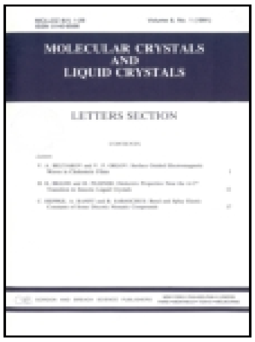

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Self-assembly of a Cd(II) coordination polymer with the 3,5L2 topology: Synthesis, structure, and properties

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ABSTRACT

A new cadmium(II) coordination polymer, $[Cd(ntdc)(dps)\cdot H_2O]_n$, was synthesized using 3-nitro-thiophene-2,5-dicarboxylic acid (H_2ntdc) and 4,4′-dipyridylsulfide (dps) as organic linkers. In the complex, adjacent Cd^{2+} ions are linked by $ntdc^{2-}$ anions adopting a new coordination mode to form a one-dimensional (1D) $[Cd(ntdc)]_n$ chain. Then dps ligands further expand the 1D chain into a corrugated two-dimensional (2D) layer network by linking neighboring Cd^{2+} ions. Topologically, the 2D network can be rationalized to a 3,5-connected 3,5L2 topology. Moreover, solid state properties such as thermogravimetric analysis and photoluminescent property were also investigated.

KEYWORDS

Cd(II) coordination polymer; crystal structure; 3-nitro-thiophene-2,5-dicarboxylic acid; 4,4′-dipyridylsulfide

Introduction

As a flourishing research field, the design and controlled assembly of coordination polymers (CPs) has attracted intensive attention both experimentally and theoretically, due to their intriguing crystalline architectures and potential applications as functional materials [1–6]. However, it remains a fundamental challenge to obtain the preferred structures with specific properties owing to many factors can influence the assembly of CPs. Generally, the coordination sites of organic ligands are closely related to the final structure of CPs, and so far, extensive work has been carried out using various organic ligands with certain features to construct high-dimensional CPs [7–9]. Among them, thiophene-based dicarboxylates linkers, such as thiophene-2,5-dicarboxylic acid, thiophene-3,4-dicarboxylic acid, and thiophene-2,3-dicarboxylic acid have been extensively employed in the construction of a rich variety of CPs with fascinating structures and potential applications [10–15].

As we know, the substituent groups in the organic ligand have significant effects on the resulting structure of CPs. From a structural point of view, the thiophene-2,5-dicarboxylic acid derivative, 3-nitro-thiophene-2,5-dicarboxylic acid (H_2ntdc) with multiple carboxylate oxygen coordination sites, steric hindrance, and electronic property is a multidentate bridging ligand on one hand. One the other hand, deprotoned H_2ntdc may act as anions when coordinating to metal ions, and thus achieve charge balance without other anions as NO_3^- or Cl^-

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Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center with registration number CCDC 1409174 (**1**). Copies of this information 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; fax: (+44) 1223-336-033.

involved in the structure. Both of these two features may increase the opportunity for novel structures and interesting properties to some extent. Recently, by employment of the H_2ntdc ligand and structurally related bis(imidazole) ligands, we have obtained four cadmium CPs and experimental results indicate H_2ntdc is an effective building block in constructing CPs with diverse architectures [16]. It is worth mentioning that the flexible bis(imidazole) ligands with excellent coordinating ability and variable conformations also play a role in regulating the structures of CPs with the H_2ntdc ligand [17–19]. As our continuous work, we attempted to synthesize CPs by varying *N*-donor ancillary ligands and further understand the coordination chemistry of the H_2ntdc ligand.

Here, we report the synthesis and crystal structure of a new compound derived from H_2ntdc and 4,4-dipyridylsulfide (dps) coligand. Furthermore, the structure stability and photoluminescent property of the complex were also discussed.

Experimental

Materials and physical measurements

H_2ntdc was prepared according to the literature procedure [16]. Other reagents were obtained commercially and used without further purification. The reaction was performed in a 15 mL Pyrex glass tube under autogenous pressure. Elemental analyses for C, H, and N were carried out on a Flash 2000 elemental analyzer. The IR spectra were recorded as KBr pellets on a Nicolet Avatar-360 spectrometer in the range of 4000–400 cm^{-1}. Thermogravimetric analyses (TGA) were carried out on a SDTQ600 thermogravimetric analyzer. A platinum pan was used for heating the sample with a heating rate of 10°C/min under a N_2 atmosphere. Fluorescence measurements were recorded with a Hitachi F4500 fluorescence spectrophotometer.

