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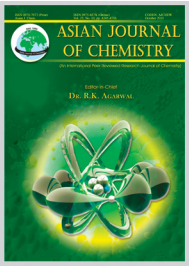

Synthesis and Crystal Structure of One-Dimensional Zig-Zag Polymer Cadmium(II): $\{[Cd(\mu\text{-}L)(NO_3)_2H_2O]_2H_2O\}_n$

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A novel 1D supramolecular complex of cadmium with molecular formula $\{[Cd(\mu\text{-}L)(NO_3)_2H_2O]_2H_2O\}_n$, was synthesized by pyridyl-pyrimidin dithioethers and $Cd(NO_3)_2$. The crystal structure of the cadmium complex, exist as the one-dimensional zig-zag polymer, showing seven-coordinate CdO_5N_2 distorted pentagonal dipyramid geometry. The formation of supramolecular networks structure is mainly due to intermolecular hydrogen bonding interactions between adjacent zig-zag polymers. The crystal is triclinic, space group P-1 with unit cell parameters: a = 12.231(2) Å, b = 14.349(2) Å, c = 16.022(2) Å, α = 85.731(4)°, β = 70.171(3)°, γ = 79.761(4)°, V = 2602.8(6)Å^3, Z = 2, Mr = 1335.90, Dc = 1.705 g/cm^3, μ = 1.058 mm^{-1}, F(000) = 1340, R = 0.0555, wR = 0.1068 for 9013 reflections with I > 2σ(I).

Key Words: Pyridyl-pyrimidin dithioether, Hydrogen bonds.

INTRODUCTION

The syntheses and characterization of coordination polymers are of considerable interest from the viewpoint of crystal engineering[1,2]. In recent years, heterocyclic thiolates and flexible thioethers have been extensively studied in that they are capable of displaying different reactions in various circumstances, giving rise to metal-organic frameworks (MOFs) with fascinating structures[3-7]. Herein, we reported an one-dimensional cadmium(II) complex, $\{[Cd(\mu\text{-}L)(NO_3)_2H_2O]_2H_2O\}_n$.

EXPERIMENTAL

All reagents for synthesis were commercially available and employed as received or purified by standard methods prior to use. 1,2-*Bis*(4-(pyridin-3-yl)pyrimidin-2-ylthio)ethane was prepared by similar procedure reported in the literature[3]. Analyses for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 1400C analyzer. Infrared spectra (4000-400 cm^{-1}) were recorded with a Bruker Vector 22 FT-IR spectrophotometer on KBr disks.

Synthesis: The title compound was prepared as following. Added a methanol (25 mL) solution of organic ligand [1,2-*bis*(4-(pyridin-3-yl)pyrimidin-2-ylthio)ethan, 40.4 mg, 1.0 mmol] to a methanol (20 mL) solution of $Cd(NO_3)_2{\cdot}6H_2O$ (30.8 mg, 1.0 mmol). The resulting solution was refluxed for 2 h, cooled to room temperature and filtered. The filtrate evaporated slowly to give colourless crystals (yield, 70 %). Anal. calcd. for $C_{40}H_{38}N_{16}O_{15}S_4Cd_2$: C: 35.96; H: 2.87; N: 16.78 %. Found: C: 35.89; H: 3.03; N: 16.81 %. IR (KBr, cm^{-1}): 3433 (m), 1595 (w), 1560 (s), 1542 (m), 1480 (w), 1403 (m), 1384 (s), 1350 (m), 1323 (m), 1200 (m), 1028 (w), 833(w).

