Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2012, 4(5):2771-2774

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Synthesis, Spectral Characterization and Biological Studies of Cd(II) complexes of 2-Substituted Benzothiazole Derivatives and Amino acids

Premlata and Gita Seth*

Department of Chemistry, University of Rajasthan, Jaipur, India

---

ABSTRACT

Cd(II) complexes of 2-substituted benzothiazole derivatives have been synthesized. The structural features have been determined from their microanalytical, magnetic susceptibility, IR, ^{1}H NMR spectral data. All the Cd(II) complexes exhibit the composition [Cd(L-L)(A-A)] where L-L HPBT, MPBT and A-A, Leucine, Isoleucine, Valine. The N, O, S donor ligands and Amino acids act as a bidentate ligands in all the complexes. Tetrahedral geometry for all the Cd(II) complexes is proposed. The monomeric nature of the complexes was confirmed from their magnetic susceptibility values. All these complexes are coloured, thermally stable and non-electrolytic in nature. These complexes have been screened for their few fungal strains Aspergillus niger and Fusarium oxysporium.

Keywords : 2-Substituted benzothiazole, Amino acids, spectral studies, Antifungal activities.

INTRODUCTION

2-Substituted benzothiazoles and its derivatives one of the most biological active classes of compound possessing a wide spectrum of activities. Literature survey shows that 2-Substituted benzothiazole nucleus is associated with diverse pharmacological activities such as antifungal[1,2], antiviral[3,4], antibacterial[5,6], analgesics[7], antitumor activity[8] and other important pharmaceutical uses[9] such as treatment of inflammatory diseases, tuberculosis[10-12] recently. Metal complexes with 2-substituted benzothiazoles have been the subject of several studies. Earlier work reported that some drugs showed greater activity. as metal complexes when compared to the parent compounds. Several work have been carried out on the transition metal complexes of 2-substituted benzothiazole derivatives. Very less work is done on the synthesis of 2-substituted benzothiazoles and its transition metal complexes involving some amino acids. In this paper efforts were taken for the synthesis, characterization and antimicrobial studies of transition metal complexes containing 2-substituted benzothiazole and amino acids leucine, Ileucine & Valine.

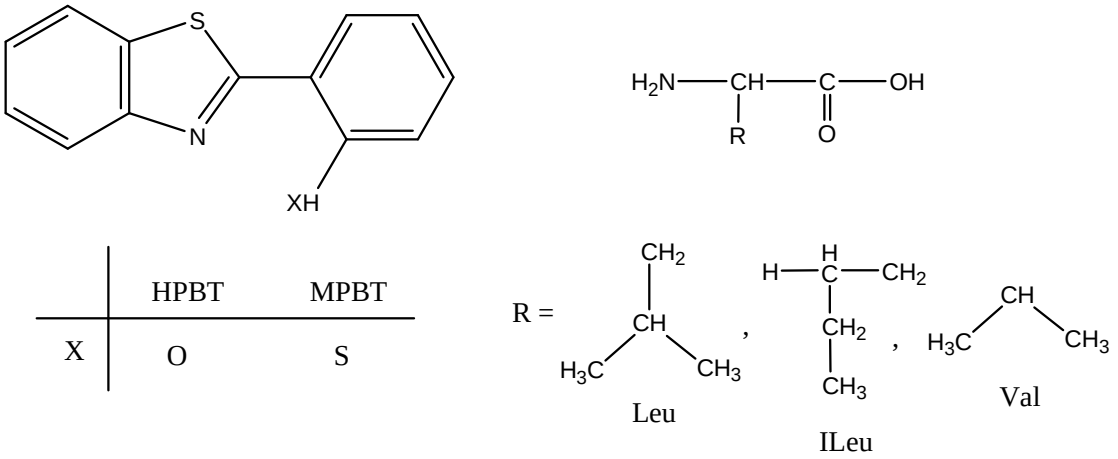
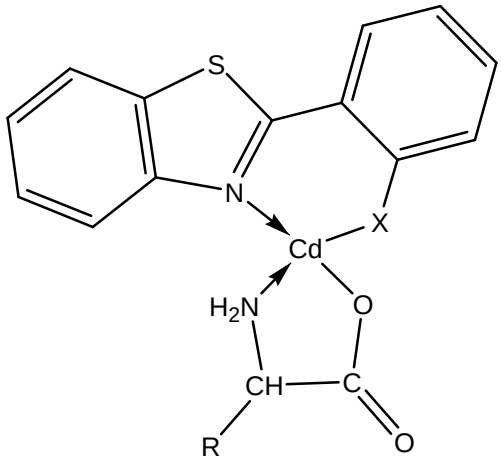