Synthesis of the compound $[Cd(ntdc)(dps)\cdot H_2O]_n$(1)

A mixture of $Cd(OAc)_2\cdot 2H_2O$ (26.7 mg, 0.1 mmol), H_2ntdc (21.7 mg, 0.1 mmol), dps (18.8 mg, 0.1 mmol), NaOH (4.00 mg, 0.1 mmol), and 7 mL deionized water was sealed in a 20-mL Pyrex glass tube and heated at 60°C for 72 h, followed by cooling to room temperature at a rate of 5°C h^{-1}. Colourless crystals were collected (yield: 32% based on Cd). Elemental analysis calcd (%) for $C_{16}H_{11}N_3O_7S_2Cd$: C, 36.02; H, 2.06; N, 7.87. Found: C, 35.92; H, 2.10; N, 7.90. IR (cm^{-1}): 3509(m), 1590(m), 1579(s), 1539(m), 1514(m), 1479(m), 1345(vs), 1312(m), 1221(w), 1135(m), 1100(w), 1091(w), 1065(w), 1051(w), 1009(m), 964(m), 898(w), 864(m), 823(s), 769(w), 756(s), 749(s), 736(w), 711(m), 690(m), 679(m).

Crystallographic data collection and refinement

The structure of **1** was determined by the single-crystal X-ray diffraction technique. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer with Mo-Ka radiation (ÿ = 0.71073 Å) at 293 K. Data reduction and absorption correction were made with SADABS software [20]. The structure was solved by direct methods with SHELXS-97 program [21] and refined with SHELXL-97 [22] by full-matrix least-squares techniques on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms on water molecules were located from difference Fourier maps and were refined using riding model. Other hydrogen atoms were placed at the calculation positions. A summary

Table 1. Crystallographic data.

Empirical formula	$C_{16}H_{11}N_3O_7S_2Cd$
Formula weight	533.80
Crystal system	Monoclinic
Space group	*P*2(1)/*c*
Unit cell dimensions	$a = 11.1535(16)$ (Å), $b = 6.7675(10)$ (Å), $c = 27.000(4)$ (Å), $\beta = 113.716(5)$ °
Volume (Å^3), Z	1865.9(5), 4
Calculated density (Kg/m^3)	1.900
μ(mm^{-1})	1.441
Reflections collected/unique	9520/3466
F(000)	1056
R (int)	0.0315
GOF on F^2	1.151
Final *R* indices [$I > 2\sigma\ (I)$]	$R_1 = 0.0319$, $wR_2 = 0.0841$
Final *R* indices (all data)	$R_1 = 0.0462$, $wR_2 = 0.1150$
Largest residuals (e Å^{-3})	0.959 / −0.694

Table 2. Selected bond lengths (Å) and bond angles (°) for **1**. (Symmetry code for **1**: #1 $-x+1, -y, -z+2$; #2 $x, y+1, z$; #3 $x-1, y, z$).

Cd(1)—O(5)	2.246(4)	Cd(1)—O(3)#1	2.273(4)	Cd(1)—O(2)#2	2.321(4)
Cd(1)—N(2)#3	2.330(4)	Cd(1)—N(1)	2.342(4)	Cd(1)—O(1)	2.371(4)
O(3)#1—Cd(1)—O(2)#2	92.54(14)	O(5)—Cd(1)—N(2)#3	91.63(16)	O(3)#1—Cd(1)—N(2)#3	171.19(13)
O(2)#2—Cd(1)—N(2)#3	85.18(14)	O(5)—Cd(1)—N(1)	164.99(16)	O(3)#1—Cd(1)—N(1)	86.01(13)
O(2)#2—Cd(1)—N(1)	92.94(13)	N(2)#3—Cd(1)—N(1)	102.59(14)	O(5)—Cd(1)—O(1)	86.65(15)
O(3)#1—Cd(1)—O(1)	97.49(13)	O(2)#2—Cd(1)—O(1)	169.74(13)	N(2)#3—Cd(1)—O(1)	84.58(14)
N(1)—Cd(1)—O(1)	89.91(12)				

of the crystallographic data, selected bond lengths and of **1** is listed in Table 1 and Table 2, respectively.