Crystal structure determination: A single crystal of compound with dimensions of 0.20 mm × 0.10 mm × 0.10 mm was selected for crystallographic data collection at 291(2) K and structure determination on a Bruker SMART CCD-4K diffractometer employing graphite-monochromated MoK_α radiation (λ = 0.71073 Å). A total of 13101 reflections were collected in the range of $1.9° \le \theta \le 25.0°$, of which 9013 reflections were unique with R_{int} = 0.080. The data were collected using SMART and reduced by the program SAINT. All the structures were solved by direct methods and refined by full-matrix least squares method on F^2_{obs} by using SHELXTL-PC software package. Non-hydrogen atoms were placed in geometrically calculated positions. Hydrogen atoms were added according to theoretical model. The final full-matrix least-squares refinement including 694 variable parameters for 9013 reflections with I>2σ(I) and converged with unweighted and weighted agreement factors of

$$R_1 = S(||F_0|-|F_c||)/S|F_0| = 0.0555 \quad (1)$$

and

$$wR_2 = \{S[w(F_0^2-F_C^2)^2]/Sw(F_0^2)^2\}^{1/2} = 0.1068 \quad (2)$$

where $w = 1/[\sigma^2(F_0^2) + (0.0011P)^2]$ and $P = (F_0^2 + 2F_C^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.54 and -0. 57 e/Å^3, respectively.

TABLE-1
SELECTED BOND DISTANCES (Å) AND ANGLES (º)

Cd1-O1	2.339(6)	Cd1-O2	2.553(7)	Cd1-O4	2.379(7)
Cd1-O5	2.440(8)	Cd1-O7	2.280(6)	Cd1-N1	2.263(6)
Cd1-N7	2.273(8)	Cd2-O8	2.346(6)	Cd2-O9	2.496(6)
Cd2-O11	2.375(7)	Cd2-O12	2.455(7)	Cd2-O14	2.281(5)
Cd2-N6	2.313(9)	Cd2 -N10	2.248(7)	O1-Cd1 -O2	51.6(2)
O1-Cd1-O4	133.5(2)	O1-Cd1-O5	81.1(2)	O1-Cd1-O7	84.2(2)
O1-Cd1-N1	136.0(3)	O1-Cd1-N7	92.2(2)	O2-Cd1-O4	174.4(2)
O7-Cd1-N7	174.8(2)	O8-Cd2-O11	131.1(2)	O8-Cd2-O14	84.9(2)
O8-Cd2-N10	138.6(3)	O9-Cd2-O11	173.2(2)	O9-Cd2-O12	130.55(19)
O9-Cd2-O14	89.9(2)	O11-Cd2-N6	97.7(3)	O14-Cd2-N6	171.0(2)

TABLE 2
HYDROGEN BOND DISTANCES (Å) AND ANGLES (º)

Type (D–H···A)	d(D–H)	d(H···A)	∠(DHA)	d(D···A)	A
O7-H7A···N12	0.8500	2.1400	135.00	2.807(9)	1-x,2-y,1-z
O7-H7B···O8	0.8500	2.0400	143.00	2.761(9)	1-x,1-y,1-z
O14-H14A···N2	0.8500	2.1700	138.00	2.860(8)	1-x,2-y,1-z
O14-H14B···O1	0.8500	2.0600	146.00	2.799(9)	1-x,1-y,1-z
C3-H3···O12	0.9300	2.6000	138.00	3.341(11)	x,y,-1+z
C4-H4···O7	0.9300	2.5600	146.00	3.371(11)	1-x,1-y,-z
C7- H7···O3	0.9300	2.4500	173.00	3.378(12)	1-x,1-y,-z
C13-H13···O8	0.9300	2.6000	144.00	3.392(12)	2-x,1-y,1-z
C23-H23···O13	0.9300	2.5400	134.00	3.248(12)	2-x,1-y,1-z
C25-H25···N13	0.9300	2.4300	103.00	2.786(12)	x,-1+y,-1+z
C28-H28···O5	0.9300	2.5800	157.00	3.458(12)	x,1+y,z

RESULTS AND DISCUSSION

The selected bond lengths and bond angles are given in Table-1. Fig. 1 shows the molecular structure of the title compound. Fig. 2 shows the packing diagram of the title compound. The Cd complex crystallizes in the monoclinic system of P-1 space group. The present complex exists as the one-dimensional zig-zag polymer, showing seven-coordinate CdO_5N_2 distorted pentagonal dipyramid geometry, the axial N7-Cd1-O7 and N6-Cd2-O14 bond angles of title complex are in the range, *ca.* 174.8(2)°and 171.0(2)°, respectively. In the case of complex, Cd(II) centers are bridged by the organic ligand to give polymer chain. It is noted that the five Cd-O bond lengths of the title complex varies within the short range of 2.280(6) - 2.553(7) Å. While the pyrimidyl ring and pyridyl unit of complex are slightly nonplanar, the dihedral angle between the two heterocyclic rings is *ca.* 27.689°.

