Scientific Journal of Impact Factor (SJIF): 4.72
e-ISSN : 2348-4470
p-ISSN : 2348-6406

International Journal of Advance Engineering and Research Development

National Conference On Nanomaterials, (NCN-2017)

Volume 4, Special Issue 6, Dec.-2017 (UGC Approved)

Supramolecular architectures in cadmium (II) - thiocyanate complex of 2-amino 4,6-dimethyl pyrimidine

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Abstract:-*In this complex, {catena- poly cadmium (II) -di-µ-thiocyanato] bis (2-amino-4,6-dimethylpyrimidine [CdAMPY]}, the asymmetric unit contains, 2-amino-4,6-dimethylpyrimidium cation, a thiocyanato ion, 2 –isocyanate ion (one in the axial & one in the equatorial position) and a cadmium ion occupying a crystallographic inversion centre. The environment around cadmium atom is octahedral. The 2-aminopyrimidine cations are not coordinated to cadmium but are hydrogen bonded to the thiocyanato ions. Symmetry related pyrimidines interact via N-H…N hydrogen bonds, forming a typical ring motif with graph set notation* $R^2_2(8)$*. The crystal structure is further stabilized by N-H...S hydrogen bonds.*

Keywords:- *2-amino-4,6-dimethylpyrimidine, X-ray analysis, Hydrogen bonding, Ring motif.*

Introduction

Investigations on the crystal structures and properties of coordination polymers are an active field in chemical research. Coordination polymers based on metal cations with unpaired electrons are of increasing interest, because of their different magnetic properties, such as spin-crossover or low-dimensional magnetism [1–3]. Recently, the design and synthesis of polymeric coordination networks have attracted much attention in supramolecular chemistry due to the fascinating structural diversity and potential applications of these networks as functional materials [4-7]. There are some reports in which N- and S-donor bridging ligands are used to form extended polymeric frameworks. [8-15]. According to the soft–hard acid–base theory, cadmium is a rather soft metal; therefore, it is expected that the N and S atoms of a thiocyanate ion can form stable bonds with cadmium, and thus thiocyanate-bridged polymeric complexes are stable [16]. Thiocyanate is an ambidentate ion which can coordinate to a metal via its S or N atoms. Thiocyanate ions can also bridge metal ions by employing both the N and S atoms for coordination. Different bridging modes of the thiocyanate ligand and cadmium can generate various types of supramolecular structures with useful properties, including nonlinear optical (NLO) behaviour [15-17]. The present study is aimed at increasing our understanding of the interplay of coordination and hydrogen bonding in determining supramolecular organization.

Experimental section

Preparation

An aqueous solution of cadmium nitrate [$Cd(NO_3)6H_2O$; 145.5 mg] in methanol (5 ml) was added to a solution of NH_4NCS (76.12 mg) in methanol (5 ml). The mixture was stirred for 20 minutes. 2-Amino-4,6-dimethylpyrimidine (61.5 mg) dissolved in methanol (10 ml) was added slowly to this mixture. The resultant solution was stirred for 30 min and left for slow evaporation at room temperature. After a few days, colourless crystals of compound (1) were obtained.

X-ray data collection

X-ray data were collected at 293K on a Bruker AXS smart single crystal diffractometer with CCD by using graphite monochromated MoKα radiation. From the cell parameters and an analysis of equivalent reflections, the crystal system was assigned as Triclinic. The absorption correction was performed by SHELXA[18].

Structure solution and refinement

In the data set of [CdAMPY], the E-statistics revealed the centrosymmetric distribution. Among the reflections of the general type *hkl* there are no systematic absences. This indicates that the lattice is primitive. The structure was solved by direct method using SHELXS97 [18] and refined by full-matrix least squares method on F^2 by SHELXL97 [18]. The H atoms are placed in idealized locations and refined as riding. The final R-value is 0.0288 for 6153 reflections I>2a(I). The geometric calculations were carried out using PLATON97 [19]. The crystal data and the details of the structure determination parameters are listed in Table 1 [CdAMPY].

