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Synthesis of Ni(II) with Shiff's base chelating ligand 4' (p-hydroxy benzal diamino)-3,5 dimercapto -1,2,4 triazole

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Abstract : The present paper deals with the preparation of ligand 4' (p - hydroxy benzal diamino) 3,5 dimercapto - 1,2,4 triazole and its complexes with Ni (II). All together five complexes compound of N1 is formed with main ligand taken and with secondary ligand H_2O, pyridine, pyridine oxide, morpholine and α-picoline on the basis of elemental Analysis, IR spectral behavior, the complexes have been found to have bidentate with two donor site sulphur and azomethine nitrogen.

(Keywords: IR spectral behavior, bidentate, secondary ligands)

Introduction

A large number of complexes of divalent transition metal of 1st transition series have been prepared with different shiff's base, hydrazones and quinazolones as ligand in presence of bases containing nitrogen, oxygen and sulphur atoms as their donar sites due to their major application in field of medicines, industry and fertilizers. In this paper, we report the formation of complexes of Ni (II) with 4'(p–hydroxy benzal diamino)–3,5 dimercapto– 1,2,4 triazole in ethanolic solution. The reported complex of Ni (II) has two donor site sulphur and nitrogen. The sulphur containing organic compounds have been found in various use in medicine e.g antituberculosis, hypnotics and local anaesthetics[1-2].

Metal complexes of Schiff's base ligand are being continuously studied due to their application of hydrogenation, hydroformylation, oxidation, reduction ,carbonylation, decarbonylation, isomerisation and alkyation, as reported in various journals, P. Viswanatha- murthi *et.al*[3].

Experimentals

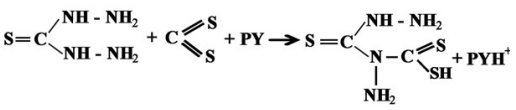
Preparation of Ligand

Preparation of 4' (p – hydroxy benzal diamino) – 3,5 dimercapto -1,2,4 triazol takes place through following way.

At first monopyridinium salt of 4 – amino – 3,5 – dimercapto – 1,2,4 – triazole was prepared by the reaction of thiocarbohydrazide with carbon disulphide in pyridine. From this precursor 4 – amino – 3,5 dimercapto – 1,2,4 – triazole was prepared by heating salt with HCl .

This Amino was used to synthesize the final ligand 4'– (p – hydroxy benzal diamino) – 3,5 dimercapto -1,2,4 trizole (a schiff's base) by its condensation with p – hydroxy benzanaldehyde.

Step 1



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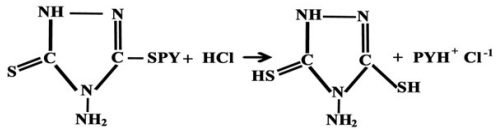

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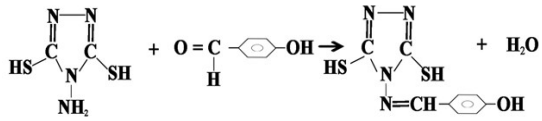

4' (p – hydroxy benzal diamino) – 2,5 – dimercapto – 1,2,4 triazole

Preparation of metal complexes:

The ligand prepared has been used for chelation with Ni (II) transition metal ions. In addition to this chelating ligand, water ,pyridine,pyridinium oxide,morpholine and α - picoline have also been used as secondary ligands.

The newly synthesiszed complexes of N_i (II) were put on microanalysis and their metal content was estimated gravimetrically.

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Result and Discussion

Table 1.1 shows the quantitative estimation of C,H,N,S and mutal-ion in complexes.

Table - 1.1

S. No	Compound	% of M calc (found)	% of C calc (found)	% of H calc (found)	% of N calc (found)	% of S calc (found)
01	$[N_1L_2(H_2O)_2]$	9.55 (9.53)	35.14 (35.16)	3.25 (3.25)	18.22 (18.20)	20.82 (20.84)
02	$[N_1L_2(PY)_2]$	8.17 (7.99)	46.75 (46.01)	3.34 (3.20)	19.48 (19.20)	17.81 (17.80)
03	$[N_1L_2(PY-O)_2]$	7.82 (7.75)	44.76 (44.60)	3.20 (3.10)	18.65 (18.50)	17.05 (17.01)
04	$[N_1L_2(Mor)_2]$	7.99 (7.88)	42.47 (42.40)	4.36 (4.32)	19.06 (19.00)	17.42 (17.20)
05	$[N_1L_2(\alpha-Pico)_2]$	7.54 (7.50)	46.23 (46.01)	3.60 (3.50)	17.98 (17.80)	16.44 (16.30)

Where

L_1 = 4' (p – hydoxy benzal diamino) – 3,5 dimercapto – 1,2,4, triazole

PY – O = Pyridinium oxide

α – Pico = α – Picoline

PY = Pyridine

Mor = Morpholine

Estimation of Ni(II)

Dimethyl glyoxime was used for the estimation of nickel[4]. Accurate weighed 0.5gm of the complex taken in 250ml pyrex beaker on repeated evaporation with HNO_3, $HClO_4$ and the complex was decomposed into clear solution.

