



NOTE

Hydrothermal Synthesis and Crystal Structure of Thiophene-2,5-dicarboxylate Cadmium(II)

S.H. Li* and W.J. Fu

College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471022, Henan Province, P.R. China

*Corresponding author: Tel/Fax: +86 379 65515113; E-mail: shihui471022@126.com

Received: 27 December 2013;

Accepted: 20 February 2014;

Published online: 10 January 2015;

AJC-16667

One new cadmium complex of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ with thiophene-2,5-dicarboxylic acid with the m.f. $\text{Cd}(\text{C}_{12}\text{H}_4\text{O}_8\text{S}_2)$ has been successfully synthesized. The compound has been characterized by X-ray single-crystal diffraction, Compound shows a one-dimensional framework. The 1D supramolecular structure is formed *via* hydrogen bonding connection.

Keywords: Coordination polymer, Crystal structure, Cadmium(II).

In recent years, the design and synthesis of novel organic-inorganic hybrid materials have provoked significant interest owing to their fascinating properties and great potential applications¹. Recently, the family of hybrid materials based on thiophene carboxylates have been synthesized under hydrothermal conditions. Herein, we report hydrothermal synthesis and crystal structure of a new hybrid material. To the best of our knowledge, this is the first example of a hybrid material constructed from thiophene-2,5-dicarboxylic acid².

All reagent and solvents employed were commercially available and used as received without further purification.

General procedure: A mixture of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.1 mmol, 0.0267 g), thiophene-2,5-dicarboxylic acid (0.50 mmol, 0.090 g) and distilled water (7 mL) was heated in a 25 mL stainless steel reactor with a Teflon liner 433 K for 2 days, followed by slow cooling to room temperature. Yellow crystals of the compound formed.

Diffraction intensity data of the single crystal of the five compounds were collected on a Bruker SMART APEXII CCD

diffractometer equipped with a graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) by using a ω -scan mode. All the structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the program SHEXL 97³. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrically calculations and their positions and thermal parameters were fixed during the structure refinement. The crystallographic data and experimental details of structural analyses for coordination polymers are summarized in Table-1. Selected bond and angle parameters are listed in Table-2. CCDC: 978132.

X-ray diffraction analysis revealed that the fundamental building unit consists of Cd(II) ion and thiophene-2,5-dicarboxylate as bridging ligands to construct a new coordination polymer. On the thiophene ring, the hydrogen atoms were assigned with $\text{Uiso}(\text{H}) = 1.2 \text{ Ueq}(\text{C})$ and included in the final refinement by using geometrical restraints, with $d(\text{C}---\text{H}) = 0.93 \text{ \AA}$. The asymmetric unit of the title structure contains one Cd(II) ion, one thiophene-2,5-dicarboxylate molecule (Fig. 1).

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE REFINEMENT SUMMARY OF $\text{Cd}(\text{C}_{12}\text{H}_4\text{O}_8\text{S}_2)$

Empirical formula	$\text{C}_{12}\text{H}_4\text{O}_8\text{S}_2\text{Cd}$	Z, Calculated density (mg/m^3)	4, 0.928
Formula weight	767.06	Absorption coefficient (mm^{-1})	0.820
Crystal system space group	Monoclinic, C2/c	F(000)	880
Unit cell dimensions	a = 14.029(7) Å b = 15.341(7) Å c = 16.463(10) Å	Limiting indices	-16 ≤ h ≤ 15 0 ≤ k ≤ 18 0 ≤ l ≤ 19
Volume (Å^3)	3240(3)	Largest diff. peak and hole ($e/\text{Å}^3$)	2.201 and -2.246
θ range for data collection	2.66 -25.50	Goodness-of-fit on F^2	1.167
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0754$; $wR_2 = 0.2267$	R indices (all data)	$R_1 = 0.0846$; $wR_2 = 0.2314$

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) OF Cd(C₁₂H₄O₈S₂)

