

Zhao-Peng Deng, Shan Gao,*
Li-Hua Huo and Hui ZhaoLaboratory of Functional Materials, School of
Chemistry and Materials Science, Heilongjiang
University, Harbin 150080, People's Republic
of ChinaCorrespondence e-mail:
shangao67@yahoo.com

Key indicators

Single-crystal X-ray study
 $T = 295$ K
Mean $\sigma(\text{C}-\text{C}) = 0.014$ Å
 R factor = 0.041
 wR factor = 0.168
Data-to-parameter ratio = 16.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**catena-Poly[[aquadiimidazolecadmium(II)]-
 μ -thiophene-2,5-dicarboxylato]**

The Cd^{II} atom has distorted pentagonal bipyramidal coordination geometry in the coordination polymer $[\text{Cd}(\text{TDA})(\text{Him})_2(\text{H}_2\text{O})]_n$ [where TDA^{2-} is the thiophene-2,5-dicarboxylate dianion ($\text{C}_6\text{H}_2\text{O}_4\text{S}^{2-}$) and Him is imidazole ($\text{C}_3\text{H}_4\text{N}_2$)]. The cadmium ion is bound by four carboxylate O atoms from two independent TDA^{2-} groups, two N atoms from two different imidazole ligands, and one water molecule. The carboxylate groups bind in bidentate mode to the Cd center, forming a linear chain structure such that the closest $\text{Cd}\cdots\text{Cd}$ distance is 10.577 (6) Å. The polymeric chains are connected *via* hydrogen bonds and π - π stacking interactions into a three-dimensional network.

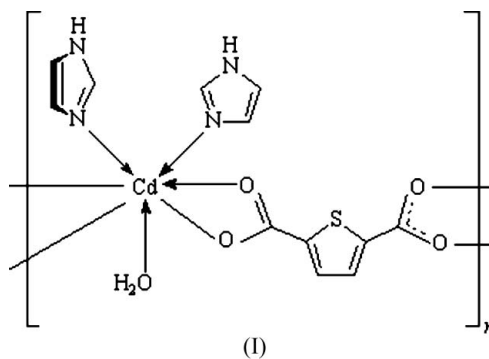
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Comment

Thiophene-2,5-dicarboxylic acid (H_2TDA) is reported to be a potential anticancer agent (Sahasrabudhe *et al.*, 1960), and additionally an excellent building block for constructing coordination polymers (Chen *et al.*, 1993). In previously studied polymers of this type, the versatile H_2TDA ligand shows a variety of binding modes to metal ions, from mono- to tetradentate (Chen *et al.*, 1998, 1999). In order to further the study of H_2TDA coordination modes, we report here the synthesis and crystal structure of the title Cd^{II} coordination polymer, $[\text{Cd}(\text{TDA})(\text{Him})_2(\text{H}_2\text{O})]_n$, (I). It was obtained by the hydrothermal reaction of cadmium dinitrate tetrahydrate, thiophene-2,5-dicarboxylic acid and imidazole (Him) in an aqueous solution.



As illustrated in Fig. 1, the asymmetric unit of (I) consists of one Cd^{II} ion, one TDA^{2-} dianion, two imidazole ligands and one coordinated water molecule. Each Cd^{II} atom is seven-coordinate and bound by four carboxylate O atoms from two independent TDA^{2-} groups, two N atoms from two different imidazole ligands, and one water molecule. The local coordination of the Cd^{II} atom can be described as distorted pentagonal bipyramidal. The equatorial pentagonal plane is

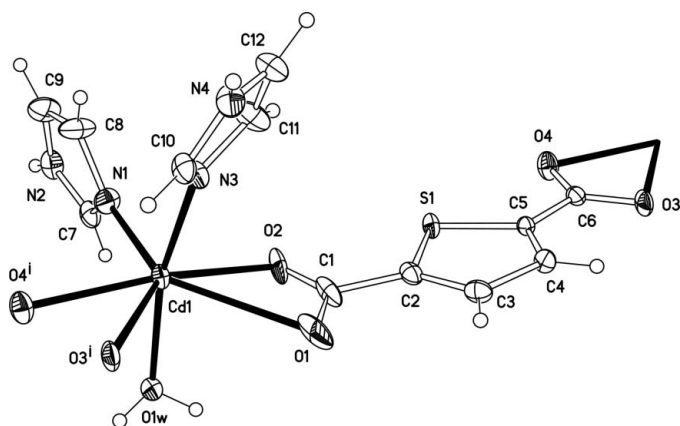


Figure 1
ORTEP plot (Johnson, 1976) of the title complex, with displacement ellipsoids drawn at the 30% probability level. [Symmetry code: (i) $x, y - 1, z$].