Results and Discussion

In the title crystal structure {catena- poly cadmium (II) -di-μ-thiocyanato] bis (2-amino-4,6-dimethylpyrimidine [CdAMPY]},2($C_3CdN_3S_3$), $C_4CdN_4S_4$, 4($C_6H_{10}N_3$) , the asymmetric unit contains one 2-amino- 4,6-dimethylpyrimidine molecule, a thiocyanato ion, and a cadmium ion, the last of these occupying an inversion centre. An ORTEP view of the asymmetric unit is shown in Figure 1. In this complex the cadmium ions are symmetrically doubly bridged by thiocyanato ions, leading to a polymeric chain motif to complete the octahedral geometry of cadmium.

The axial positions are coordinated by N-atoms of thiocyanate ion & equatorial positions are coordinated by 2 S atoms & 2 N atoms of thiocyanate ions. The bond distances [Cd1-N19 / Cd2-N20 = 2.295 (2) / 2.247 (3) Å, Cd1-S2 / Cd2-S4 = 2.797 (7) / 2.631 (8) Å]. The thiocyanato ligands are almost linear. The N20-C20-S3 angle is 178.7(3)°. The selected bond distances and angles involving the non-hydrogen atoms are listed in Table 2.

Hydrogen bonding

In this complex, the 2-amino-4,6-dimethylpyrimidine molecule are not coordinated to cadmium but are hydrogen-bonded to the thiocyanato ions. The thiocyanate ligands play different roles in the buildup of the structure; one role results in the formation of [Cd2(NCS)2] building blocks, while the other links the building blocks and cations via N—H**…**S hydrogen bonds. The N—H**…**S hydrogen bonds and weak π- π stacking interactions are involved in the formation of both a two-dimensional network structure and the supramolecular network. Intermolecular N—H**…**S hydrogen-bonding interactions between the protonated AMPY+ cation and the nonbridging thiocyanate S atom (Table-3). There are pyrimidine-pyrimidine interaction observed between a unprotonated N3/N13 & N4 &N14 amino groups. Both the pyrimidine molecules are protonated at one of the pyrimidine N atoms (increase in internal angle at N1 & N11, C2-N1-C6=122.7(3)°, C2-N11-C16=122.1(2)°. When compared with the unprotonated N atoms N3, N13, C2-N3-C4=117.5(3)°, C12-N13-C14=118.1(2)°. Here, one of the hydrogen atom of (H4A) 4-amino group interacts with the unprotonated N3 atom via N-H...N hydrogen bonds to form a ring motif with graph-set notation $R_2^2(8)$. Similarly, one the hydrogen atom of (H14A) amino group interacts with the unprotonated N13 atom via N-H...N hydrogen bonds to form a same ring motif. A view of crystal packing is shown in Figure 2. The hydrogen-bonding geometries are given in Table 3. In addition, the π-π stacking interactions are observed between two pyrimidinium cations with interplanar distance of 3.386Å, a centroid -to-centroid (Cg2-Cg2) distance of 3.7871(15)Å and slip angle (the angle between the centroid vector and the normal to the plane) of 26.62°.

Supplementary Materials

The atomic coordinates and the isotropic displacement parameters for all the hydrogen atoms, the anisotropic displacement parameters for all the non-hydrogen atoms, the bond distances and bond angles involving the hydrogen atom and the torsion angles [CdAMPY] are given in Tables 1- 3.

Acknowledgements

MS thanks Collegiate Education Chennai- Tamil Nadu, for financial support (College Research student Fellowship). Ref.No:28696/K2/12. The authors are thankful to Bharathidasan University – Tiruchirappalli, for providing the single-crystal X-ray diffraction facility.

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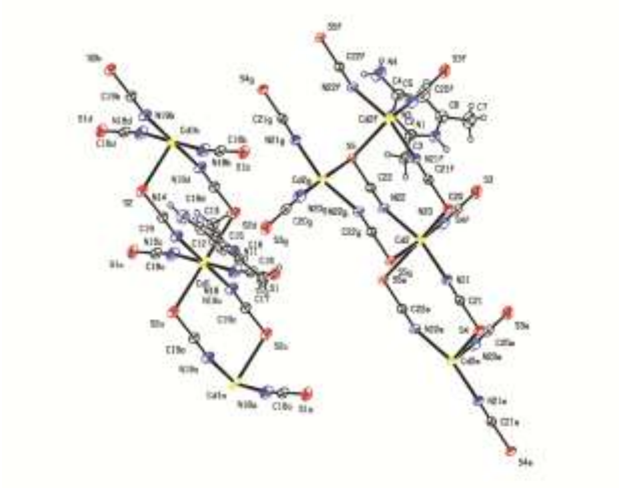

