

STUDIES OF SOME NOVEL METAL COMPLEXES OF SOME MACRO ORGANIC LIGANDS CONTAINING NITROGEN AND SULPHUR AS POTENTIAL DONOR ATOMS

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ABSTRACT

Some novel complexes of ligands N – (5-Bromo-Naphthyl) -2- mercapto propanamide and N- (5-methoxy Naphthyl) -2- mercapto propanamide with Cu(II), Ni(II) and Co(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 Cu(II) complexes, octahedral Ni(II) complexes and square planar as well as octahedral Co(II) complexes.

Keywords: N-(5-Bromo-Naphthyl) -2- mercapto propanamide (L), N-(5-methoxy- Naphthyl) -2- mercapto propanamide (L').

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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 works¹⁻¹⁷ 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 Cu (II), Co(II) and Ni(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. Jensen¹⁷ first observed the formation of Ni (II) complexes of 2-amino ethane thiol in solution. The stability constants for the complexes with Co (II), Ni(II) had been determined¹⁸ 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=Ni) and tri nuclear cationic complexes of which nickel derivative have been confirmed by x-ray diffraction.

EXPERIMENTAL

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-Naphtyl)-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 110⁰-120⁰ C 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 (122⁰c 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.

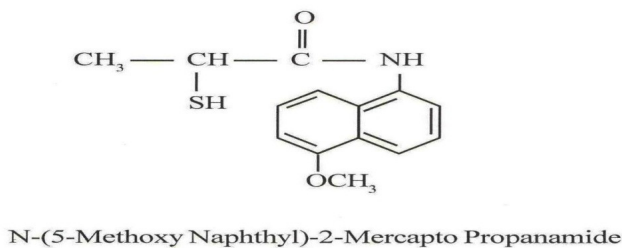
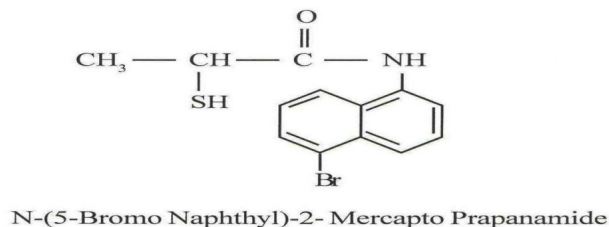


Fig.-1

General Procedure

Metal complexes were formed when 0.0051M of metal halide and 0.11M of ligand were dissolved separately in minimum quantity of alcohol and then mixed together. The mixture was refluxed on water bath for one hour with few drops of acetic acid in case of acetate. The pH of refluxed solution was raised to eight and diluted with distilled water. The solid chelate so obtained in each case was filtered and washed several times with hot water. It was finally washed with alcohol and dried in a desiccator over calcium chloride.

Detection Method

About 0.5 gm of complex was weighed and decomposed in pyrex beaker by repeated evaporation with HNO₃ and HClO₄ until the clear solution was obtained with HCl, the solution was reduced after dilution with water. The clear solution of copper is used to estimate the value of copper either Iodometrically or Gravimetrically. In the presence of acetic acid, at pH 2.6, copper salicyldoximate, [Cu (C₇H₆O₂N)₂] was obtained as green precipitate. The calculation of quantity of copper was done by using the chemical factor 0.18922. In slightly ammonical medium the precipitation of nickel was carried out. For removal of excess of ammonia the red complex of nickel dimethylgly oxime formed was digested over steam bath. The precipitate was cooled to room temperature and filtered through previously washed sintered glass crucible. After drying the complex at 110-120⁰C as Ni(C₄H₇O₂N₂), the precipitate was weighed. The metal content was calculated by the factor 0.20319.

0.5 gm of cobalt complex was weighed in a weighed silica crucible and ignited slowly on free flame for about half an hour. The crucible was cooled and placed in an electric furnace. To the ignited cobalt complex a few drops of HNO₃ and conc. H₂SO₄ was added to convert it in to sulphate. The crucible was covered and heated in electric furnace maintained at 450 – 500⁰C. By repeated addition of HNO₃, H₂SO₄ and heating in electric furnace the cobalt was completely converted in to sulphate. The crucible was cooled in desiccators and cobalt content weighed as CoSO₄. The metal content was calculated by multiplying the weight of CoSO₄ with the factor 0.38023.

RESULTS AND DISCUSSION

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

as the molar conductance values of these complexes were very low²¹⁻²³. However, the analytical data for the metal complexes given in the table were found to be in agreement with the proposed molecular formula.