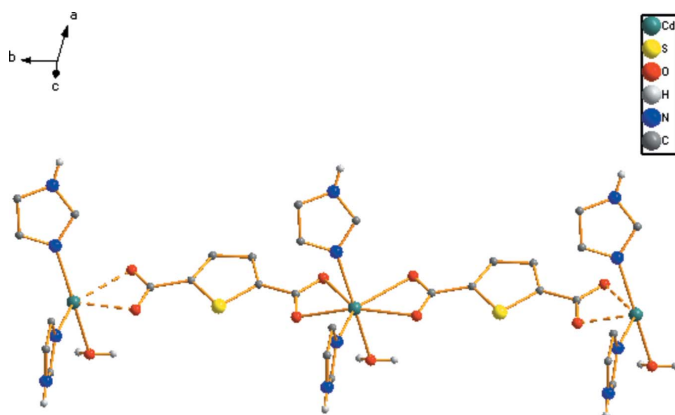


Figure 2
The linear chain structure of the title complex. H atoms attached to C atoms have been omitted.

defined by atoms O1, O2, O3ⁱ, O4ⁱ and N1 [symmetry code: (i) $x, y - 1, z$]. Atom N3 and the water molecule occupy the axial sites. The smallest O—Cd—O angle, 49.1 (3)°, is attributed to the bis-chelate coordination of the TDA²⁻ ligand that forms two four-membered rings. It should be noted that the two C—O bond distances of the carboxylate group (O3/C6/O4) are almost equivalent, and so in agreement with its delocalized state, whereas the O2—C1 distance is longer than the O1—C1 distance, in accordance with the formal double-bond character of the O1—C1 bond. The dihedral angles between the two carboxylate groups and the thiophene ring are 5.3 (4)° (O1/C1/O2) and 6.0 (4)° (O3/C6/O4), respectively, demonstrating that the TDA²⁻ ligand is basically planar.

Each TDA²⁻ group binds in bis-bidentate chelating mode to link neighboring Cd^{II} atoms to form a one-dimensional linear chain structure which is propagated parallel to the *b* axis (Fig. 2), in which the closest Cd···Cd distance is 10.577 (6) Å. Furthermore, the water and imidazole molecules form extensive intermolecular hydrogen bonds with carboxylate O atoms (Table 2). There are π - π stacking interactions between adjacent thiophene rings, the centroid-centroid separation being 3.694 (6) Å. The polymeric chains align in a manner that

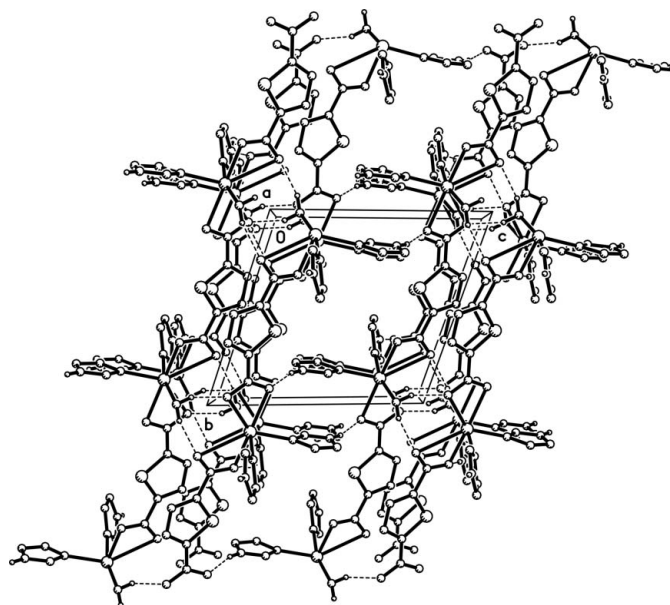


Figure 3
Packing diagram of the title complex, viewed along the *a* axis. The hydrogen bonds are shown as dashed lines. H atoms attached to C atoms have been omitted.

facilitates both hydrogen-bonding and π - π stacking interactions, leading to a three-dimensional supramolecular network (Fig. 3).