Figure 1. An ORTEP view of the molecule in the asymmetric unit in the crystal structure of compound CdAMPY

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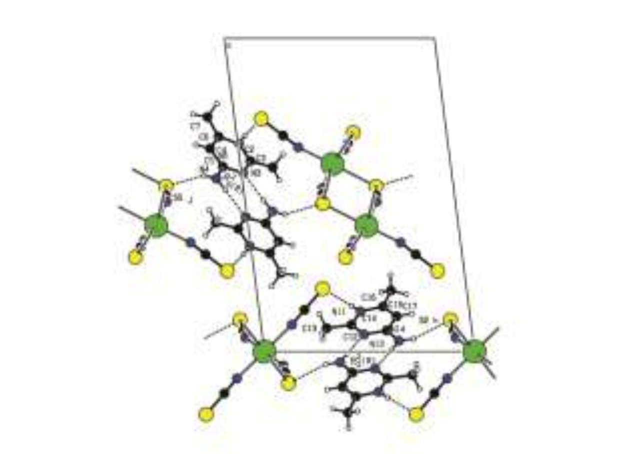

Figure 2. Hydrogen bonding patterns in CdAMPY

International Journal of Advance Engineering and Research Development (IJAERD)
National Conference On Nanomaterials, (NCN-2017), Volume 4, Special Issue 6, Dec 2017
UGC Approved,e-ISSN:2348-4470, p-ISSN:2348-6406

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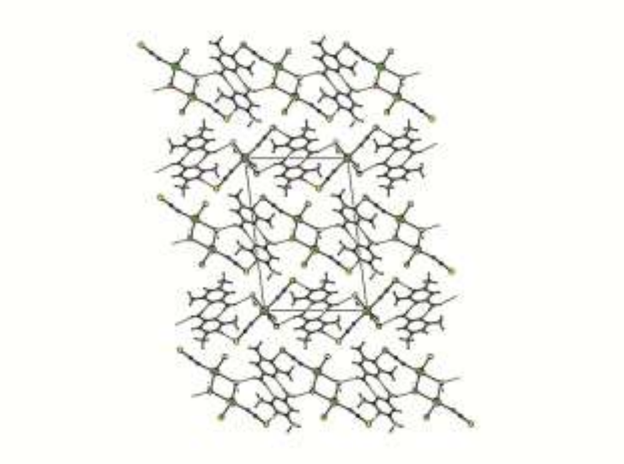

Figure 3. A view of the molecular packing in CdAMPY

Table 1 - Crystal Data and Details of the Structure Determination for compound CdAMPY

Formula	$2(C_3\,Cd\,N_3\,S_3)$, $C_4\,Cd\,N_4\,S_4$, $4(C_6\,H_{10}\,N_3)$
Formula Weight	1414.68
Crystal System	Triclinic
Space group	P-1 (No. 2)
a, b, c [Å]	5.9351(2) 12.5406(3) 18.5485(4)
alpha, beta, gamma [°]	5.9351(2) 12.5406(3) 18.5485(4)
V [Å^3]	1356.05(6)
Z	1
D(calc) [g/cm^3]	1.732
Mu(MoK□) [/mm]	1.601
F(000)	702
Crystal Size [mm]	0.05 x 0.05 x 0.30
Temperature (K)	293(2)
Radiation [Å]	MoKα 0.71073
Theta Min-Max [°]	3.7, 27.4
Dataset	-6: 7; -16: 16; -24: 24
Tot., Uniq. Data, R(int)	11132, 6153, 0.023
Observed data [I > 2.0 σ (I)]	4930
Nref, Npar	6153, 317
R, wR2, S	0.0288, 0.0694, 1.05
$w = 1/[\backslash^{2}(Fo^{2})+(0.0581P)^{2}]$	where $P=(Fo^{2}+2Fc^{2})/3$
Min. and Max. Resd. Dens. [e/ Å^3]	-0.63, 0.40