Results and discussion

Complex **1** is a corrugated 2D coordination polymer. Single crystal X-ray structural analysis exhibits that **1** crystallizes in the monoclinic system with a space group of *P*2(1)/c. As shown in Fig. 1, the asymmetric unit has one crystallographically independent Cd^{2+} ion, one ntdc^{2-} anion, one dps ligand as well as one coordinated water molecule. The Cd^{2+} ion is six-coordinated with four O atoms and two N atoms, constructing a distorted octahedral coordination geometry with three carboxylate O atoms from three individual ntdc^{2-} anions, one O

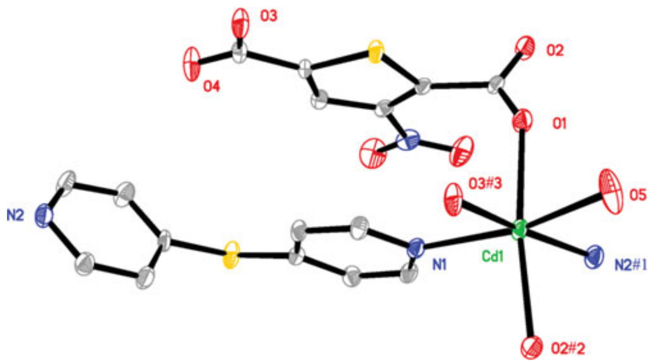
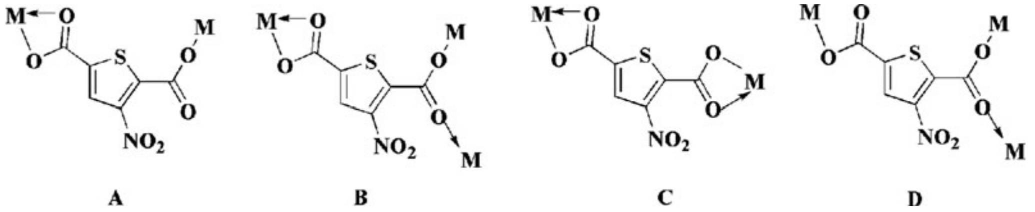


Figure 1. View of the Cd^{2+} ion coordination environment in **1**. (Symmetry codes: #1 $x-1, y, z$; #2 $x, 1+y, z$; #3 $1-x, -y, 2-z$)



Scheme 1. The coordination modes of ntdc^{2-} anions.

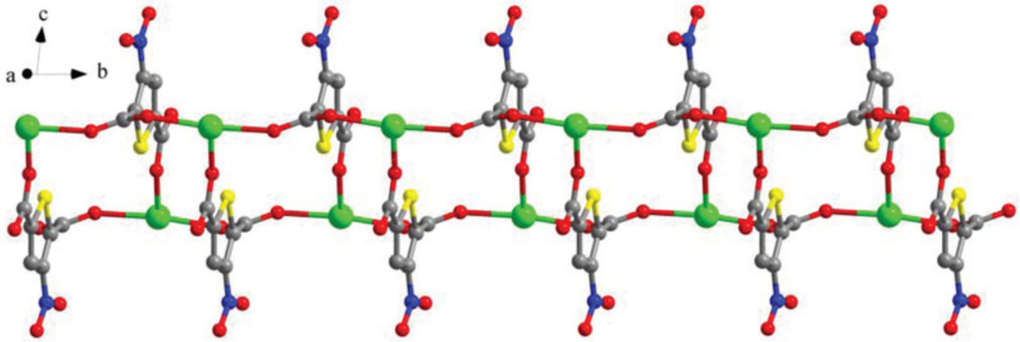


Figure 2. View of the 1D double chain of **1**, linked *via* bridging ntdc^{2-} ligands.

atom of one coordinated water molecule, and two N atoms from two individual dps ligands. The lengths of Cd—O bonds range from 2.246(4) to 2.371(4) Å, the Cd—N bonds vary from 2.330(4) to 2.342(4) Å, which are within the normal ranges in other Cd^{2+} complexes [23–24]. Scheme 1 shows the different coordination modes observed for ntdc^{2-} anions; modes A, B, and C were reported previously, and coordination mode D has been found for the first time in Compound **1**. Each ntdc^{2-} anion in **1** adopts the μ_3-(η^1,η^1)-(η^1) coordination mode, linking adjacent Cd^{2+} ions to yield a one-dimensional (1D) $[Cd(ntdc)]_n$ structure along the *b*-axis (Fig. 2). The dihedral angle between two coordinated carboxylates is 67.407°. Then, flexible dps ligands further expand the 1D chain into a corrugated two-dimensional (2D) network by linking neighboring Cd^{2+} ions (Fig. 3a). In topology, the structure manifests a 3,5-connected 3,5L2 topology with a point symbol of $\{4^2.6^7.8\}\{4^2.6\}$ regarding ntdc^{2-} anions as 3-connected nodes and Cd^{2+} ions as 5-connected linkers. Notably, analysis of the crystal structure of **1** indicates that there are two kinds of intramolecular hydrogen bonds (Fig. 4). The coordinated water molecule acts as H-donors and offers two hydrogen atoms (H1W and