Experimental

Cadmium dinitrate tetrahydrate (3.08 g, 10 mmol) was added to an aqueous solution of thiophene-2,5-dicarboxylic acid (1.72 g, 10 mmol). The pH was adjusted to 6 with 0.1 M sodium hydroxide. Imidazole (1.34 g, 20 mmol) was then added. The mixture was stirred for 1 h and then sealed in a 50 ml Teflon-lined stainless steel bomb and held at 383 K for 3 d. The bomb was cooled naturally to room temperature, and colorless prismatic crystals of (I) were obtained. Analysis calculated for C₁₂H₁₂N₄O₅SCd: C 33.00, H 2.77, N 12.83%; found: C 32.96, H 2.74, N 12.85%.

Crystal data

[Cd(C₆H₂O₄S)(C₃H₄N₂)₂(H₂O)]
 $M_r = 436.72$
 Triclinic, $P\bar{1}$
 $a = 7.7486$ (15) Å
 $b = 10.577$ (2) Å
 $c = 10.947$ (2) Å
 $\alpha = 103.71$ (3)°
 $\beta = 101.57$ (3)°
 $\gamma = 108.43$ (3)°
 $V = 789.1$ (4) Å³

$Z = 2$
 $D_x = 1.838$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 7316 reflections
 $\theta = 3.0$ – 27.5 °
 $\mu = 1.55$ mm⁻¹
 $T = 295$ (2) K
 Prism, colorless
 0.36 × 0.24 × 0.18 mm

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\min} = 0.641$, $T_{\max} = 0.761$
 7628 measured reflections

3564 independent reflections
 2125 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.086$
 $\theta_{\max} = 27.5$ °
 $h = -9 \rightarrow 10$
 $k = -13 \rightarrow 13$
 $l = -14 \rightarrow 11$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.168$
 $S = 1.06$
 3564 reflections
 214 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0795P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.78 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -1.65 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cd1—O1 _w	2.341 (6)	Cd1—N3	2.269 (7)
Cd1—O1	2.829 (6)	O1—C1	1.227 (14)
Cd1—O2	2.318 (6)	O2—C1	1.249 (14)
Cd1—O3 ⁱ	2.503 (6)	O3—C6	1.244 (9)
Cd1—O4 ⁱ	2.413 (6)	O4—C6	1.248 (10)
Cd1—N1	2.267 (8)		
N3—Cd1—O1	80.4 (3)	O2—Cd1—O1 _w	83.2 (2)
O1 _w —Cd1—O1	86.1 (3)	N1—Cd1—O4 ⁱ	84.6 (3)
O2—Cd1—O1	49.1 (3)	N3—Cd1—O4 ⁱ	103.5 (2)
O1—Cd1—O3 ⁱ	84.4 (3)	O2—Cd1—O4 ⁱ	165.8 (2)
O1—Cd1—O4 ⁱ	136.0 (2)	O1 _w —Cd1—O4 ⁱ	84.1 (2)
O1—Cd1—N1	139.2 (2)	N1—Cd1—O3 ⁱ	136.3 (2)
N1—Cd1—N3	96.3 (3)	N3—Cd1—O3 ⁱ	86.4 (2)
N1—Cd1—O2	90.5 (3)	O2—Cd1—O3 ⁱ	133.2 (2)
N3—Cd1—O2	90.2 (2)	O1 _w —Cd1—O3 ⁱ	89.3 (2)
N1—Cd1—O1 _w	95.8 (2)	O4 ⁱ —Cd1—O3 ⁱ	52.7 (2)
N3—Cd1—O1 _w	166.2 (2)		

Symmetry code: (i) $x, y - 1, z$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1 _w —H1 _w 1 \cdots O3 ⁱⁱ	0.85 (7)	1.93 (4)	2.732 (8)	157 (8)
O1 _w —H1 _w 2 \cdots O1 ⁱⁱⁱ	0.85 (6)	1.96 (3)	2.770 (10)	160 (7)
N2—H14 \cdots O4 ^{iv}	0.86	1.92	2.758 (10)	165
N4—H15 \cdots O2 ^v	0.86	1.97	2.826 (10)	171

Symmetry codes: (ii) $-x, -y + 1, -z$; (iii) $-x, -y, -z$; (iv) $-x, -y + 1, -z + 1$; (v) $x + 1, y, z$.

The H atoms attached to C atoms and imidazole N atoms were placed in calculated positions, with C—H = 0.93 Å, N—H = 0.86 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$, and were refined with the riding-model approximation. Water H atoms were located in a difference Fourier map and refined with O—H and H \cdots H distance restraints of 0.85 (1) and 1.39 (1) Å, respectively, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The largest residual peak is 1.08 Å from the Cd atom and the deepest is hole is 0.9 Å from the same atom.

Data collection: *RAPID-AUTO* (Rigaku Corporation, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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