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Synthesis and Crystal Structure of [1,2-*bis*(4-(Pyridine-2-yl)pyrimidine-2-ylthio)ethane-κ^4N,N,N',N'] *bis*[Diiodidocadmium(II)]: $(CdI_2)_2C_{20}H_{16}N_6S_2\cdot(CHCl_3)_2$

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A novel 3D supramolecular complex [1,2-*bis*(4-(pyridine-2-yl)pyrimidine-2-ylthio)ethane-κ^4N,N,N',N'] *bis*[Diiodidocadmium(II)] with molecular formula as $(CdI_2)_2C_{20}H_{16}N_6S_2\cdot(CHCl_3)_2$, was synthesized by the reaction of 1,2-*bis*(4-(pyridin-2-yl)pyrimidin-2-ylthio)ethane with CdI_2, in which each ligand connects two identical Cd ions in N,N' chelation modes to form a discrete dinuclear cadmium coordination complex, which crystallizes in the monoclinic space group P-1. The coordination geometry around each Cd(II) cation is a distorted tetrahedron completed by two N atoms from one arm and two I atoms. Both pyridyl and pyrimidyl rings at the end of each arm are not coplanar with a deviation of 4.6°. The average Cd-N and Cd-I bond lengths are 2.310 and 2.667 Å, respectively. The crystal packing also exhibits weak intermolecular C-H···I hydrogen bonds. The crystal is monoclinic, space group P-1 with unit cell parameters: a = 8.2429(13) Å, b = 9.5001(15) Å, c = 13.633(2) Å, α = 81.843(3)º, β = 78.902(3)º, γ = 68.244(2)º, V = 970.1(3)Å^3, Z = 1, Mr = 1375.68, Dc = 2.355 g/cm^3, μ = 4.824 mm^{-1}, F(000) = 634.0, R = 0.0735, wR = 0.2298 for 3353 reflections with I > 2σ(I).

Key Words: Cd(II) complex, 1,10-Phenanthroline-5,6-dione, Supramolecule, Hydrogen bonds.

INTRODUCTION

Heterocyclic thiolates and flexible thioethers have been frequently used for constructing supramolecular architectures in recent years[1-4]. Within these molecules, heterocyclic donors containing N atoms are attached to the central linking aryl core *via* the -SCH_2- spacer. In continuation of our study, herein reported are metallosupramolecular cadmium complex of 1,2-*bis*(4-(pyridin-2-yl)pyrimidin-2-ylthio)ethane.

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-2-yl)pyrimidin-2-ylthio)ethane was prepared by similar procedure reported in the literature[2]. Analyses

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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: To a suspension of ligand *i.e.*, 1,2-bis(4-(pyridin-2-yl)pyrimidin-2-ylthio)ethane (24.0 mg, 0.050 mmol) in chloroform (5 mL) in a tube, a solution of CdI_2 (18.3 mg, 0.05 mmol) in methanol (5 mL) was very slowly dropped on the top of the ligand solution. Crystals formed after 10 days. Anal. calcd. (%) for $C_{22}H_{18}N_6S_2I_4Cd_2$: C, 19.21; H, 1.32; N, 6.11. Found. (%): C, 19.23; H, 1.34; N, 6.09. IR (KBr, ν_{max}, cm^{-1}): 3420 (w), 1605 (w), 1596 (s), 1547 (s), 1480 (w), 1432 (m), 1404 (m), 1346 (m), 1327 (w), 1205 (m), 1183 (w), 1046 (w), 806 (w).

Crystal structure determination: A single crystal of present compound with dimensions of 0.30 mm × 0.22 mm × 0.18 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 ($\lambda = 0.71073$ Å). A total of 4827 reflections were collected in the range of $2.3° \leq \theta \leq 25.0°$, of which 3353 reflections were unique with $R_{int} = 0.115$. 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 190 variable parameters for 3353 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of

$$R_1 = \Sigma(||F_0| - |F_c||)/\Sigma|F_0| = 0.0735 \quad (1)$$

and

$$wR_2 = \{\Sigma[w(F_0^2 - F_C^2)^2]/\Sigma w(F_0^2)^2\}^{1/2} = 0.2298 \quad (2)$$

where $w = 1/[\sigma^2(F_0^2) + (0.2000P)^2]$ and $P = (F_0^2 + 2F_C^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 1.92 and -1.69 e/Å^3, respectively.

RESULTS AND DISCUSSION

The selected bond lengths and bond angles in Table-1. Figs. 1 and 2 show the molecular structure and the packing diagram of the title compound, respectively. As depicted in Fig. 1, each ligand connects two identical Cd ions in N, N' chelation modes to form a discrete dinuclear cadmium coordination complex, which crystallizes in the triclinic space group P-1. The coordination geometry around each Cd atom is a distorted tetrahedron completed by two N atoms from one arm and two I atoms. The average Cd-N and Cd-I bond lengths are 2.310 and 2.667 Å, respectively. Whilst the dihedral angle between the two heterocyclic rings of each arm is decreased to 3.36°. In addition, the mean plane of pyrimidinyl ring is nearly perpendicular to that of central phenyl ring in sharp contrast with the situation in the free ligand. As shown in Fig. 2, weak intermolecular C-H···I hydrogen bonds link near molecules into 3D network (Table-2).

