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RESEARCH ARTICLE

Crystal and Molecular Structure Study of the Complex $Cd(L)_2Br_2.C_2H_5OH$ (L=2-(4-Methylsulfanyl phenyl)-1*H*-benzimidazole)

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Abstract: The complex, $Cd(L)_2Br_2.C_2H_5OH$, contains an ethanol molecule and dibromocadmate(II) coordinated to two benzimidazole moiety. In the crystal structure, the ethanol molecule is involved in four hydrogen bonds, *viz.* N-H…O, C-H…O, C-H…Br and O-H…Br intermolecular interactions network. Further the supramolecular assembly is stabilized by π-π stacking interactions between the benzimidazole and thiomethyl phenyl rings. Additionally, the metal ion, Cd(II) exhibits a distorted tetrahedral coordination of the bromine atoms.

Keywords: Benzimidazole derivative, Metal ligand complex, Crystal structure, Weak interactions

Indrotuction

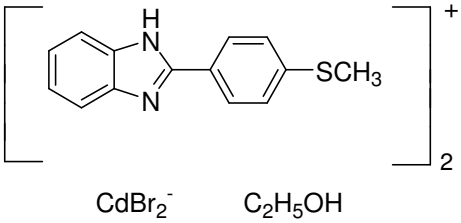
Benzimidazole derivatives exhibit a number of important structures in pharmaceutical chemistry because of their biological activities and clinical applications. They exhibit antitumor, antihelmintic, antibacterial, virucidal and fungucidal properties in addition, benzimidazole derivatives are effective against the human cytomegalovirus (HCMV)[1] and are also efficient selective neuropeptide Y Y1 receptor antagonists[2]. The described methods for the synthesis of benzimidazoles make use of solid-phase synthesis via *o*-nitroanilines[3,4] or the condensation of *o*-phenylenediamines with carboxylic acid derivatives, aldehydes and aryl halides. Some of these derivatives, particularly nitro derivatives, are used as photographic materials in photography and on the other hand, the development of the chemistry of the benzimidazole dyes has been remarkable[5,6].

As a part of our ongoing investigations of benzimidazole derivative, the benzimidazole derivative was synthesized as a ligand for complexation with cadmium metal to give the title metal complex and its crystal structure is reported herein.

Experimental

Preparation of the complex, $Cd(L)_2Br_2.C_2H_5OH$

An ethanolic solution (15 mL) of the 2-(4-methylsulfanyl phenyl)-1*H*-benzimidazole) (0.960 mg, 2 mmol) was added to a solution of cadmium(II) bromide (0.272 mg, 1 mmol) in ethanol (25 mL). The mixture was then treated with 48% HBr (2-3 mL) followed by liquid bromine (2-3 mL). The mixture was refluxed for nearly 6 h during which yellow crystals suitable for x-ray analysis were obtained (Scheme 1). The crystals were collected, washed with cold ethanol and dried *in vacuum* over P_2O_5 (yield 1.23 mg, 85 %).



Scheme 1. $Cd(L)_2Br_2.C_2H_5OH$ (where, L=2-(4-methylsulfanyl phenyl)-1*H*-benzimidazole)

X-ray crystallographic analysis

The crystal structures of the complex $Cd(L)_2Br_2.C_2H_5OH$ was determined by single crystal x-ray diffraction technique. Single crystals were obtained from the mother liquor on slow evaporation of the solvent at ambient temperature over a week. X-ray diffraction data were collected on an Oxford Xcalibur diffractometer[7] equipped with an Eos CCD detector (Mo Kα radiation, graphite monochromator, λ = 0.71073 Å). Intensity data were collected using a single crystal with dimensions 0.2x0.18x0.18 mm up to a maximum of 26.81° in the ω–ϕ scan mode. The data were reduced using SAINTPLUS[8]. The structures were solved by direct methods[9] using SHELXS-97 and refined with full matrix least-squares technique[9] by using SHELXL-97. The non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were fixed geometrically and refined isotropically. The H atoms were placed at calculated positions in the riding model approximation (C---H 0.93Å), with their temperature factors set to 1.2 times those of the equivalent isotropic temperature factors of the parent atoms. All other non-H atoms were refined anisotropically. The R factor for observed data finally converged to R=0.0420. The maximum and minimum values of residual electron density were 1.717 and -0.884eÅ^{-3}. Geometry calculations were performed using PLATON[10], ORTEP representations were prepared[11] using ORTEP-3 and packing diagrams[12] were made using CAMERON incorporated in the WinGX[11] software packing. The mean plane calculation was done using the program PARST[13].

