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Synthesis and Crystal Structure of A Novel 1D Supramolecular Complex: $[C_{21}H_{18}N_6S_2I_2Hg]_2 \cdot CH_3OH$

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A novel 1D supramolecular complex with a formula as $[C_{21}H_{18}N_6S_2I_2Hg]_2 \cdot CH_3OH$, was formed by the reaction of 1,3-*bis*(4-(pyridine-3-yl)-pyrimidine-2-ylthio)propane with HgI_2, in which metal ion was in a four-coordinated environments with a distorted tetrahedral geometry. Then independent zigzag chains are linked each other and pack in 3D-superamolecular network *via* hydrogen bonds. The crystal is triclinic, space group P-1 with unit cell parameters: a = 11.1806(14) Å, b = 15.4729(19) Å, c = 16.875(2) Å, α = 75.028(2)°, β = 86.737(2)°, γ = 71.171(2)°, V = 2668.2(6) $Å^3$, Z = 2, Mr = 1777.9, Dc = 2.213 g/cm^3, μ = 8.263 mm^{-1}, F(000) = 3078, R = 0.0428, wR = 0.0831 for 9220 reflections with $I > 2\sigma(I)$.

Key Words: 1,3-*Bis*(4-(pyridine-3-yl)pyrimidine-2-ylthio)propane, Zigzag chain, Hydrogen bonds.

INTRODUCTION

Several researchers show remarkable attention in the rational design and assembly of new coordinated frameworks about heterocyclic thiolates and flexible thioethers for their fascinating structural topologies and potential use as functional materials in recent years[1-7]. Previously, some 3D supramolecular complexes derived from pyridyl-pyrimidine dithioethers[8-10] are reported. Herein, a new 1D zigzag chain supramolecular mercury complex $[C_{21}H_{18}N_6S_2I_2Hg]_2 \cdot CH_3OH$ is reported.

EXPERIMENTAL

All the commercially available chemicals were of reagent grade. Ligand was prepared according to reported method[11]. 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.

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Synthesis: To a stirred solution of ligand (209 mg, 0.50 mmol) in 40 mL of methanol, the solution of HgI_2 (227 mg, 0.50 mmol) in methanol (50 mL) was added. A pale yellow precipitate formed immediately which was filtered under vacuum and dried in air (yield: 70 %). Anal. Calcd. for $C_{21}H_{18}N_6S_2HgI_2$: C, 28.89; H, 2.08; N, 9.63 %. Found: C, 28.94; H, 1.93; N, 9.58 %. IR (KBr, cm^{-1}): 3433 m, 1597 m, 1559 vs, 1542 w, 1480 w, 1428 w, 1405 m, 1346 s, 1324 m, 1203 s, 1118 w, 807 w. The filtrated solution evaporated slowly to give the pale yellow single crystals at room temperature.

Crystal structure determination: A single crystal of compound with dimensions of 0.3 mm × 0.2 mm × 0.1 mm was selected for crystallographic data collection at 291(2) K and structure determination on a Bruker SMART CCD-4K diffractometer employing graphite-monochromated MoKα radiation (λ = 0.71073 Å). A total of 13367 reflections were collected in the range of $1.6° \leq \theta \leq 25.0°$, of which 9220 reflections were unique with R_{int} = 0.033. 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 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 595 variable parameters for 9220 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of:

$$R_1 = \Sigma(||F_0|-|F_c||)/\Sigma|F_0| = 0.0428 \quad (1)$$

and

$$wR_2 = \{\Sigma[w(F_0^2-F_C^2)^2]/\Sigma w(F_0^2)^2\}^{1/2} = 0.0831 \quad (2)$$

where $w = 1/[\sigma^2(F_0^2) + (0.0267P)^2]$ and $P = (F_0^2 + 2F_C^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 1.03 and -0.91 e/Å^3, respectively.

RESULTS AND DISCUSSION

The selected bond lengths and bond angles (Table-1, Fig. 1) show the molecular structure of the title compound. Fig. 2 shows the packing diagram of the title compound. From the Fig. 1, it is easy to observe that the mercury(II) ion is four-coordinated with two N donors from different ligands and two coordinated I-counter ions to arrange distorted tetrahedral coordination sphere with Hg-N and Hg-I distance in the range of those found in the other complexes[11,12].

In crystal packing, it is interesting to observe that the C–H···N and C–H···I intermolecular hydrogen bonds are formed between adjacent 1D chains resulting in a 3D supramolecular framework.