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

I1-Cd1	2.6635(11)	I2-Cd1	2.6740(11)	Cd1-N1	2.313(7)
Cd1-N3	2.307(8)	I1-Cd1-I2	127.84(3)	I1-Cd1-N1	114.51(19)
I1-Cd1-N3	107.3(2)	I2-Cd1-N1	111.41(18)	I2-Cd1-N3	109.7(2)
N1-Cd1-N3	71.2(3)	–	–	–	–

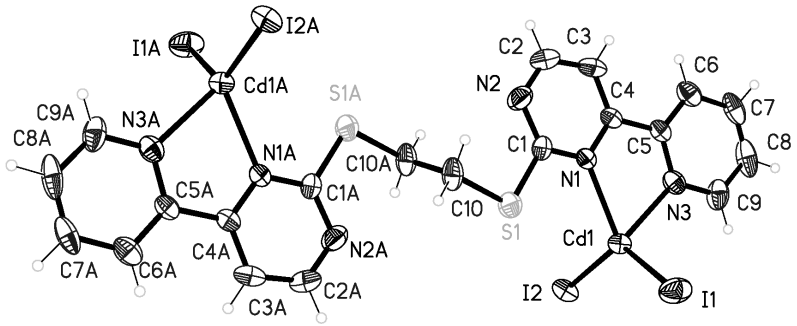

Fig. 1. Structure of the Cd(II) compound, showing 30 % probability displacement ellipsoids and the atom-numbering. Two chloroform molecules are omitted for clarity [symmetry code: 1 - x, 1 - y, -z]

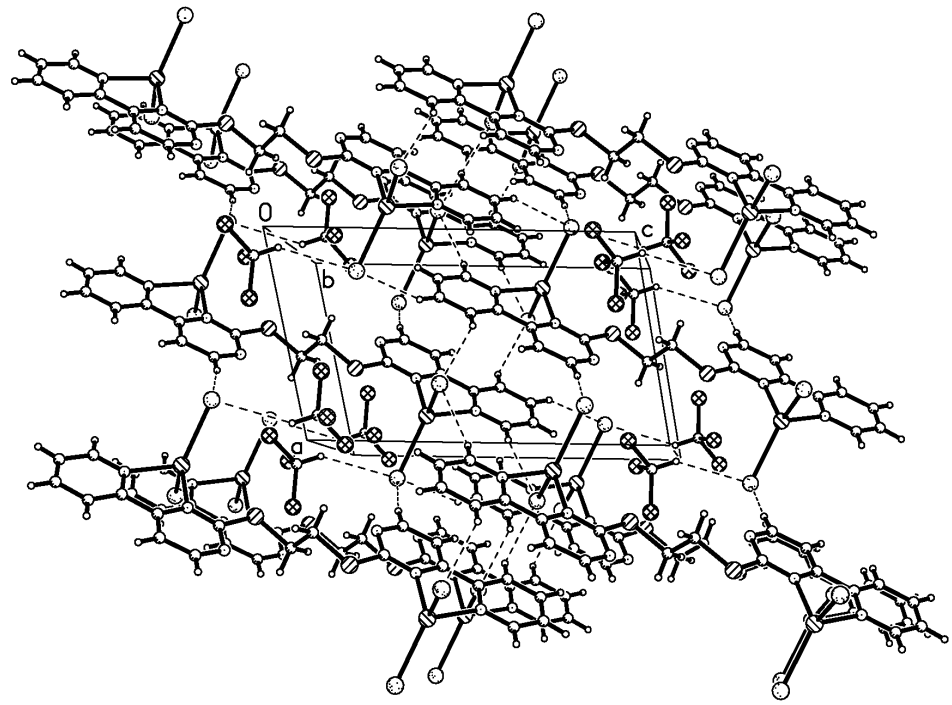

Fig. 2. View of a 3D supramolecular framework of the Cd(II) complex showing the intermolecular hydrogen bonding

TABLE-2
HYDROGEN BOND DISTANCES (Å) AND ANGLES (°)

Type (D-H···A)	d(D-H)	d(H…A)	∠(DHA)	d(D…A)	A
C6-H6···I1	0.9300	3.0600	146	3.862(11)	1 - x, 1-y, 1-z
C9-H9···I1	0.9300	2.9900	155	3.852(13)	2-x, -y, 1-z

Conclusion

Crystal structure of a novel 3D supramolecular cadmium(II) complex has been synthesized and characterized by IR, 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 760048.

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