_2$
Formula weight	807.38
Crystal system	Monoclinic
Space group	$C2/c$
$a / \text{\AA}$	14.517(3)
$b / \text{\AA}$	20.069(4)
$c / \text{\AA}$	9.4241(18)
$\beta / ^\circ$	108.434(3)
$V / \text{\AA}^3$	2604.8(9)
$D_{\text{calc}} / \text{g}\cdot\text{cm}^{-3}$	2.059
F(000)	1584
Limits of data collection / $^\circ$	$2.51 \leq \theta \leq 26.99$
Reflections collected	7419
Independent reflections (R_{int})	2843 (0.0603)
Goodness of fit	1.032
R indices ($I > 2\sigma(I)$)	$R_1 = 0.0365, wR_2 = 0.1053$
R indices (all data)	$R_1 = 0.0379, wR_2 = 0.1067$

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]^{1/2}}$$

4-pytH ligand from 4,4'-dithiodipyridine under hydrothermal conditions, which is characterized by IR, elemental analysis, thermal analysis and single-crystal X-ray diffraction. The crystal structure of complex **1** shows a novel two-dimensional framework with 4-connected (4, 4) topology. In addition, complex **1** exhibits strong fluorescent emissions in the solid state at room temperature.

Experimental

General. All reagents and solvents were commercial available and used without further purification. Infrared spectrum was recorded on a VECTOR 22 spectrometer, over the range 4000–400 cm^{-1} , using KBr pellet. Elemental analysis data (C, H, N) were obtained using a Perkin-Elmer model 240C automatic instrument. The luminescence spectrum was obtained with a Fluoro Max-P spectrophotometer on solid crystalline samples anchored to quartz microscope

Table 2. Selected bond distances (\AA) and angles ($^\circ$) for **1**

Cd(1)-O(1)	2.444(3)	Cd(1)-O(2)	2.368(2)
Cd(1)-S(1)	2.5372(9)	Cd(1)-O(1) ⁱ	2.444(3)
Cd(1)-O(2) ⁱ	2.368(2)	Cd(1)-S(1) ⁱ	2.5372(9)
Cd(2)-O(2)	2.418(2)	Cd(2)-O(3)	2.507(2)
Cd(2)-O(6)	2.501(4)	Cd(2)-O(3) ⁱ	2.507(2)
Cd(2)-O(2) ⁱ	2.418(2)	Cd(2)-O(4) ⁱⁱ	2.171(2)
O(1) ⁱ -Cd(1)-O(1)	163.0(2)	O(1)-Cd(1)-S(1)	93.43(6)
O(1)-Cd(1)-S(1) ⁱ	94.25(8)	O(1) ⁱ -Cd(1)-S(1)	94.25(8)
O(1) ⁱ -Cd(1)-S(1) ⁱ	93.43(6)	O(2)-Cd(1)-O(1)	54.02(9)
O(2)-Cd(1)-O(1) ⁱ	110.7(2)	O(2)-Cd(1)-S(1)	133.99(7)
O(2)-Cd(1)-S(1) ⁱ	91.34(7)	O(2) ⁱ -Cd(1)-O(1)	110.7(2)
O(2) ⁱ -Cd(1)-O(1) ⁱ	54.02(9)	O(2) ⁱ -Cd(1)-O(2)	75.0(2)
O(2) ⁱ -Cd(1)-S(1)	91.34(7)	O(2) ⁱ -Cd(1)-S(1) ⁱ	133.99(7)
S(1) ⁱ -Cd(1)-S(1)	126.21(5)	O(2)-Cd(2)-O(3)	73.41(8)
O(2)-Cd(2)-O(6)	143.42(6)	O(2)-Cd(2)-O(3) ⁱ	143.47(8)
O(2)-Cd(2)-O(2) ⁱ	73.2(2)	O(2) ⁱ -Cd(2)-O(3)	143.47(8)
O(2) ⁱ -Cd(2)-O(6)	143.42(6)	O(2) ⁱ -Cd(2)-O(3) ⁱ	73.41(8)
O(3) ⁱ -Cd(2)-O(3)	142.4(2)	O(4) ⁱⁱ -Cd(2)-O(2)	87.09(9)
O(4) ⁱⁱ -Cd(2)-O(3)	81.80(8)	O(4) ⁱⁱ -Cd(2)-O(6)	79.14(7)
O(4) ⁱⁱ -Cd(2)-O(2) ⁱ	110.70(9)	O(4) ⁱⁱ -Cd(2)-O(3) ⁱ	91.21(9)
O(4) ⁱⁱ -Cd(2)-O(4) ⁱⁱⁱ	158.3(2)	O(4) ⁱⁱⁱ -Cd(2)-O(2)	110.70(9)
O(4) ⁱⁱⁱ -Cd(2)-O(3)	91.21(9)	O(4) ⁱⁱⁱ -Cd(2)-O(6)	79.14(7)
O(4) ⁱⁱⁱ -Cd(2)-O(2) ⁱ	87.09(9)	O(4) ⁱⁱⁱ -Cd(2)-O(3) ⁱ	81.80(8)
O(6)-Cd(2)-O(3)	71.18(5)	O(6)-Cd(2)-O(3) ⁱ	71.18(5)