Conclusion

Crystal structure of a novel 1D zigzag chain mercury(II) complex has been synthesized and characterized by IR, elemental analysis and X-ray diffraction analysis.

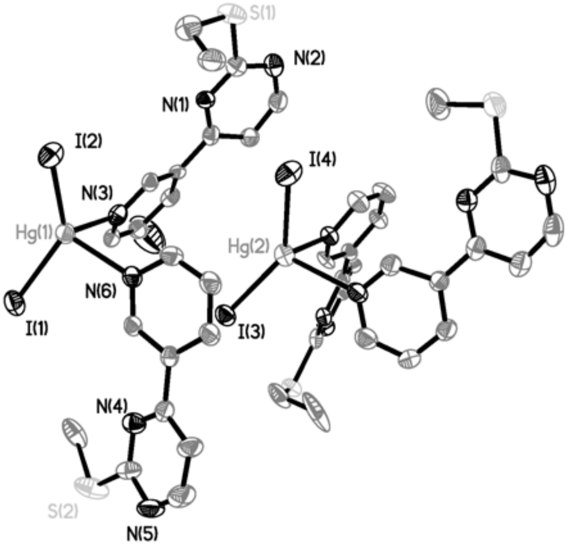

Fig. 1. Molecular structure of the title complex

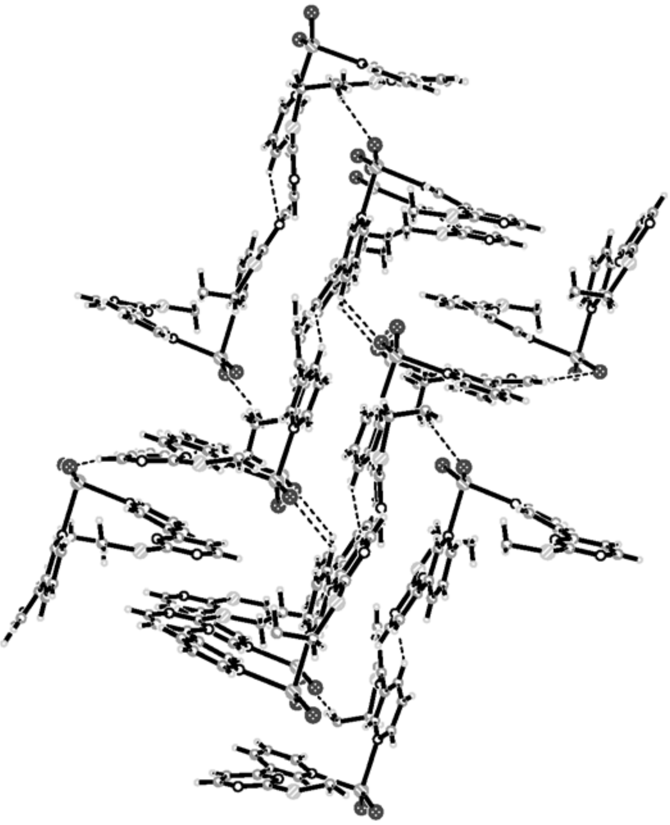

Fig. 2. Hydrogen bonds among 1D network in the complex

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

Hg1-I1	2.6424(11)	Hg1-I2	2.6238(11)
Hg1-N3	2.412(8)	Hg1-N6	2.390(8)
Hg2-N12	2.426(8)	Hg2-I3	2.6229(10)
Hg2 -I4	2.6257(11)	Hg2-N9	2.421(8)
I1-Hg1-I2	138.33(3)	I1-Hg1-N3	102.3(2)
I1-Hg1-N6	101.1(2)	I2 -Hg1-N3	103.8(2)
I2 -Hg1-N6	111.3(2)	N3-Hg1-N6	89.1(3)
I3-Hg2-N9	112.5(3)	I3-Hg2-N12	103.9(2)
I4-Hg2-N9	99.4(3)	I4-Hg2-N12	99.8(2)
N9-Hg2-N12	84.5(3)	I3-Hg2-I4	141.56(3)

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

Type (D-H···A)	d(D-H)	d(H···A)	∠ (DHA)	d(D···A)	A
O1-H1···N7	0.850	2.610	128.0	3.21	N7 [1+x,y,1+z]
C10-H10b···N2	0.930	2.550	102.0	2.906(2)	N2 [-1+x,y,z]
C18-H18···N11	0.930	2.590	143.0	3.375(2)	N11 [1-x,-y,1-z]
C43-H43···N10	0.930	2.550	137.0	3.32	N10 [1+x,y,1+z]

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 705226.

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