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Synthesis and Crystal Structure of Di(thiocyanato-κN) *bis*(1,10-phenanthroline-5,6-dione-κ^2N,N') Cadmium(II): $\{[Cd(C_{12}H_6N_2O_2)_2(H_2O)_2]\cdot(ClO_4)_2\cdot(H_2O)\}$

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A novel 3D supramolecular complex di(thiocyanato-κN)*bis*(1,10-phenanthroline-5,6-dione-κ^2N,N') cadmium(II) synthesized with a formula as $\{[(C_{12}H_6N_2O_2)_2Cd(H_2O)_2]\cdot(ClO_4)_2\cdot(H_2O)\}$, was synthesized by 1,10-phenanthroline-5,6-dione and $Cd(ClO_4)_2$. In the crystal structure of the present complex, cadmium ion located in a six-coordinated environments with a distorted octahedral geometry. The intermolecular hydrogen bonds interactions among the near mononuclear units are playing an important role in the construction of 3D-superamolecular network. The crystal is monoclinic, space group $P2_1/c$ with unit cell parameters: a = 16.027(2) Å, b = 13.0521(17)Å, c = 15.365(2)Å, α = 90º, β = 115.889(2)º, γ = 90º, V = 2891.6(6)Å^3, Z = 4, Mr = 785.73, Dc = 1.805 g/cm^3, μ = 1.022 mm^{-1}, F(000) = 1568, R = 0.0532, wR = 0.1731 for 6317 reflections with I > 2σ(I).

Key Words: 1,10-Phenanthroline-5,6-dione, Supramolecule, Hydrogen bonds.

INTRODUCTION

Recent years have witnessed an explosion of great interest in the coordinated complexes with physical and chemical properties derived from 1,10-phenanthroline-5,6-dione[1-4]. Here we report a new monomeric cadmium(II) complex di(thiocyanato-κN)*bis*(1,10-phenanthroline-5,6-dione-κ^2N,N') cadmium(II) with the molecular formula $\{[Cd(C_{12}H_6N_2O_2)_2\cdot(H_2O)_2]\cdot(ClO_4)_2\cdot(H_2O)\}$.

EXPERIMENTAL

All reagents for synthesis were commercially available and employed as received or purified by standard methods prior to use. 1,10-Phenanthroline-5,6-dione was prepared by similar procedure reported in the literature[2]. Analyses for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 1400C analyzer.

Synthesis: For the synthesis of present compoud, a solution of the ligand (0.2 mmol), $Cd(ClO_4)_2\cdot6H_2O$ (0.1 mmol) in 50 mL methanol was refluxed for 2 h and then cooled to room temperature and filtered. Single crystals suitable for X-ray analysis were grown from the methanol solution by slow evaporation at room temperature in air. Anal. calcd. (%) for $C_{24}H_{18}N_4O_{15}Cl_2Cd$: C, 36.69; H, 2.31; N, 7.13. Found. (%): C, 36.73; H, 2.38; N, 7.10.

Crystal structure determination: A single crystal of compound with dimensions of 0.31 mm × 0.26 mm × 0.20 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 16647 reflections were collected in the range of $2.1° \leq \theta \leq 27.0°$, of which 6317 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 371 variable parameters for 6317 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of

$$R_1 = \Sigma(||F_0| - |F_c||)/\Sigma|F_0| = 0.0532 \quad (1)$$

and

$$wR_2 = \{\Sigma[w(F_0^2 - F_C^2)^2]/\Sigma w(F_0^2)^2\}^{1/2} = 0.1731 \quad (2)$$

where $w = 1/[\sigma^2(F_0^2) + (0.1014P)^2]$ and $P = (F_0^2 + 2F_C^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 1.25 and -0.75 e/Å^3, respectively.

RESULTS AND DISCUSSION

The selected bond lengths and bond angles are given in Table-1. Fig. 1 shows the molecular structure of the present compound. Fig. 2 shows the packing diagram of the present compound. The present compound crystallizes in the monoclinic system of $P2_1/c$ space group. The asymmetric unit consists of one camium cation, two coordinated water molecules and two 1,10-phenanthroline-5,6-dione ligands, as well as two free perchlorate anions and one lattice water molecule. As shown in Fig. 1, each Cd(II) ion is surrounded by two oxygen atoms and four nitrogen atoms, in which four nitrogen atoms from two ligands and two oxygen atoms from two water molecule, forming a CdO_2N_4 core. The average Cd-N bond distance for CdO_2N_4 core is 2.352 Å while the average Cd-N bond distance is 2.265 Å.