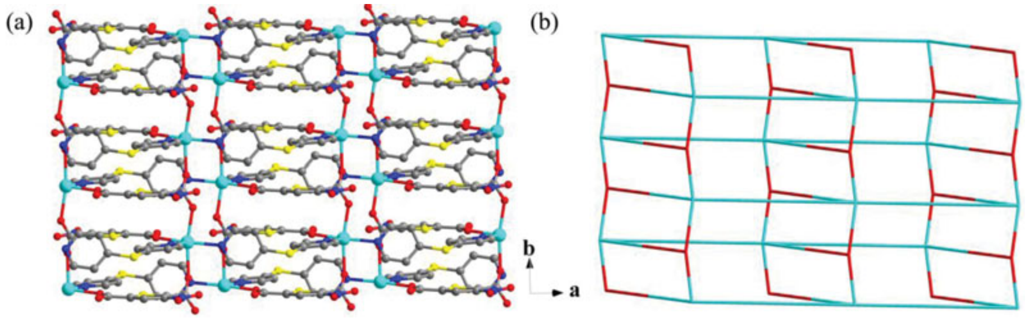


Figure 3. (a) View of the 2D network of **1**, extending in the *bc* plane. H atoms have been omitted for clarity and (b) view of the topological structure of **1**.

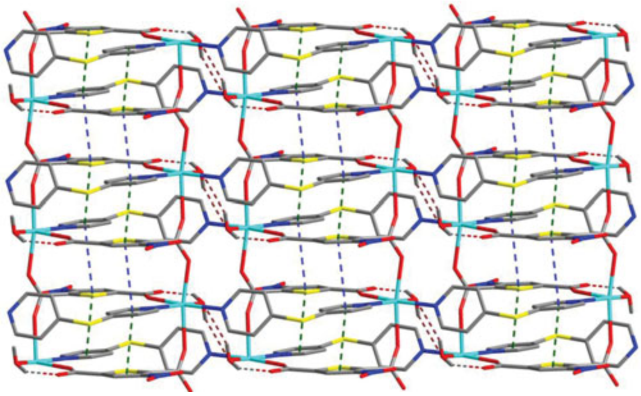


Figure 4. View of intramolecular hydrogen bonds (dark red dotted lines) and $\pi\cdots\pi$ (green or blue dotted lines) interactions. All H atoms except those related to H-bonding interactions have been omitted for clarity.

H2W) to H-acceptors of the ntdc^{2-} anions (O4) and the coordinated water molecule (O5). Moreover, it deserves to point out that the 2D framework is further stabilized by two types of $\pi\cdots\pi$ *s*tacking interactions between the pyridyl rings of dps ligands and ntdc^{2-} anions moiety, which are confirmed by the centroid-to-centroid distances of 3.800(2) and 3.815(6) Å, respectively, as calculated by the PLATON program.

In order to check the bulk purity of **1**, powder X-ray diffraction (PXRD) technique has been measured and compared with the simulated from the single-crystal structure. The measured PXRD pattern is in good accord with the result simulated from the respective single-crystal data, indicative of pure product (Fig. 5a). The differences in intensity may be owing to the variation in the preferred orientation of the powder sample. At room temperature, **1** is air-stable and insoluble in common solvents such as water, acetone, methanol, ethanol, acetonitrile, toluene, and *N, N*-dimethylformamide. In the IR spectra of **1**, the broad medium intensity bands from about 3509 cm^{-1} could be assigned to the lattice water molecules. The characteristic stretching vibrations of the carboxylate groups, of which the absorbance peaks in the range of 1539∼1579 cm^{-1} and 1312∼1514 cm^{-1} are attributed to the asymmetric stretching and symmetric stretching, respectively. The absence of bands at the region of 1675∼1710 cm^{-1} suggests the complete deprotonation of carboxylate groups in H_2ntdc, which are in agreement with the crystallographic structural analysis. Thermal property of **1** was investigated by TGA experiments. The TGA curve of **1** suggests that the first weight loss of 3.41% occurs

