



NOTE

Hydrothermal Synthesis and Crystal Structure of *bis*-(2,2'-Bipyridinyl) thiophene-3,4-dicarboxylate Cadmium(II) [Cd(C₁₀H₈N₂)₂(C₆H₃O₄S)₂]

Y. ZHAO^{1*} and M. ZHU²

¹College of Physics and Electronic Information, Luoyang Normal University, Henan, P.R. China

²College of Chemistry and Chemical Engineering, Luoyang Normal University, Henan, P.R. China

*Corresponding author: Tel/Fax: +86 379 65515016, E-mail: luoyangchangchun@126.com

Received: 23 December 2013;

Accepted: 15 April 2014;

Published online: 5 June 2014;

AJC-15316

A new cadmium complex with formula Cd(C₁₀H₈N₂)₂(C₆H₃O₄S)₂ is formed by the reaction of Cd(OAc)₂·2H₂O, thiophene-3,4-dicarboxylic acid and ([2,2']bipyridinyl). 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 conditions². Herein, we report the 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-3,4-dicarboxylic acid².

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

A mixture of Cd(OAc)₂·2H₂O (0.1 mmol, 0.0267 g), thiophene-3,4-dicarboxylic acid (0.25 mmol, 0.043 g), bpp ([2,2']bipyridinyl (0.25 mmol, 0.050 g)) and distilled water (7 mL) was heated in a 25 mL stainless steel reactor with a Teflon liner 413 K for five days, followed by slow cooling to room temperature. Yellow crystals of the compound formed.

Detection method: Diffraction intensity data of the single crystal of the five compounds were collected on a Bruker SMART APEX-II CCD diffractometer equipped with a graphite monochromated MoK_α radiation (λ = 0.71073 Å) by using a ω-scan mode. All the structures were solved by direct methods and refined by full-matrix least-squares methods on F² using the program SHELXL 97³. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrical 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.

TABLE-1
CRYSTALLOGRAPHIC DATA AND STRUCTURE
REFINEMENT SUMMARY FOR Cd(II) COMPLEX

Empirical formula	C ₃₂ H ₂₂ O ₈ N ₄ CdS ₂
Formula weight	767.06
Crystal system space group	Triclinic, P-1
Unit cell dimensions	a = 7.7788(6) Å; b = 10.8548(9) Å; c = 18.8303(15) Å
Volume (Å ³)	1511.7(2)
θ range for data collection	2.74-25.50
Final R indices [I > 2σ(I)]	R ₁ = 0.0206; wR ₂ = 0.0535
Z, calculated density (mg/m ³)	2, 1.685
Absorption coefficient (mm ⁻¹)	0.921
F(000)	772
Limiting indices	-9 ≤ h ≤ 9; -13 ≤ k ≤ 13; -22 ≤ l ≤ 22
Largest diff. peak and hole (e/Å ³)	0.269 and -0.428
Goodness -of-fit on F ²	1.008
R indices (all data)	R ₁ = 0.0223; wR ₂ = 0.0547

The molecular structure of Cd(C₁₀H₈N₂)₂(C₆H₃O₄S)₂ is given in Fig. 1.

X-ray diffraction analysis revealed that the fundamental building unit consists of thiophene-3,4-di-carboxylate and bpp (bpp = [2,2']bipyridinyl) as bridging ligands to construct a new coordination polymer. The asymmetric unit of the title structure contains one Cd²⁺ ion, two thiophene-3,4-di-carboxylate

TABLE-2
SELECTED BOND LENGTHS (Å) AND
ANGLES (°) FOR Cd(II) COMPLEX

Cd(1)-O(9)	2.3375(16)	Cd(1)-N(2)	2.3972(16)
Cd(1)-O(2)	2.3681(16)	Cd(1)-N(3)	2.4192(15)
Cd(1)-N(4)	2.3967(15)	Cd(1)-N(1)	2.4306(16)
O(9)-Cd(1)-O(2)	79.86(6)	S(1)-C(4)	1.702(2)
O(9)-Cd(1)-N(4)	112.42(6)	N(4)-Cd(1)-N(3)	67.86(5)
O(2)-Cd(1)-N(4)	127.28(5)	N(2)-Cd(1)-N(3)	90.18(5)
O(9)-Cd(1)-N(2)	151.61(6)	O(9)-Cd(1)-N(1)	84.59(6)
O(2)-Cd(1)-N(2)	101.99(6)	O(2)-Cd(1)-N(1)	81.65(5)
N(4)-Cd(1)-N(2)	89.26(5)	N(4)-Cd(1)-N(1)	147.44(5)
O(9)-Cd(1)-N(3)	81.97(6)	N(2)-Cd(1)-N(1)	67.89(6)
O(2)-Cd(1)-N(3)	160.06(6)	N(3)-Cd(1)-N(1)	88.54(5)

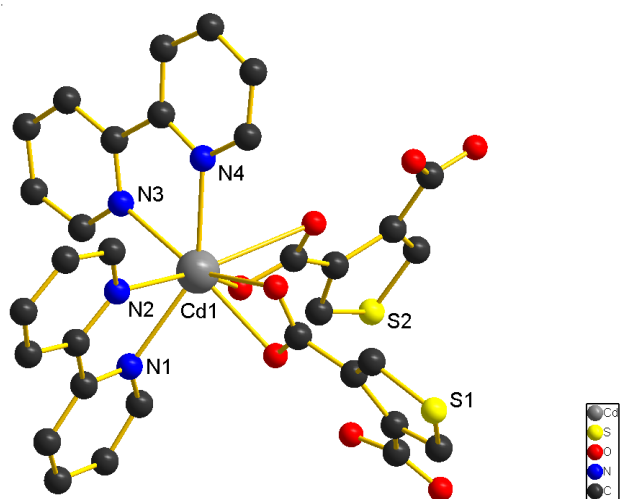


Fig. 1. Molecular structure of $\text{Cd}(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{C}_6\text{H}_3\text{O}_4)_2$ at 30% probability displacement ellipsoids

and two bpp molecules. The cadmium atom is six-coordinated in a distorted octahedral manner and four nitrogen atoms (N1, N2, N3 and N4) from two [2,2']bipyridinyl ligands (Fig. 1). The Cd-N bond lengths are 2.4306 (16) Å, 2.3972 (16) Å, 2.4192 (15) Å and 2.3967 (15) Å, respectively. and two oxygen atoms (O2 and O9) from two thiophene-3,4-di-carboxylate molecules. The Cd-O bond lengths are 2.3681 (16) Å and 2.3375 (16) Å, respectively. The chains are further assembled by the intermolecular hydrogen bonding interaction leading to the formation of a 1D framework (Fig. 2).

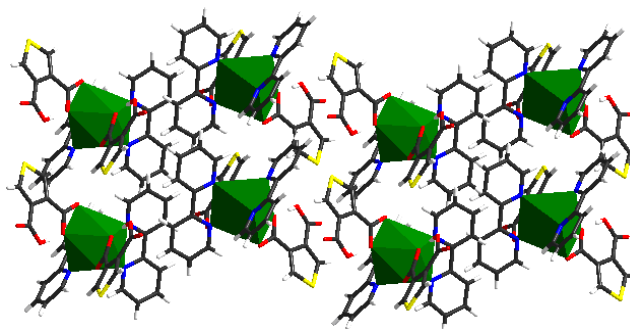


Fig. 2. 1D structure formed via hydrogen bonding interactions

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).