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Preparation and Characterization of Binuclear Complexes of NN'NN" tetrakis (2-methylbenzimidazolyl) *p*-phenylenediamine with Zn (II) and Cd (II)

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ABSTRACT: The binuclear complexes of NN'NN" tetrakis (2-methylbenzimidazolyl) *p*-phenylenediamine (L) with Zn (II) and Cd (II) having composition M_2LX_4 (M=Zn^{II} and Cd^{II}, X=Cl , NCS and CH_3COO) have been prepared and characterized from the studies of elemental analysis, electrical conductance measurement, magnetic susceptibility, UV and IR spectral analysis. The electrical conductance value of complexes in DMF shows negligible electrical conductance value at 30°C (~ 10-12 Ohm^{-1} mol^{-1} cm^2) supported the coordination of anions with metal ions. IR data of thiocyanato complexes suggested N-bonding of NCS group in Zn (II) and through S atom in Cd (II) complexes. The stoichiometric and spectral data supported trigonal bipyramidal geometry of these binuclear complexes.

Keywords: Binuclear complexes; Elemental analysis; tetrakis (benzimidazole) and derivative complexes.

INTRODUCTION: Benzimidazole is a heterocyclic binuclear aromatic compound formed by the fusion of benzene and imidazole nucleus. Benzimidazole and substituted benzimidazoles have been found to form stable complexes with various metal ions and some of them have been found to be analytical reagents for gravimetric estimation of metal ions.[1-2]

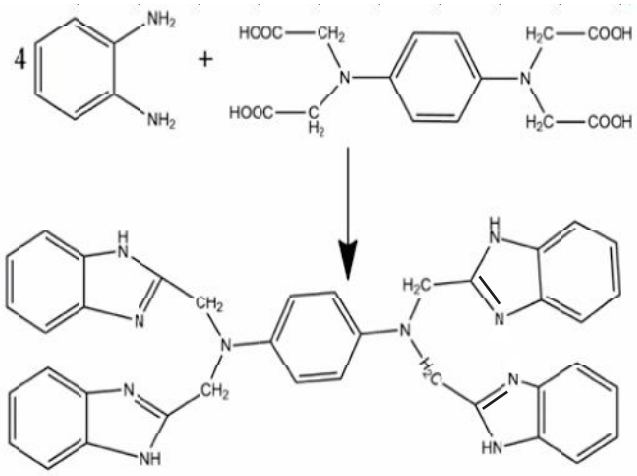
Benzimidazole derivatives play an important role in medicinal uses having a number of pharmacological activities and used as antidiabetic, anticancer, antibacterial, antiparasitic, antihypertensive, antiulcer, antifungal, antitumor, anti-inflammatory, antioxidant, antiprotozoal medicines. [3-8]

The immense pharmacological industrial and medicinal potentiality of benzimidazole derivative and their metal complexes tempted us to persue research work on some metal complexes of new benzimidazole derivatives of biological interest. [9-13]

In present investigation, we have prepared and characterized the complexes of Zn (II) and Cd (II) with NN'NN" tetrakis (2-methylbenzimidazolyl) *p*-phenylenediamine (tmbzp).

MATERIALS AND METHODS: Metal salts and solvents used were extra pure reagent of E. Merck or Anal-R Grade chemical of B.D.H. The result of elemental analyses and IR, UV spectra were obtained from CDRI Lucknow.

Preparation of ligand:



[Structure of The ligand NN' NN" tetrakis (2-methylbenzimidazolyl) *p*-phenylenediamine]

The ligand NN' NN" tetrakis (2-methylbenzimidazolyl) *p*-phenylenediamine ($C_{38}H_{32}N_{10}$) was prepared by condensing *p*-phenylene-N,N'-tetra acetic acid with 4-molar proportion of o-phenylenediamine in polyphosphoric acid at 160-170ºC. The ligand was recrystallised with hot ethanol and the m.p. of product found was, 212ºC. It has satisfactory elemental analysis.

Preparation of complexes: About 10 milimole of metal chloride / acetate / thiocyanate was dissolved in hot methanol and treated with methanol solution of five milimole of ligand (tmbzp) and refluxed on steam bath for one hour. The resulting solution was concentrated to small volume and kept at room temperature for crystallization. The products separated were collected on buckner funnel and washed with a little cold methanol. The complexes were dried over $CaCl_2$ in a 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 with composition of M_2LX_4 (L=tmbzp, X=Cl^-, NCS^- and CH_3COO^- and M = Zn^{II} or Cd^{II}).

Table 1: Analytical Results of lignad and its complexes.