Table-1

S. No.	Complexes	Mode	% M	% C	% H	% N	% S	% Br
1.	[Cu L ₂ 2H ₂ O]H ₂ O	Found	8.61	42.45	3.81	3.79	8.71	21.72
		Cal	8.64	42.43	3.80	3.80	8.70	21.73
2.	[Cu L ₂ Py ₂]	Found	7.56	51.45	3.82	6.68	7.61	19.06
		Cal	7.57	51.46	3.81	6.67	7.62	19.05
3.	Cu L ₂ ' (Py-O)	Found	7.28	49.59	3.68	6.41	7.33	18.33
		Cal	7.29	49.51	3.67	6.42	7.34	18.36
4.	[Cu L ₂ ' 2H ₂ O]H ₂ O	Found	9.95	52.71	5.33	4.38	10.02	-----
		Cal	9.96	52.70	5.33	4.38	10.03	-----
5.	[Cu L ₂ ' (α-pic) ₂]	Found	8.26	62.34	5.45	7.29	8.32	-----
		Cal	8.25	62.37	5.46	7.28	8.31	-----
6.	[Cu. L ₂ ' (α-pic-O) ₂]	Found	7.91	59.87	5.23	6.99	7.99	-----
		Cal	7.93	59.88	5.25	6.98	7.98	-----
7.	[Ni L ₂ 2H ₂ O]H ₂ O	Found	8.04	42.72	3.82	3.82	8.75	21.89
		Cal	8.03	42.71	3.83	3.83	8.76	21.87
8.	[Ni L ₂ ' Py ₂]	Found	7.02	51.79	3.82	6.70	7.68	19.16
		Cal	7.03	51.76	3.83	6.71	7.67	19.15
9.	[Ni L ₂ ' (Py-O) ₂]	Found	6.76	49.84	3.70	6.47	7.36	7.39
		Cal	6.77	49.85	3.69	6.46	7.38	7.38
10.	[Ni L ₂ 2H ₂ O]H ₂ O	Found	9.26	53.09	5.36	4.43	10.11	-----
		Cal	9.27	53.10	5.37	4.42	10.10	-----
11.	[Ni L ₂ ' (α-pic) ₂]	Found	7.65	62.76	5.50	7.32	8.38	-----
		Cal	7.67	62.76	5.49	7.32	8.37	-----
12.	[Ni L ₂ ' (α-pic-O) ₂]	Found	7.33	60.26	5.26	7.04	8.05	-----
		Cal	7.36	60.24	5.27	7.03	8.03	-----
13.	[Co L ₂ 2H ₂ O]H ₂ O	Found	8.04	42.68	3.84	3.82	8.75	21.88
		Cal	8.06	42.69	3.83	3.83	8.75	21.87
14.	[Co L ₂ ' Py ₂]	Found	7.06	51.76	3.82	6.72	7.65	19.13
		Cal	7.06	51.75	3.83	6.71	7.66	19.14
15.	[Co L ₂ ' (Py-O) ₂]	Found	6.81	49.82	3.70	6.47	7.39	18.42
		Cal	6.80	49.84	3.69	6.46	7.38	18.44
16.	[Co L ₂ ' (2H ₂ O)]H ₂ O	Found	9.30	63.09	5.36	4.41	10.10	-----
		Cal	9.31	63.08	5.37	4.42	10.11	-----
17.	[Co L ₂ ' (α-pic-O) ₂]	Found	7.71	62.72	3.48	7.30	8.37	-----
		Cal	7.70	62.75	5.49	7.32	8.36	-----
18.	[Co L ₂ ' (α-pic) ₂]	Found	7.38	60.25	5.26	7.01	8.02	-----
		Cal	7.39	60.23	5.27	7.02	8.03	-----

Magnetic Susceptibility

The moments for the complexes of Cu(II)d⁹, Ni(II)d⁸, and Co(II)d⁷ were found to be 1.73 BM, 2.7 BM and 2.83 BM which were within the expected spin only values¹.

Moreover, the higher value of the magnetic moment for (Ni(II) d⁸ complex was 2.80 BM which is attributed to the orbital contribution. Furthermore, the μ_{eff} of the Cu (II) d⁹ complex was found to be 2.10 BM which is within the expected value for one electron. Finally the complexes of Co(II), Ni(II) and Cu(II) were found to be paramagnetic as expected from their electronic configuration²⁴. The magnetic moment values are listed in Table-2.

Table-2

Complexes	μ_{eff} .B.M.
[Co L ₂ ' 2H ₂ O]H ₂ O	2.20
[Co L ₂ ' Py ₂]	2.16
[Co L ₂ ' (Py-O) ₂]	2.12
[Co L ₂ ' 2H ₂ O]H ₂ O	2.10
[Co L ₂ ' (α -pic-O) ₂]	2.15
[Co L ₂ ' (α -pic) ₂]	2.18
[Ni L ₂ ' 2H ₂ O]H ₂ O	2.80
[Ni L ₂ ' Py ₂]	2.90
[Ni L ₂ ' (Py-O) ₂]	2.85
[Ni L ₂ ' 2H ₂ O]H ₂ O	2.82
[Ni L ₂ ' (α -pic) ₂]	2.85
[Ni L ₂ ' (α -pic-O) ₂]	2.90
[Cu L ₂ 2H ₂ O]H ₂ O	2.10
[Cu L ₂ Py ₂]	2.12
[Cu L ₂ (Py-O) ₂]	2.15
[Cu L ₂ 2H ₂ O]H ₂ O	2.10
[Cu L ₂ ' (α -pic) ₂]	2.14
[Cu. L ₂ ' (α -pic-O) ₂]	2.12

CONCLUSION

The magnetic moment values of Cu(II) complexes under investigation are in the range of 2.10 to 2.15 BM at 305K. These values fall in the range expected for six co-ordinate octahedral copper (II) and four co-ordinated tetrahedral complexes.

The magnetic moment values of nickel (II) complexes under investigation have been determined at room temperature (305K). The magnetic moment values of complexes as observed are in the range of 2.80 to 2.90 B.M. The μ_{eff} of bis chelated complexes are straight forward and are in the range expected for octahedral nickel (II) complexes.

Cobalt (II) complexes display magnetic moment values between 2.10 to 2.20 B.M. (given in the table) at room temperature. These values clearly indicate that the complexes are four co-ordinated square planar complexes of cobalt (II), as in the principle, for both cases the moment should be close to the spin only value for one unpaired electron. Four co-ordinated planar complexes are easily oxidized to diamagnetic octahedral cobalt (III) on exposure to air. In the present case, on exposure to air for several days there is no change in colors and magnetic moment values of these complexes. Because the cobalt (II) is not oxidized readily to its cobalt (III) complexes. These consideration lead to the conclusion that the complexes do not have planar stereo-chemistry rather they possess low spin octahedral structures.

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