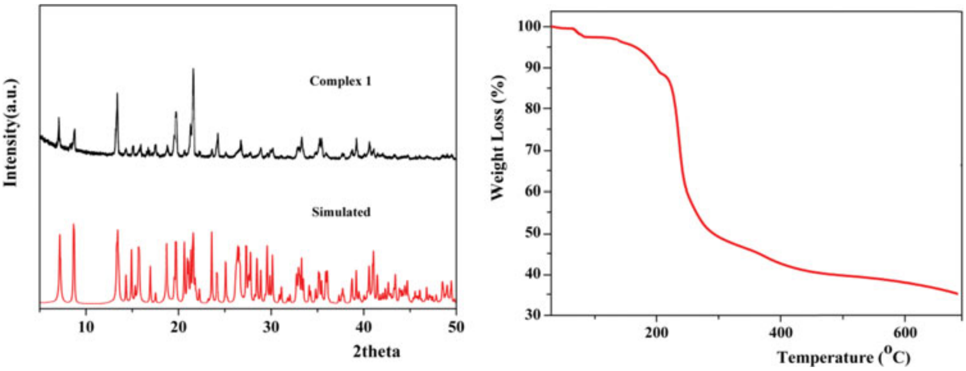


Figure 5. PXRD patterns of **1** simulated from X-ray single-crystal diffraction data and experimental data (left) and TGA curve for **1** (right).

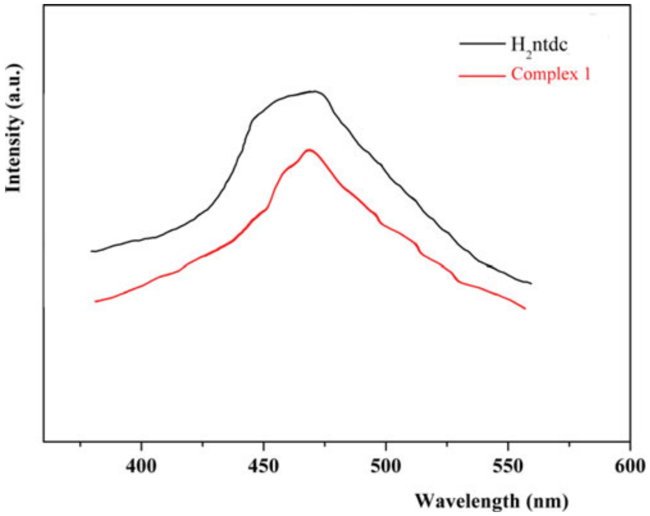


Figure 6. Solid-state emission spectrum of **1**.

between 45 and 72°C, which corresponds to the expulsion of one lattice water molecule (calculated: 3.37%). The main framework keeps stable up to 115°C followed by the weight loss, which is attributed to the decomposition of the framework (Fig. 5b).

At present, luminescent CPs are of great interest due to their various applications in photochemistry and chemical sensors. Therefore, the solid-state photoluminescent spectra of complex **1**, H_2ntdc and free dps ligand were investigated. The free ligand H_2ntdc displays an emission maximum at 474 nm when excited at 300 nm, which may be attributed to the $\pi * \rightarrow \pi$ or $\pi * \rightarrow n$ transition within the ligand. While, almost no luminescence was detected for dps ligand at room temperature, As shown in Fig. 6, the main emission peaks of **1** was observed at 469 nm (λ_{ex} =330 nm). It is well known that the Cd^{2+} ion is difficult to oxidize or reduce due to the d^{10} configuration. As a result, the emission of **1** is neither ligand-to-metal charge transfer nor metal-to-ligand charge transfer in nature. According to the literatures and our experiments, it could be assigned to a characteristic of intraligand charge transition [25–26].

Conclusion

In summary, a new Cd(II) coordination polymer based on H_2ntdc and dps mixed ligands has been successfully synthesized. In the compound, Cd^{2+} ions are connected together by H_2ntdc and dps ligands to get a 2D network with 3,5-connected 3,5L2 topology. Furthermore, luminescent property of the compound has also been investigated at room temperature. The result provides the modulation of ancillary ligand is an effective method for continuing to synthesize CPs constructed from H_2ntdc. We are presently exploring the other CPs constructed from H_2ntdc and studying the relationship between their structures and properties.

Acknowledgments

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