Results and Discussion

Figure 1 shows the ORTEP diagram of the molecule with thermal ellipsoids drawn at 50% probability. Figure 2 and 3 shows the hydrogen bond interactions and crystal packing in the compound. The details of crystal data and refinements are given in Table 1. Table 2 shows the respective hydrogen bond interactions for compound.

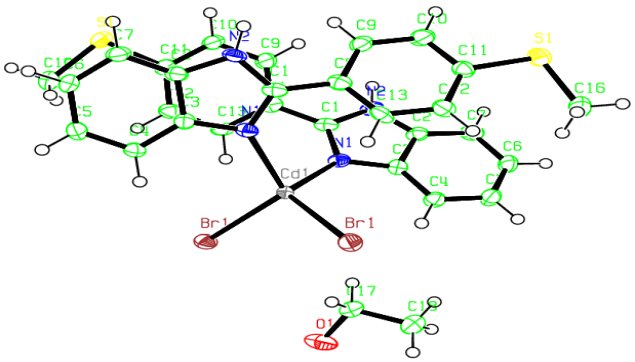


Figure 1. ORTEP view of $Cd(L)_2Br_2.C_2H_5OH$ compound showing 50% probability ellipsoids and the atom numbering scheme

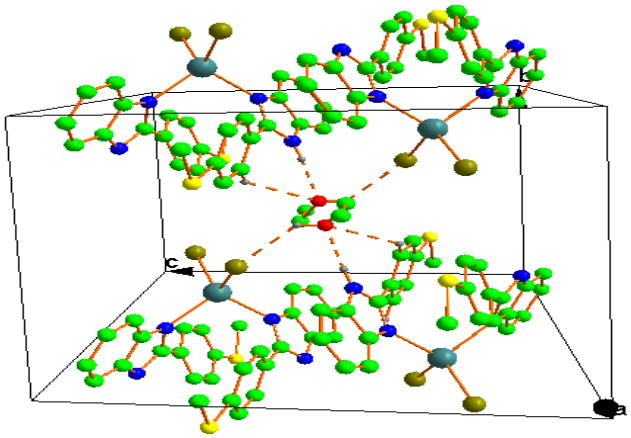


Figure 2. Crystal structure of $Cd(L)_2Br_2.C_2H_5OH$ viewed along '*a*' axis. (Dotted lines indicate intermolecular C─H···Br, N─H···O, O-H…Br and C─H···O interactions)

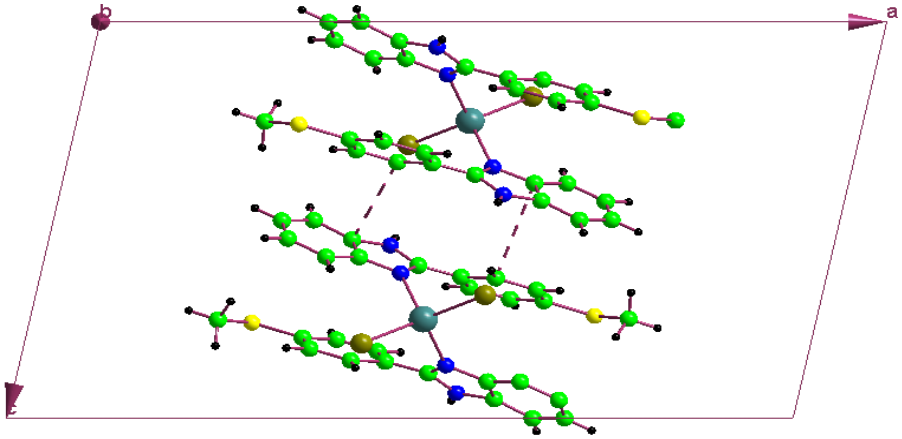


Figure 3. Crystal structure of $Cd(L)_2Br_2.C_2H_5OH$ viewed along '*a*' axis. (Dotted lines indicate π-π stacking interactions between the benzimidazole and thiomethyl phenyl rings)

