



Studies Of Zinc (II), Cadmium (II) & Lead (II) Complexes Of N-(5-Bromo-Naphthyl)-2- Mercapto Propanamide & N-(5-Methoxy Naphthyl)-2- Mercapto Propanamide Macro Organic Ligands

V. K. Pathak

Department of Chemistry*, Institute of Technology and Management, GIDA, Gorakhpur, Uttar Pradesh, India

P. R. Pandey

Department of Chemistry, J.P. University, Chapra, Bihar, India

ABSTRACT Some novel complexes of ligands N – (5-Bromo-Naphthyl) -2- mercapto propanamide and N- (5-methoxy Naphthyl) -2- mercapto propanamide with Zn(II), Cd(II) and Pb(II) were prepared. The ligands and their metal complexes were characterized by Physico – chemical spectroscopic techniques. The spectral data suggested the deprotonation of thiol (-SH) group and its coordination to the metal ions in complexes. It was also suggested to involve NH group in coordination to the metal ion through nitrogen atom. Further, spectroscopic studies suggested tetrahedral, octahedral Zn(II) complexes, tetrahedral, distorted octahedron Cd(II) complexes and square pyramidal geometry Pb (II) complexes.

KEYWORDS : N – (5-Bromo-Naphthyl) -2- mercapto propanamide (L), N – (5-methoxy- Naphthyl) -2- mercapto propanamide (L'), deprotonation, thiol.

1. Introduction

Ligands containing sulphur and Nitrogen donors are quite interesting and form an active field of current research in co-ordination chemistry. A large volume of works have been reported on the complex behavior of sulphur and nitrogen donor ligands, yet donor characteristics of ligands N- (5-Bromo-Naphthyl) -2- mercapto propanamide and N – (5-methoxy- Naphthyl) -2- mercapto propanamide offer scope for further studies. In the present work an attempt has been made to investigate the donor behavior of the above ligands with Zn (II), Cd(II) and Pb(II). To study the co-ordination behavior of chelates having sulphur and nitrogen atoms, a survey of work on such ligands (already reported) have been made. 2- amino ethane thiol is the simplest representative of this class of chelating agent. In our work the approach developed by Garrels and Thompson (1962) has been expanded to include higher order complexes and applied to the divalent ions of Zn, Cd, Pb. The stability constants for the complexes with Zn (II), Cd(II) had been determined [18] earlier. Jicha and Bush [19, 20] made detailed study of the complexes of these ligands and observed that two type of complexes are formed with transition metal ions viz. the monomeric bis ligand complexes $M(H_2NCH_2S)_2$ ($M=Zn$) and tri nuclear cationic complexes of which Pb(II) derivative have been confirmed by x-ray diffraction. Single crystal x-ray diffraction analysis showed that the Cd (II) lies in distorted octahedron co-ordination geometry. Larkworthy *et. al.* [48] reported the preparation of 2-amino benzene thiol complexes of Zn (II) under anaerobic conditions. The Cd (II) and Pb (II) complexes of the dibasic form have been reported. Complexes of 2-mercapto benzothiazole with Zn (II), Pb (II), and Cd (II) have been reported by Agrawal *et. al.* [47].

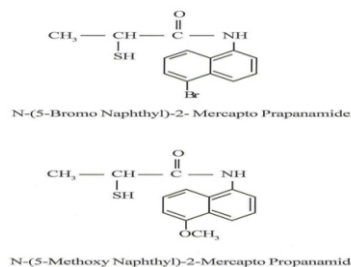
2. Experimental

2.1 Materials and Preparation

All chemicals were obtained from commercial sources and used without further purification. 5-Bromo-1-naphthyl amine and 2-mercapto acetic acid were taken from MERCK.

N-(5-Bromo-Naphthyl)-2-mercapto propanamide was prepared by the method reported in literature [1, 2]. Equimolecular proportions of 5-Bromo-1-naphthyl amine 0.1 mole and 2- mercapto acetic acid were mixed in a 500ml conical flask and heated in a glycerine bath maintained at 110^o-120^oC for about 2 to 2.5 hours in a slow current of CO₂. A solid was obtained when the ligand was poured in to a beaker of water. It was filtered and crushed to powder in a mortar and then washed with dil.HCl and water to remove unchanged amine and thio acetic acid respectively.

Further purification of the obtained compound was made by repeated recrystallisation from dil. Alcohol (122^oC melting point). It was then dried in vacuum desiccator. N- (5-methoxy- Naphthyl) -2- mercapto propanamide was prepared as above except 5-methoxy-1-naphthyl amine was used in the place of 5-Bromo-1- naphthyl amine.



2.2 General Procedure

The alcoholic solution of 0.0051M metal bromide/acetate alcoholic solution of 0.11M ligand was added slowly and refluxed for one hour. The pH of refluxed solution was raised to 8. The separated solid complex was filtered, washed with alcohol and dried. Ethanol solution of metal chloride ethanolic ligand solution was mixed together in 0.11M ratio. About 2 ml of appropriate base at low temperature. On cooling ppt separated out. The contents on dilution with water ensured the complete precipitation. The precipitate was filtered, washed with water, followed by several portions of alcoholic water and aqueous pyridine solution. The precipitate was dried in desiccators over CaCl₂.