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

Cd1-O5	2.264(5)	Cd1-O6	2.267(4)	Cd1 -N1	2.340(4)
Cd1-N2	2.367(4)	Cd1-N3	2.358(4)	Cd1-N4	2.342(4)
O5-Cd1-O6	86.88(17)	O5 -Cd1-N1	87.17(16)	O5 -Cd1 -N2	95.64(16)
O5-Cd1-N3	156.98(14)	O5-Cd1-N4	96.07(17)	O6 -Cd1-N1	160.21(13)
O6-Cd1-N2	90.93(14)	O6-Cd1-N3	110.23(16)	O6 -Cd1-N4	89.22(14)
N1-Cd1-N2	70.92(12)	N1-Cd1-N3	81.27(15)	N1 -Cd1-N4	110.18(12)
N2-Cd1-N3	99.24(16)	N2-Cd1-N4	168.28(18)	N3-Cd1 -N4	69.79(16)

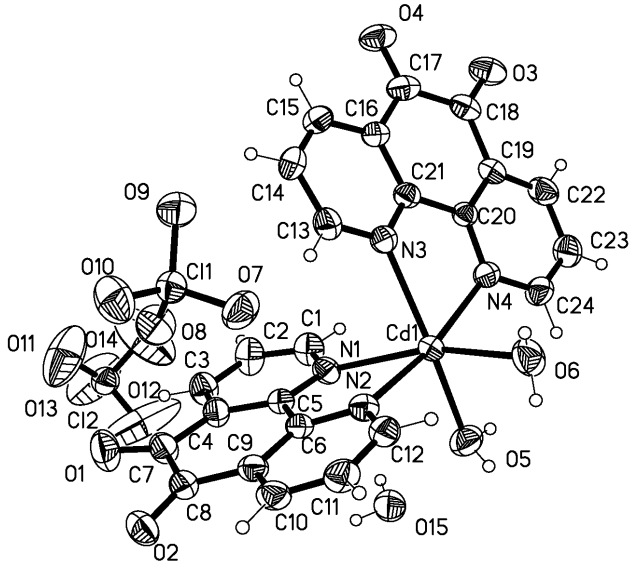

Fig. 1. Molecular structure of the title complex

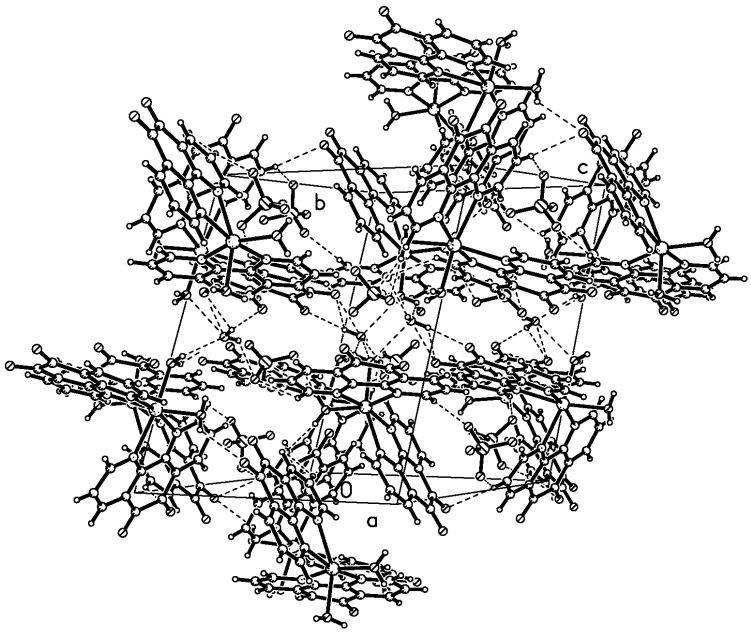

Fig. 2. View of a 3D supramolecular framework of tiltle complex showing the intermolecular hydrogen bonding

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

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

Type (D-H···A)	d(D-H)	d(H···A)	∠(DHA)	d(D···A)	A
O5- H5A···O15	0.8500	2.3400	2.785(7)	113.00	1-x, 2-y, -z
O5-H5B···O15	0.8500	2.4800	2.785(7)	102.00	1-x, 2-y, -z
O6-H6A···O13	0.8500	2.1200	2.966(10)	179.00	x, 1+y, z
O6-H6B···O3	0.8500	2.4800	3.033(6)	124.00	-x, 1/2+y, -1/2-z
O15-H15B···O11	0.8500	2.4900	3.193(11)	140.00	1-x, 1/2+y, 1/2-z
O15-H15C···O1	0.8500	2.3700	2.878(6)	119.00	x, 3/2-y, -1/2+z
O15-H15C···O2	0.8500	2.1900	3.007(6)	162.00	x, 3/2-y, -1/2+z
C1-H1···O8	0.9300	2.4800	3.347(7)	154.00	x, 3/2-y, -1/2+z
C12-H12···O11	0.9300	2.5700	3.297(9)	135.00	x, 1+y, z
C14-H14···O9	0.9300	2.5200	3.255(7)	136.00	–
C14-H14···O3	0.9300	2.5000	3.241(8)	137.00	x, 3/2-y, 1/2+z

Conclusion

Crystal structure of a novel 3D superamolecular cadmium(II) complex has been synthesized and characterized by 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 760045.

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