

## **PREPARATION AND CHARACTERIZATION OF Zn (II) AND Cd (II) COMPLEXES WITH N, N-BIS (2-METHYLBENZIMIDAZOLYL)-p-TOLUIDINE**

**IRSHAD ALI**

*Department of Chemistry, B.N. College, Patna University, Patna*

**AND**

**MD. ATHAR SHADIQUE**

*Department of Chemistry, L.N. Mithila University, Darbhanga*

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N, N-Bis(2-methylbenzimidazolyl)- p-toluidine (C<sub>23</sub> H<sub>11</sub> N<sub>5</sub>) is tripodal ligand (NNN) and coordinates as neutral molecule and form diacido complexes MLX<sub>2</sub> (M = Zn<sup>II</sup> or Cd<sup>II</sup> and X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> CH<sub>3</sub>COO<sup>-</sup> and NCS<sup>-</sup>). The electrical conductance values of freshly prepared DMF solution of complexes show negligible electrical conductance values (10-12 ohm<sup>-1</sup> mol<sup>-1</sup> cm<sup>2</sup>) suggesting coordination of acid ions in complexes. The ir spectral studies of diacetato and diisothiocyanato complexes indicated mono coordination of anions. The NCS<sup>-</sup> group  $\nu$ (C = N) stretch (2080 and 2095 cm<sup>-1</sup>) suggested N-bonding of thiocyanate group. The infrared  $\nu$ (C = N) stretch of free ligand observed at 1632 cm<sup>-1</sup> shifted to lower frequencies and observed near 1610-1595 cm<sup>-1</sup> in complexes due to withdrawal of electron cloud of lone pair of donor nitrogen atoms towards metal atom in bond formation. From Stoichiometry and considering d<sup>10</sup> electronic system of Zn (II) and Cd (II) five coordinated trigonal bipyramidal structure (sp<sup>3</sup>d) hybrid bonding is suggested in these complexes.

**KEYWORDS :** Bis (2-methylbenzimidazolyl)-p-toluidine, Tripodal ligand.

### **INTRODUCTION**

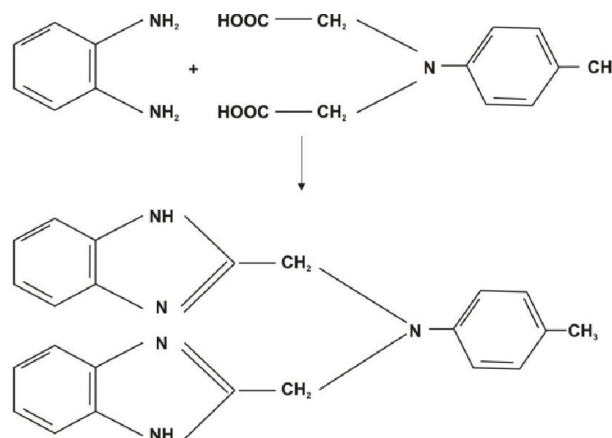
The interest towards coordination complexes of benzimidazole derivatives arose due to medicinal and biologically active imidazole nucleus present in it and till date more than hundred benzimidazole derivatives are used clinically for the treatment of most of the chronic, viral and bacterial diseases in living system [1-10]. The zinc (II), next to iron, is the most vital metal in physiological system, which is responsible for various enzymatic reactions taking place in body. Carboxypeptidase and carbonicanhydrase are most vital zinc enzymes among them [11]. Cadmium is one of the heavy pollutants and it inhibits various enzymatic reactions in physiological system [11]. It is one of the hazardous element and affect central nervous system as well. Due to biological significance of zinc and cadmium, we have prepared some diacido complexes of zinc (II) and cadmium (II) and characterise them from physicochemical studies.

## EXPERIMENTAL

The chemicals used were obtained from E. Merck. The results of elemental analysis and IR spectra were obtained from CDRI Lucknow.

### Preparation of ligand

The ligand bis (2-methylbenzimidazolyl) p-toluidine ( $C_{23}H_{11}N_5$ ) was prepared by condensing p-toluidine-N, N-diacetic acid with 2-molar proportion of o-phenylenediamine in polyphosphoric acid at 160-170°C.



N, N-bis (2-methyl benzimidazolyl)-p-toluidine

The ligand was recrystallised with ethanol and the m.p. of product found was, 189°C. It has satisfactory elemental analysis.

### Preparation of complexes

About 10 milimole of metal halide, acetate or thiocyanate was dissolved in hot methanol and treated with equimolar proportion of ligand in methanol. The resulting solution was concentrated to small volume and kept at room temperature for crystallization. The products separated were collected at buckner funnel and washed with a little cold methanol. The products were dried over  $CaCl_2$  in desiccator and analysed. The results of elemental analysis of ligand and its complexes are given in Table-A. The analytical results of the products correspond well to composition of  $MLX_2$  ( $X = Cl^-, Br^-, I^-, NCS^-$  and  $CH_3COO^-$  and  $M = Zn^{II}$  or  $Cd^{II}$ ).