2.3 Detection Method

About 0.5 gm of complex was decomposed with HNO₃ and HClO₄ mixture. After decomposition, the zinc content was precipitated as oxinate. The precipitate was dried at 130^o-140^oC in an oven. It was weighed as dried at 130^o-140^o C in oven. It was weighed as Zn(C₇H₆NO)₂. The chemical factor for Zinc is 0.1849.

The cadmium complex was decomposed with HClO₄ and HNO₃. After decomposition the cadmium content of the complex was estimated as salicyldoximate. In the presence of sodium acetate as hite granular and acetic acid at pH=5.6, cadmium salicyldoximate was separated. The complex was digested on steam bath, cooled, filtered, washed thoroughly with water and weighed after drying at 100-105^oC as Cd(C₇H₆O₂N)₂.

The lead complex was decomposed with HClO₄ and HNO₃. After decomposition the lead content of the complex was estimated as salicyldoximate. In the presence of sodium acetate as hite granular and acetic acid at pH=5.6, lead salicyldoximate was separated. The complex was digested on steam bath cooled, filtered, washed thoroughly with water and weighed after drying at 110-115^oC as Pb(C₇H₆O₂N)₂.

3. Results and Discussion

The prepared complexes were found to be solid, insoluble in water but they were soluble in dimethyl sulfoxide (DMSO). Moreover the metal complexes were found to be non-conducting in DMSO as the molar

conductance values of these complexes were very low (Burger, 1973; Kettel, 1975; Shayma et al, 2009-2010). Luminescence behavior in the presence of quenching Pb(II) and non-quenchingness e.g. Cd(II) & Zn(II). However, the analytical data for the metal complexes given in the table were found to be in agreement with the proposed molecular formula.

Joshi & Bhattacharya determined the formation constants of Cd (II), Zn(II) and Pb(II) by using the Irving –Rossotti titration method.

Table 1: Formation constants for complexes at 0.1M ionic strength.

Complexes	Zn	Pb	Cd
ML ₂	16.3	18.2	16.5
ML ₂	4.9	4.8	3.8
ML ₄	6.5	6.1	5.4
ML ₄	7.2	6.8	7.0
ML ₆	6.5	7.0	6.0
ML ₆	7.3	7.2	7.1

The thermodynamic stability of the Pb(II), Cd(II), Zn(II) complexes with the diammine macro organic ligands has been investigated by pH potentiometric titration at 25°C in 0.1M KNO₃. The stability constant vary in the following order Cd(II) > Zn(II) ~ Pb(II).

3.1 Electronic Spectral Studies of Complexes

The Cd and Zn complexes show only the charge transfer transitions which can be assigned to charge transfer from the ligand to the metal and vice-versa, no d-d transition are expected for d¹⁰ Zn(II) and Cd(II) complexes. In the electronic spectra of both complexes recorded in aceto nitrile solution.

3.2 I.R. Spectral Studies of Ligand and Complexes

The ligand contains the following main moieties active to I.R spectral studies:

Amide, -NH, -SH, aromatic nucleus, C-S, C=O Amide skew strong absorption owing to carbonyl stretching vibrations in the region 1785-1625cm⁻¹. The absorption owing to the carbonyl stretching vibration of amide is very markedly dependent upon the method of determination. N-methylacetamide is reported to absorb at 1715cm⁻¹ in the vapor state.

Table 2: I.R. Bands of ligands and metal complexes

Compounds	-NH cm ⁻¹	(C=O) cm ⁻¹	-SH cm ⁻¹	M-N cm ⁻¹	M-S cm ⁻¹	MO cm ⁻¹
LH	3255 s	1655 s	2565 w	—	—	—
LH	3260 s	1653 s	2560 w	—	—	—
[Zn L ₂]	3248	1653	—	306	272	—
[Zn]	3250	3650	—	305	270	—
[Pb L ₂]	3250	1647	—	307	270	—
[Pb]	3250	1650	—	307	273	—
[Cd L ₂]	3245	1650	—	306	270	—
[Cd]	3248	1648	—	303	275	—

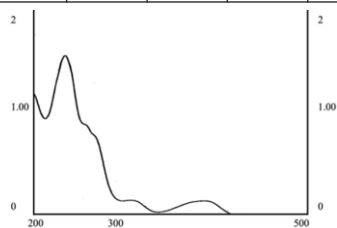


Figure 1: Electronic Spectrum of [ZnL₂]Cl

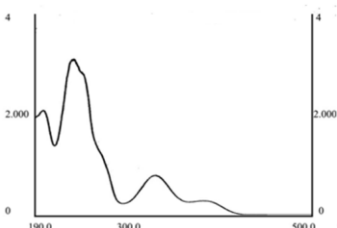


Figure 2: Electronic Spectrum of [CdL₂]NO₃

4. Conclusions

The electronic absorption and reflectance spectra at Cd(II) complex were determined and the bands position of these complexes have been recorded. The electronic absorption spectra I ethanol or acetone of the ligands do not exhibit any d-d bond rather they exhibit two intense bands near 220-225 nm and 270-275 nm region (LH-224-280, L/H-220-275 nm) respectively. These bands are attributed to (C=O) and (C=N) groups of the ligand molecules.

The IR spectra of the ligands and complexes have to be interpreted in terms of shifts of absorptions and/or change in intensity of frequency of groups involved in co-ordination. The ligand LH and L/H has possibilities of co-ordination through the following donor groups or atoms.

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