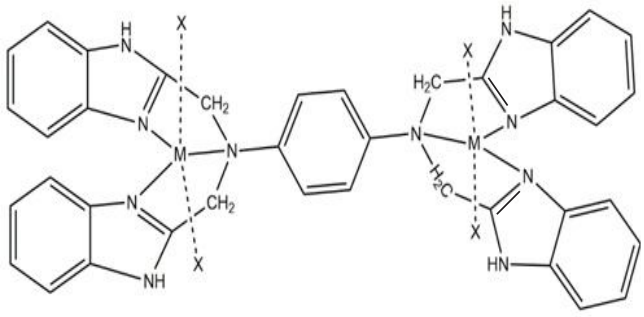
Compound	% of elemental found (calculated)				
	Metal M	**Carbon C**	**Hydrogen H**	**Nitrogen N**	**Anion X/S**
Ligand =L ($C_{38}H_{32}N_{10}$)	-	72.33 (72.61)	4.93 (5.09)	22.01 (22.29)	- -
Zn_2LCl_4	14.35 (14.51)	50.52 (50.62)	3.22 (3.55)	15.21 (15.54)	15.64 (15.76)
$Zn_2L(NCS)_4$	13.18 (13.19)	50.46 (50.86)	3.32 (3.22)	19.58 (19.78)	12.72 (12.91)
$Zn_2L(CH_3COO)_4$	13.12 (13.14)	55.32 (55.48)	4.12 (4.42)	14.01 (14.07)	- -
Cd_2LCl_4	22.42 (22.59)	45.73 (45.83)	3.11 (3.21)	14.01 (14.07)	14.15 (14.27)
$Cd_2L(SCN)_4$	20.62 (20.72)	46.32 (46.45)	2.85 (2.94)	18.03 (18.06)	11.87 (11.79)
$Cd_2L(CH_3COO)_4$	20.63 (20.64)	50.78 (50.69)	4.02 (4.04)	12.95 (12.85)	- -

RESULTS AND DISCUSSION: The ligand NN'NN" tetrakis (2-methylbenzimidazolyl- *p*-phenylendiaminine (tmbzp) is a potential hexadentate coordinating molecule and forms diacido complexes with zinc (II) and cadmium (II) of composition $[M_2(tmbzp)X_4]$ in hot methanol (M = Zn^{II} or $Cd^{II}$and X = Cl^-, NCS^- and CH_3COO^-).

The complexes were unaffected by air and were stable to heat below 150º C and decomposes above 290-295º C without giving clear melting point. The complexes are diamagnetic as expected for compounds of element having d^{10} electronic system. The ethanol solution of ligand shows three prominent electronic transitions located at 212, 258 and 298 nm attributable $\sigma - \sigma*, \pi - \pi*$ and n– n* transitions.[14-15] The electronic absorption spectra of complexes shows a strong absorption band near 340-350 nm attributed to (M→L) charge transfer transition.[15] The complexes are fairly soluble in DMF. The DMF solution of complexes show negligible electrical conductance value (10-12 ohm^{-1} $mol^{-1}cm^2$ at 30º C) indicating that complexes [M(tmbzp) X_2] are non-conducting and anions X are bonded and coordinated to metal atoms[17]. The ligand has, donor sites (NNN) as tripod molecule and anions must be attached at axial position forming trigonal bipyramidal shape of complexes having sp^3d hybrid bonding.

The IR spectrum of ligand shows benzimidazole ring υ(NH) band at 3241-3252 cm^{-1} and is retained in its complexes suggesting that NH nitrogen is not involved in coordination. The υ(C = N) of benzimidazole ring is observed at 1642 cm^{-1} which get shifted to

lower frequency and observed at 1612-1598 cm^{-1}, supporting coordination of tertiary benzimidazole ring pyridine nitrogen atoms.[14-16] The tertiary amine (-Ṅ-) group (C-N) stretch of ligand located at 1250 cm^{-1} is affected and raised to high frequency on coordination . The shift of υ(C-N) of tertiary amine nitrogen indicated that tertiary amine nitrogen is third donor site of tmbzp. The thiocyanates group υ(C = N) vibrations of complexes were observed at 2095 cm^{-1} as strong and broad band for Zn (II) and at 2115 cm^{-1} as sharp band for Cd (II) complexes respectively, supported the coordination of NCS through nitrogen atom in Zn(II)and through S atom in Cd (II) complexes.[10] From the above observations a trigonal bipyramidal structure may be suggested for these [M_2 (tmbzp) X_4] complexes, as shown below.



M_2 (tmbzp) X_4]
[X=Cl^-, NCS^- or CH_3COO^- and M=Zn^{II} and Cd^{II}]

[Probable Structure of Complexes]

CONCLUSION: In summary we have reported here a suitable and facile method for preparation of Zn and Cd metal complexes having benzimidazole based ligand. All the characterization data and elemental analysis results were in good agreement with illustrated structures of metal complexes. Our present study is very useful for synthetic as well as medicinal perspective.

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