Table A

Compound	% of elemental found (calculated)				
	Metal M	Carbon C	Hydrogen H	Nitrogen N	Anion X
Ligand =L ( $C_{23}H_{11}N_5$ )	-	74.99 (75.20)	5.78 (5.72)	18.95 (19.07)	-
$ZnLCl_2$	12.60 (12.91)	54.65 (54.82)	3.98 (4.17)	12.78 (13.90)	14.50 (14.10)

ZnLBr <sub>2</sub>	11.80 (11.03)	46.98 (46.59)	3.99 (3.54)	11.67 (11.80)	27.27 (27.08)
ZnLI <sub>2</sub>	9.68 (9.52)	40.43 (40.21)	3.56 (3.05)	10.28 (10.19)	37.50 (37.00)
ZnL(NCS) <sub>2</sub>	11.79 (11.92)	54.98 (54.70)	3.87 (3.82)	18.00 (17.87)	11.40 (11.60)
ZnL(CH <sub>3</sub> COO) <sub>2</sub>	11.56 (11.88)	58.67 (58.86)	4.25 (4.90)	12.56 (12.71)	11.20 (11.62)
CdLCl <sub>2</sub>	20.32 (20.42)	49.9 (50.14)	3.73 (3.81)	12.51 (12.71)	12.56 (12.89)
CdLBr <sub>2</sub>	18.00 (17.58)	43.13 (43.14)	3.83 (3.28)	10.08 (10.94)	24.98 (25.02)
CdLI <sub>2</sub>	15.23 (15.32)	38.12 (37.63)	2.58 (2.86)	9.32 (9.54)	35.60 (34.63)
CdL(SCN) <sub>2</sub>	18.78 (18.87)	49.80 (50.38)	3.42 (3.52)	16.28 (16.45)	10.82 (10.74)
CdL(CH <sub>3</sub> COO) <sub>2</sub>	18.02 (18.81)	53.98 (54.23)	4.35 (4.51)	11.31 (11.71)	10.25 (10.71)

## RESULTS AND DISCUSSION

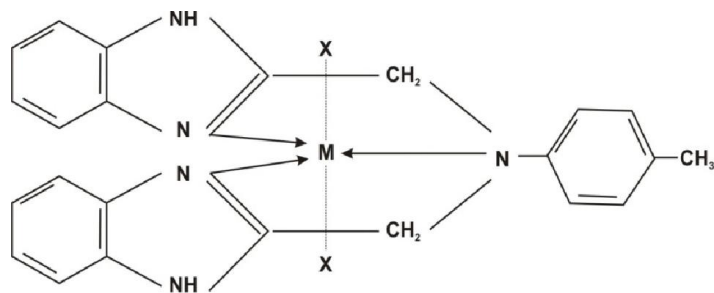
The ligand N, N-bis (2-methylbenzimidazolyl-p-toluidine (bmbzt) is potential tridentate coordinating molecule and forms diacido complexes with zinc (II) and cadmium (II) of composition [M (bmbzt) X<sub>2</sub>].



The complexes were unaffected by air and were stable to heat below 280-300°C. The complexes are diamagnetic as expected for compound of element having d [10] electronic system. The ligand is soluble in organic solvents. The ethanol solution of ligand shows three prominent electronic transitions located at 215, 248 and 292 nm attributable  $\sigma - \sigma^*$ ,  $\pi - \pi^*$  and  $n - n^*$  transition. The electronic absorption spectra of complexes shows a strong absorption band near 340-350 nm attributed to charge transfer transition. The complexes are fairly soluble in DMF. The DMF solution of complexes show negligible electrical conductance value indicating that complexes [M(bmbzt) X<sub>2</sub>] are non-conducting and anions X are bonded and coordinated to metal atom [12]. The ligand has donor sites (NNN) as tripod and anions must be attached at axial position forming trigonal bipyramidal shape of complexes.

The ir spectrum of ligand shows benzimidazole ring  $\nu(\text{NH})$  band at 3248-3254  $\text{cm}^{-1}$  and is retained in complexes suggesting that NH nitrogen is not involved in coordination. The  $\nu(\text{C} = \text{N})$  of benzimidazole ring is observed at 1632  $\text{cm}^{-1}$  which is shifted to lower frequency and observed at 1610-1595  $\text{cm}^{-1}$ , supporting coordination of tertiary benzimidazole ring nitrogen atoms [13, 14, 15]. The tertiary amine (-N-) group (C-N) stretch of ligand located at 1250  $\text{cm}^{-1}$  is affected and raised to high frequency on coordination. The thiocyanates group  $\nu(\text{C} = \text{N})$  vibrations in complexes were observed at 2080 and 2095  $\text{cm}^{-1}$  for Zn (II) and Cd (II) complexes respectively, supporting the coordination of NCS through nitrogen atom

[15]. From above observation a trigonal bipyramidal structure may be suggested for these  $[M(\text{bmbzt})\text{X}_2]$  complexes, as shown below.



( $X = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{NCS}^-$  or  $\text{CH}_3\text{COO}^-$ )  
 $M = \text{Zn}^{II}$  or  $\text{Cd}^{II}$ )

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