In slightly ammonical medium the precipition of nikel dimethyl glyoxime was carried out. The Filtrate dried at 115 – 120° C as $Ni(C_4H_7O_2H_2)$ and weighed. The metal content was calculated by the factor 0.20319.

Estimation of Sulphur

The accurate weight of the complex in a 500ml capacity round bottom flask containing 2-3ml liquid bromine and 20-30ml conc HNO_3. The mouth of the flask was covered with conical funnel[5-6]. The sulphur is precipitated as barium sulphate by adding excess of $BaCl_2$ solution. The gravimetric factor for sulphur is 0.13736.

Infrared Spectral Studies of Complexes and Ligand:

Table 1.2 shows important absorption bands in I.R spectrum of the ligand and their assignment.

Table 1.2

S.No	Prequency (cm^{-1})	Assignment
01	3260	ν(> N – H) Stretching
02	3150	ν(O – H) Phenolic
03	3020	ν(> C – H) Stretching
04	2560	ν(- S – H) Stretching
05	1520, 1455	Skeletal vibration of benzene ring
06	750	δ (C – H)
07	690	t (C – S)

Now, Table 1.3 shows importants IR. Band of LH and metal complexes, where L = 4' (P–hydroxy benzal diamino) – 3,5 dimercapto -1,2,4 – triazole.

Table 1.3

S. No	Complexes	NH (cm^{-1})	OH (cm^{-1})	SH (cm^{-1})	M – N (cm^{-1})	M – S (cm^{-1})	M – O (cm^{-1})
01	LH	3260	-	2560	-	-	-
02	$[N_iL_2(H_2O)_2]$	3250	2850	-	315	270	455
03	$[N_iL_2(PY)_2]$	3245	-	-	310	275	-
04	$[N_iL_2(PY-O)_2]$	3240	-	-	315	275	460
05	$[N_iL_2(Mor)_2]$	3245	-	-	315	275	450
06	$[N_iL_2(\alpha-Pico)_2]$	3245	-	-	315	275	450

From the Table 1.2, infrared spectra of phenolic (- OH) group is 3150 cm^{-1} indicating appreciable hydrogen bonding in phenolic – OH group. The N – H strectching frequency is 3260 which is in the range of 3570 – 3125cm^{-1}. The weak bond found at 2560 cm^{-1}in the I.R spectrum of the ligand may be contributed to S – H stretching vibration.

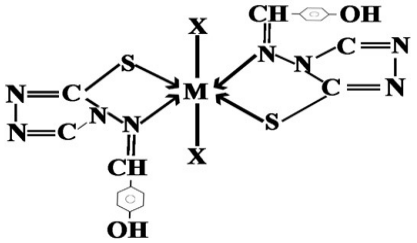
The C – S group weak absorption is obtained at 690 cm^{-1} in the range of 700–600 cm^{-1} owing to t (C – S) stretching vibration the presence of skeletal vibration of benzene ring is best recognized in the range 1600–1450cm^{-1} region[7].The band at 1455cm^{-1} and 1520cm^{-1} arises in the ligand spectrum due to contribution of benzene ring with skeletal vibration.

Infrared spectrum of ligands and complexes have been studied and the band position of important achieve group and those of M – N, M – S and M – O have been tabulated.

The bands position have been assigned tentatively on the basis of work reported earlier[8-9]. A sharp and strong bands near 3265 cm^{-1}, 2850 cm^{-1}, 2550 cm^{-1} have been assigned to stretching (t_{vib}) vibration. The lower value of NH and OH bands are assignable due to hydrogen bonding intramolecular / intermolecular[10-11]. The – OH band position indicates, the non – involvement of OH group in the complexes.

New bands in the lower range near 450, 315, 275 cm^{-1} are assigned to M – O, M – N, M – S respectively. Thus the ligand behaves as bidentate monoamine co-ordinating through one deprotonated mercapto sulphur and azomethine nitrogen and thus behaving as heterochelating agent.

The presence of some new band in I.R spectra of complexes indicates the presence of pyridine, pyridine oxide, morpholine and α–picoline.



[M^{+2}=Ni (II)]

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