Table 2. Selected bond lengths (Å) and bond angles (°) for compound CdAMPY

Cd2-N20	2.247(3)	Cd2-N21	2.247(2)
Cd2-N22	2.315(2)	N11-C16	1.371(3)
Cd2-S5_e	2.8417(8)	N11-C12	1.347(3)
Cd2-S4_f	2.6313(8)	N13-C14	1.367(3)
Cd2-S5_g	2.8959(7)	N13-C12	1.311(3)
Cd1-N19	2.295(2)	N14-C14	1.327(4)
Cd1-S2_a	2.7979(7)	C2-C3	1.500(4)
Cd1-N18	2.291(3)	S3-C20	1.632(3)
S4-C21	1.649(3)	C6-C7	1.484(5)
S5-C22	1.661(2)	S1-C18	1.638(3)
S2-C19	1.646(3)	N20-C20	1.154(4)
N21-C21	1.146(3)	N22-C22	1.148(3)
N19-C19	1.155(3)	C12-C13	1.480(4)
N1-C2	1.341(4)	C14-C15	1.402(4)
N1-C6	1.352(4)	C15-C16	1.352(4)
N3-C2	1.310(4)	C16-C17	1.497(5)
N3-C4	1.364(4)	N4-C4	1.327(4)
N20-Cd2-N21	95.98(10)	N18-Cd1-N19_c	89.25(10)
N20-Cd2-N22	92.42(10)	S2_d-Cd1-N18	89.07(7)
S5_e-Cd2-N20	99.50(8)	Cd2_e-S4-C21	98.35(9)
S4_f-Cd2-N20	97.12(8)	Cd2_f-S5-C22	104.95(9)
S5_g-Cd2-N20	178.70(8)	Cd2_g-S5-C22	100.19(9)
N21-Cd2-N22	164.62(8)	Cd2_f-S5-Cd2_g	100.30(2)
S5_e-Cd2-N21	84.35(6)	Cd1_b-S2-C19	100.64(10)
S4_f-Cd2-N21	93.08(6)	Cd2-N20-C20	163.7(3)
S5_g-Cd2-N21	84.97(6)	Cd2-N21-C21	170.9(2)
S5_e-Cd2-N22	81.57(6)	Cd2-N22-C22	153.6(2)
S4_f-Cd2-N22	98.64(6)	Cd1-N18-C18	171.3(2)
S5_g-Cd2-N22	86.45(6)	Cd1-N19-C19	155.9(2)
S4_f-Cd2-S5_e	163.36(3)	C2-N1-C6	122.7(3)
S5_e-Cd2-S5_g	79.70(2)	C2-N3-C4	117.5(3)
S4_f-Cd2-S5_g	83.70(2)	S2_a-Cd1-N19	86.85(7)
N18_c-Cd1-N19	89.25(10)	N19-Cd1-N19_c	180
S2_d-Cd1-N19	93.15(7)	C12-N11-C16	122.1(2)
C12-N13-C14	118.1(2)	S2_a-Cd1-S2_d	180
S2_d-Cd1-N18_c	90.94(7)	N18-Cd1-N19	90.75(10)
S2_a-Cd1-N18	90.94(7)	S3-C20-N20	178.7(3)
N18-Cd1-N18_c	180	S4-C21-N21	177.6(2)
S5-C22-N22	179.6(3)	S1-C18-N18	179.4(3)
N11-C12-C13	117.6(2)	S2-C19-N19	177.5(3)
N13-C12-C13	120.4(2)	N3-C2-C3	119.5(3)
N11-C12-N13	122.0(2)	N1-C2-N3	122.2(2)
N13-C14-C15	121.1(3)	N1-C2-C3	118.3(3)
N14-C14-C15	123.0(2)	N3-C4-C5	121.4(3)
N13-C14-N14	116.0(3)	N3-C4-N4	115.3(3)
C14-C15-C16	119.3(2)	N4-C4-C5	123.3(3)
N11-C16-C17	117.7(3)	C4-C5-C6	118.9(3)
C15-C16-C17	124.9(3)	N1-C6-C5	117.3(3)
N11-C16-C15	117.4(3)	C5-C6-C7	125.1(3)
N1-C6-C7	117.5(3)		

Table 3. Hydrogen bonding geometry (Å, °) for compound CdAMPY

D*–H···*A	**Distance, Å**			***D*–H···*A* (°)**
	***D*–H**	**H···*A***	***D*···*A***	
N1--H1···S3	0.86	2.47	3.328(3)	174
N4--H4A···N3	0.86	2.21	3.073(4)	177
N4--H4B···S5	0.86	2.55	3.343(3)	153
N11--H11···S1	0.86	2.47	3.328(2)	172
N14--H14A···N13	0.86	2.18	3.039(4)	176