Fig. 1. Structure of the ligands HPBT, MPBT, Leu, Ileu and Val.



X = O, S

R = Leu, Ileu, Val

Fig. 2. The suggested Chemical structures of the Cd(II) ternary complexes.

EXPERIMENTAL SECTION

All the solvents were distilled prior to use, o-aminothiophenol, salilylic acid, thiosalicylic acid, $CdCl_2$ were purchased from Merck and used as such. Microanalysis was carried out at the CDRI Lucknow, India. Melting points were determined on a capillary melting point apparatus and are uncorrect, IR spectra were recorded (with KBr pellets on a SHIMADZU 8400 SPIR spectrophotometer). Molecular weights were determined by the Rast comphor method. Nitrogen was determined by the Kjeldhal's method and sulfur was estimated by the messenger's method. Chloride was determined by the Volhard's method. Cadmium was estimated gravimetrically.

Synthesis of 2-Substituted benzothiazoles (HPBT, MPBT)

The 2-substituted benzothiazoles *viz.* 2(2´-hydroxyphenyl) benzothiazole (HPBT), 2(2´-merceptophenyl) benzothiazole (MPBT) were prepared by o-aminothiophenol (0.1 mol, 1.25 ml) and salicylic acid (0.01 mole, 1.38 g), thiosalicylic acid (0.01 mole, 1.54 g) in polyphosphoric acid (20 ml) using the method reported in literature[17]. The reaction mixture was heated to 200°C under reflux with constant stirring for 4h. The temperature was brought down to 100°C and the contents were poured into a large volume of rapidly stirred water. The resultant stury was made alkaline with 50% NaOH. The crude product was collected by filtration and washed with sufficient amount of water, dried in vacuo and recrystallized from ethanol.

Preparation of Cd(II) ternary complex

To a solution of $CdCl_2$ (0.46 g, 0.1 mole) is dry MeOH (25 ml) was added HPBT (0.56 g, 0.1 mol)/MPBT (0.60, 0.1 mol) and Leucine (0.32 g, 0.1 mol)/ Ileucie (0.33 g, 0.1 mol) / Valine (0.29 g, 0.1 mol) in dry MeOH (25 ml). The reaction mixture was then refluxed in the presence of a drop of pyridine with constant stirring for 4h and allowed to stand at room temperature overnight. These were filtered, recrystallized from EtOH and dried in vaccuo.

RESULTS AND DISCUSSION

Analytical data given in table-1 suggest that ten metal ligand stoichiometry is 1:1:1 and the complexes are monomeric in nature. All the Cd(II) complexes are coloured solids, which are stable to air and moisture and soluble in DMSO and DMF.

Table 1. Analytical data & physical properties of ligands and their Cd(II) ternary complexes .