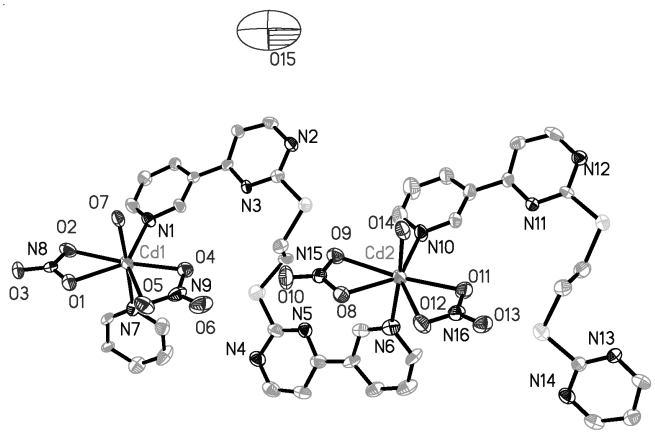

Fig. 1. Molecular structure of the Cd complex

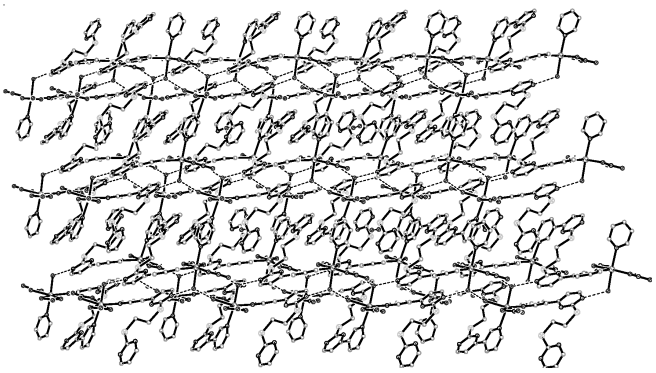

Fig. 2. View of a 3D supramolecular framework of Cd complex showing the intermolecular hydrogen bonding.

In crystal packing, it is observed that the C–H···O, C–H···N, O–H···O and O–H···N intermolecular hydrogen bonds are formed between adjacent chains resulting in a 3D supramolecular framework. All hydrogen bond patterns are given in Table-2.

Conclusion

Crystal structure of a novel 3D superamolecular cadmium(II) complex has been synthesized elemental analysis and X-ray diffraction analysis.

Supplementary material

Crystallographic data for the structure reported in this communication have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC 760046.

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REFERENCES

1. J.P. Zhang and X.M. Chen, *Chem. Commun.*, 1689 (2006).
2. X.M. Zhang, *Coord. Chem. Rev.*, **249**, 1201 (2005).
3. H.Z. Dong, J. Yang, X. Liu and S.H. Gou, *Inorg. Chem.*, **47**, 2913 (2008).
4. H.Z. Dong, J. Zhao, S.H. Gou and H.B. Zhu, *Polyhedron*, **28**, 1040 (2009).
5. H.Z. Dong, W.T. Bi and H.B. Zhu, *Asian J. Chem.*, **21**, 5607 (2009).
6. H.Z. Dong, H.B. Zhu, X. Liu and S.H. Gou, *Polyhedron*, **27**, 2167 (2008).
7. H.Z. Dong, H.B. Zhu, T.F. Tong and S.H. Gou, *J. Molecul. Struc.*, **891**, 266 (2008).