Table 1. Crystallographic data and structure refinements summary for the compound $Cd(L)_2Br_2.C_2H_5OH$

Empirical formula	$C_{32}H_{36}N_4O_2S_2Br_2Cd.C_2H_5OH$
Formula weight	844.99
Temperature	90(2)K
Wavelength	0.71073Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 24.290(2) Å b = 10.1672(9) Å c = 13.8342(12) Å β = 102.094(5)°
Volume	3340.6(5)Å^3
Z	4
Calculated density	1.680 g/mL
Absorption coefficient	3.206 mm^{-1}
F(000)	1688
Crystal size	0.40x0.35x0.30 mm
Theta range for data collection	1.71 to 26.81°
Limiting indices	-30<=h<=30, 0<=k<=12, 0<=l<=17
Reflections collected / unique	7272 / 7272 [R(int) = 0.0000]
Completeness to theta	26.81 and 99.7%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7272/0/199
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.1007
R indices (all data)	R1 = 0.0539, wR2 = 0.1046
Largest diff. peak and hole (e.Å^{-3})	1.717 and -0.884
Measurement	Bruker SMART CCD diffractometer
Program system	SAINTPLUS
Structure determination	Direct methods (SHELXL97, SHELXS97)
Molecular graphics	ORTEP-3

Table 2. Non-bonded interactions and possible hydrogen bonds (Å) for the complex, $Cd(L)_2Br_2.C_2H_5OH$ (D-donor; A-acceptor; H-hydrogen)

D-H· · ·A	D-H	H···A	D-A	D-H···A
C13-H13…Br1$^{(0)}$	0.950(3)	2.945	3.781(3)	147
N2-H2…O1$^{(1)}$	0.880(3)	1.964(2)	2.842(4)	174
C9-H9…O1$^{(1)}$	0.950(4)	2.733(3)	3.434(4)	131
O1-H1…Br1$^{(1)}$	0.840(3)	2.637	3.241(3)	130

Symmetry code: (0) x, y, z (i) -x,-y,-z+1 (ii) –x+1,-y+1,-z+2

Structure description of the complex, $Cd(L)_2Br_2.C_2H_5OH$

The complex crystallizes in monoclinic crystal system space group C2/c. The benzimidazole and thiomethyl phenyl groups are non-planar and are inclined at a dihedral angle of 35.36°. The thiomethyl group is *cis* to the benzimidazole ring. The molecular structure is primarily stabilized by intramolecular C─H···Br hydrogen bond interaction [C-H = 0.950 Å, H4…N2 = 2.945Å, C4-N2 = 3.781 Å and the angle C─H···N = 147°] leading to the formation of a pseudo seven-membered hydrogen-bonded pattern with graph-set motif S(7), thus locking the molecular conformation and eliminating conformational flexibility.

The N-C and N=C distances were found to be 1.339 Å and 1.355 Å respectively. The *cis* orientation of the thiomethyl group and phenyl ring is characterized by the torsional angle C(11)-C(12)-S(1)-C(16))[6.43(4)°]. The bond lengths and bond angles for the benzimidazole moiety of the molecule are in good agreement, within the experimental errors, with those observed in other benzimidazole derivatives[14].

The crystal structure is stabilized by intermolecular interactions which lead to three dimensional framework structures by the combination of C─H···O, N─H···O. C-H…Br and O─H···Br interactions. The C─H···O and N─H···O interactions generate bifurcated bonds from two donors, N2 and C9 to the same acceptor, O1 linking the dimers so formed into a tape like pattern along '*b*' axis. Further, the O─H···Br and C-H…Br hydrogen bond connects the molecules into chains along '*a*' axis (Figure 1). Additionally, the supramolecular assembly is further stabilized by π-π stacking interactions between the benzimidazole and thiomethyl phenyl rings separated by a centroid-centroid distance of 3.620 Å.

Conclusion

The complex, $Cd(L)_2Br_2.C_2H_5OH$ has been solved by single crystal x-ray diffraction studies. In the crystal structure, the metal ion, Cd(II) exhibits a distorted tetrahedral coordination of the bromine atoms and is located on a general position.

Acknowledgment

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