	Compd. & empirical formula	Colour	M.P. (°C)	Elemental analysis found (Calcd.)					Molecular weight Found (Calcd.)
				C	H	N	S	Cd	
1.	[Cd(HPBT)(leu)] $Cd(C_{19}H_{20}N_2O_3S)$	Light orange	234	48.60 (48.67)	4.20 (4.30)	5.90 (5.97)	6.80 (6.84)	23.18 (23.98)	466.77 (468.85)
2.	[Cd(MPBT)(leu)] $Cd(C_{19}H_{20}N_2O_2S_2)$	Gray	236	47.00 (47.06)	4.15 (4.16)	5.18 (5.78)	13.20 (13.23)	23.10 (23.18)	484.13 (484.91)
3.	[Cd(HPBT)(Ileu)] $Cd(C_{19}H_{20}N_2O_3S)$	Ligh yellow	234	48.65 (48.67)	4.20 (4.30)	5.90 (5.97)	6.80 (6.84)	23.90 (23.98)	468.54 (468.85)
4.	[Cd(MPBT)(Ileu)] $Cd(C_{19}H_{20}N_2O_2S_2)$	Yellowish	235	47.01 (47.06)	4.15 (4.16)	5.68 (5.78)	13.20 (13.23)	23.10 (23.18)	484.74 (484.91)
5.	[Cd(HPBT)(val)] $Cd(C_{18}H_{18}N_2O_3S_2)l$	Creamish	203	47.50 (47.53)	3.00 (3.99)	6.10 (6.16)	7.00 (7.07)	24.16 (24.72)	453.67 (454.82)
6.	[Cd(MPBT)(val)] $Cd(C_{18}H_{18}N_2O_2S_2)l$	Whitish	205	45.11 (45.91)	3.15 (3.85)	5.75 (5.95)	13.60 (13.62)	23.17 (23.87)	468.27 (470.89)

Table 2. IR spectral data (cm^{-1}) of ternary complexes of Cd(II) complexes of 2-substituted benzothiazole and Leucine, Ileucine and Valine.

Compound	γ (C=C)	γ C=N)	γ (C=O)	γ (NH_2) Asym.	γ (NH_2) Sym.	γ □ (Cd γ N)	γ □ O)	(Cd-	γ □ S)	(Cd-
[Cd(HPBT)(leu)]	1435	1605	1608	3350	3208	320	480		-	
[Cd(HPBT)(Ileu)]	1430	1595	1609	3348	3201	322	475		-	
[Cd(HPBT)(Val)]	1461	1605	1611	3345	3208	326	485		-	
[Cd(MPBT)(leu)]	1465	1592	1612	3355	3265	328	662		240	
[Cd(MPBT)(Ileu)]	1466	1590	1608	3350	3264	335	663		230	
[Cd(MPBT)(Val)]	1469	1909	1615	3352	3260	340	665		260	

The broad band at 3400-3350 cm^{-1} due to γ (O-H) phenolic mode of HPBT, disappears in the Cd(II) ternary complexes, indicating the deprotonation of the OH group and coordination of phenolic oxygen to the Cd atom with the formation of Cd-O bond. This gets further support by the appearance of bond in the region 450-670 cm^{-1} due to γ (Cd-O) vibration[18]. The IR spectrum of MPBT shows a band at 2575-2560 cm^{-1} due to γ (S-H) (thiophenolic) vibrations, which disappears in the Cd(II) ternary complexes, suggesting the deprotonation of -SH group and coordination through thiophenolic sulfur with the Cd atom. It is further supported by the appearance of new band in the region 240-260 cm^{-1} due to γ (Cd-S) vibration.

A medium or relatively weak band in the region 1500-1600 cm^{-1} due to γ (C=N) stretching vibrations[19]. This band is shifted to lower frequency by 10-20 cm^{-1} in Cd(II) ternary complexes indicating the bonding of the benzothiazole moiety with Cd atom. It is further confirmed by the appearance of band in the region 320-360 cm^{-1} due to γ (Cd γ N) vibration[20].

Biological activity

The antifungal activity of ligands (HPBT, MPBT) and their ternary Cd(II) complexes were carried out against pathogenic fungi namely *Aspergillus niger* and *Fusarium oxysporium* by radial growth methods. The solution of the test compound were prepared (50, 100 and 200 ppm) in dimethyl formamide. The linear growth of the fungus was recorded by measuring the diameter of the fungus colony after 72 h and the percentage inhibition was calculated as 100 (C-T) /C, whre T are the diameter of the fungus colony in the control and text plates respectively. The results of antifungal activity of the ligands and Cd(II) ternary complexes have been compared with the conventional fungicial bavistin taken as standards (Table-3).