Symmetry transformations used to generate equivalent atoms: i $-x, y, -z+1/2$, ii $x, -y, z-1/2$, iii $-x, -y, -z+1$.

slides. Thermogravimetric analysis (TGA) was performed under flowing N_2 on a Perkin-Elmer Pyris 1 TGA analyzer with a heating rate of 20 $^\circ\text{C min}^{-1}$ up to 900 $^\circ\text{C}$.

Synthesis of $[\text{Cd}_2(\text{odpa})(4\text{-pytH})_2\cdot\text{H}_2\text{O}]_n$ (1**).** A mixture of $\text{Cd}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.0346 g, 0.100 mmol), H_4odpa (0.0346 g, 0.100 mmol) and 4-dtdp (0.0441 g, 0.200 mmol) in H_2O (10 mL) was sealed in a 16 mL Teflon-lined stainless steel container and heated at 180 $^\circ\text{C}$ for 72 h. After cooling to room temperature, colorless block crystals were collected by filtration and washed by water and ethanol several times. (yield 41.2%, based on H_4odpa). Elemental analysis for $\text{C}_{26}\text{H}_{18}\text{Cd}_2\text{N}_{10}\text{O}_{10}\text{S}_2$ ($M_r = 807.38$): C 38.68%, N 3.47%, H 2.25%; found: C 38.79%, N 3.48%, H 2.26%. IR (KBr pellets)/ cm^{-1} : 3539 (m), 3199 (m), 3119 (m), 2356 (w), 1680 (m), 1577 (s), 1526 (s), 1420 (s), 1379 (s), 1259 (s), 1171 (s), 1142 (m), 987 (s), 855 (s), 722 (s), 476 (w).

Structural Determination and Refinement. Crystallographic diffraction data for complex **1** was recorded on a Siemens (Bruker) SMART CCD diffractometer using monochromated Mo-K α radiation ($\lambda = 0.71073 \text{\AA}$) at 291 K. Absorption correction was applied using multi-scan technique. The structure was solved by direct method using the program SHELXL-97 and refined by full-matrix least-squares technique on F^2 with SHELXL-97.¹⁸ All non-hydrogen atoms were located in difference Fourier maps and refined with anisotropic temperature parameters. The H atom of N(pyridine) atom was located in a difference Fourier map. All other H atoms were refined isotropically, with the

isotropic vibration parameters related to the non-H atom to which they are bonded. A summary of the structural determination and refinement for the title complex is listed in Table 1 and the selected bond distances and angles are shown in Table 2.

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Supporting Information. CCDC-987017 (1) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Telephone: (44) 01223 762910; Facsimile: (44) 01223 336033; E-mail: deposit@ccdc.cam.ac.uk].

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