Cd(1)-O(1)	2.314(7)	Cd(1)-O(4)#2	2.523(6)
Cd(1)-O(2)	2.479(6)	Cd(1)-O(2)#3	2.479(6)
Cd(1)-O(3)#1	2.295(7)	S(1)-C(5)	1.716(8)
O(3)#1-Cd(1)-O(3)#2	88.1(6)	O(3)#1-Cd(1)-O(2)#3	87.3(3)
O(3)#1-Cd(1)-O(1)	169.3(2)	O(3)#2-Cd(1)-O(2)#3	136.2(2)
O(3)#2-Cd(1)-O(1)	92.8(5)	O(1)-Cd(1)-O(2)#3	84.8(3)
O(1)-Cd(1)-O(1)#3	88.3(6)	O(1)#3-Cd(1)-O(2)#3	54.4(2)
O(2)#3-Cd(1)-O(2)	124.1(3)	O(3)#1-Cd(1)-O(4)#1	54.2(2)
O(1)-Cd(1)-O(4)#1	136.5(2)	O(3)#2-Cd(1)-O(4)#1	84.0(3)
O(1)#3-Cd(1)-O(4)#1	87.9(3)	O(2)#3-Cd(1)-O(4)#1	126.0(2)
O(2)-Cd(1)-O(4)#1	82.07(18)	O(4)#1-Cd(1)-O(4)#2	122.7(3)

Symmetry codes: #1 $x-1/2, y-1/2, z$; #2 $-x+1/2, y-1/2, -z+1/2$; #3 $-x, y, -z+1/2$

The cadmium atom is eight-coordinated in a distorted Polyhedron manner and four oxygen atoms (O1, O2, O3 and O4) from two thiophene-2,5-dicarboxylate molecules. The Cd-O bond lengths are 2.314(7) Å, 2.479(6) Å, 2.295(7) Å and 2.523(6) Å. Symmetry codes: #1 $x-1/2, y-1/2, z$; #2 $-x+1/2, y-1/2, -z+1/2$. The chains are further assembled by the intermolecular hydrogen bonding interaction leading to the formation of a 1D framework (Fig. 2).

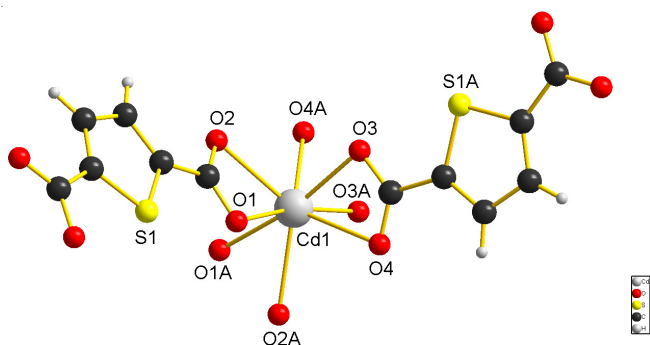


Fig. 1. Molecular structure of the Cd(C₁₂H₄O₈S₂) at 30 % probability displacement ellipsoids

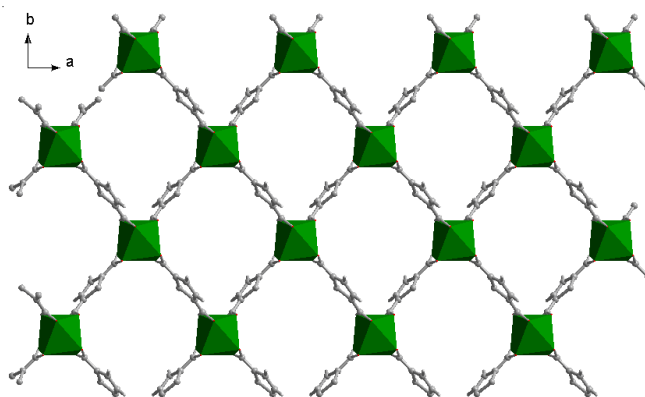


Fig. 2. 1D structure formed via hydrogen bonding interactions

REFERENCES

1. Y.C. Liang, R. Cao, W.P. Su, M.C. Hong and W.J. Zhang, *Angew. Chem. Int. Ed.*, **39**, 3304 (2000).
2. B. Zhao, P. Cheng, X.Y. Chen, C. Cheng, W. Shi, D.Z. Liao, S.P. Yan and Z.H. Jiang, *J. Am. Chem. Soc.*, **126**, 3012 (2004).
3. G.M. Sheldrick, SHELXTL97, Program for the Refinement of Crystal Structure, University of Gottingen, Germany (1997).