Table 3 : Fungicidal screening data for ligands HPBT, MPBT and their Cd(II) ternary complexes.

Table 3. Fungicidal screening data for the ligands (HPBT, MPBT) and their Cd(II) ternary complexes

Complex	Average % inhibition (concentration in ppm)					
	Aspergillus niger			*Fusarium oxysporium (ppm)*		
	50	100	200	50	100	200
HPBT	28	39	55	30	40	57
MPBT	38	47	60	40	48	64
[Cd(HPBT)(leu)]	71	81	89	73	82	91
[Cd(HPBT)(Ileu)]	72	82	90	74	83	92
[Cd(MPBT)(leu)]	74	84	92	75	88	92
[Cd(MPBT)(Ileu)]	75	85	94	76	90	96
Bavistin	80	90	100	85	92	100

Acknowledgement
This work was supported by grants from the Rajiv Gandhi National fellowship, New Delhi for the award of fellowship.

REFERENCES

[1] P Selvam; PP Radhika; S Janagaraj; AS Kumar, *Res. Biotech.*, **2011**, 2(3).
[2] O Sanja; Podunavac-Kuzmanovic Dragoljub D Cvetkovic, *Chemical Industry & Chemical Engineering Quarterly*, **2011**, 17(1), 9.
[3] G Along; G Kaur; R Kaur; A Singh; R Tiwari, *J Young Pharm.*, **2010**, 2(4), 394.
[4] N Pal; M Kumar;G Seth, *E J Chem.*, **2011**, 8(3), 1174.
[5] NK Sharma; MS Priyanka; KK Jha , *J Pharm Res.*, **2010**, 3(5), 969.
[6] HM El-Shaaer; SA Abdel-Aziz; HA Allimony; UF Ali; RM Abdel-Rahman, *Pharmazi.*, **1997**, 52(8), 285.
[7] A Gupt; S Raat, *J Curr Pharma Res.*, **2010**, 3(1), 13.
[8] I Hutchinson; SA Jennings; BR Vishnuvajjala; AD Westwell; Stevens M F G, *J Med Chem.*, **2002**, 45, 744.
[9] CA Mathis; YM Wang; DP Holt; GF Huang; ML Debnath; WE Lunk, *J Med Chem*., **2003**, 46, 2740.
[10] J Das J, RV Moquin; C Liu; AM Doweyko; HF Defex; Q Fang; S Pang; S Pitt; DR Shen; GL Schiever; JC Barrish, *Bioorg Med Chem Lett.*, **2003**, 13, 2587.
[11] B Gong; F Hong; C Kohm; L Bonham; P Klin, *Bioorg Med Chem Lett.*, **2004**, 14, 1455.
[12] I Hutchinson; TD Bradshaw; CS Matthew; MFG Stevens; AD Westwell, *Bioorg Med Chem Lett*., **2003**, 13, 471.
[13] AM Khedr; DF Draz, *J Coord Chem.*, **2010**, 63(8), 1418.
[14] A Patra; S Sarkar; R Chakraborty; MGB Drew; P Chattopadhyay , *J Coord Chem.*, **2010**, 63(11), 1913.
[15] M Sonmez; M SederwM, *Synth React Inorg Met-Org Chem.*, **2004**, 34, 485.
[16] M Sonmez; MR Bayram; M Celebi, *J Coord Chem.*, **2009**, 62(16), 2728.
[17] PC Vyas; CK Ojha; AK Goyal, *Chem Ind*., 1980, 287.
[18] KM Ibrahim; MM Bekheit; AGM Reash, *Transition Met Chem.*, **1991**, 16, 189.
[19] B Ulkuseven; A Tavman, *Trans Met Chem.*, **2001**, 26, 723.
[20] Shivakumaraiah ;N M N Gowda, *Indian J Chem.*, **2003**, 42A, 1856-1860.