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Magnetic and Spectral Study of Some Mixed Ligand Complexes

BISHWANATH KUMAR[1], RAJEEV KUMAR[2] and BIRENDRA KUMAR*

*Department of Chemistry, Jagjiwan College, Gaya, India.
[1] Department of Chemistry, S D College, Paraiya, , India.
[2]Department of Chemistry, Maha Bodhi College, Belaganj, India.
*Corresponding author E-mail: birendra5556@yahoo.in

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ABSTRACT

Complexes of Fe(II), Co(II) and Ni(II) metal ions have been prepared with 4-(p-hydroxyl benzalidimino)-3,5-dimercapto-1,2,4-triazole (LH) as primary ligand while pyridine has been used as secondary ligand. The analytical data suggest 1:2 (M:L) stoichiometric composition of complexes . The electrical conductivity indicates their non- electrolytic nature. The magnetic and spectral character favour octahedral geometry of Fe(II), Co(II) and Ni(II) complexes.

Key words: Precursor, Heterochelates.

INTRODUCTION

The schiff's bases of triazole derivative and their metal complexes possess pharmacological acivities.[1-8] It is found that pharmacological activity of triazole derivative is enhanced ridiculously on coordination with metal ions.[6] Present paper deals with some mixed ligand complexes of Fe(II), Co(II) and Ni(II) metal ions

MATERIAL AND METHODS

The organic reagent and solvent used in present investigation were procured from B.D.H. and Bengal chemicals. Metal salts of Iron (II), Nickel (II) and Cobalt (II) used were all of either Merck or of B.D.H., A.R Grade quality. The primary ligand, 4-(p-hydroxyl -benzalidimino)-3,5-dimercapto-1,2,4-triazole was prepared. For this at first monopyridinium salt of 4-amino-3,5 dimercapto-1,2,4-triazole was prepared by refluxing the mixture of thiocarbohydrazide and carbon disulphide in pyridine on an oil bath for 1 hr. From boiling solution a precipitate appeared and after cooling, pale yellow prismatic crystal was obtained. The precursor, 4-amino-3,5 dimercapto-1,2,4-triazole was prepared by heating the obtained pyridinium salt with HCl. This amine was used to synthesize the primary ligand, i.e., 4-(p-hydroxylbenzalidimino) -3,5-dimercapto-1,2,4-triazole, by refluxing the equimolor quantity of 4-amino-3,5 dimercapto-1,2,4-triazole and p-hydroxybenzaldehyde in ethanol for 1 hr. The reaction mixture was allowed to stand overnight at room temperature where by yellow crystal was obtained.

The alcoholic solution of 0.005M metal chloride and the alcoholic solution of 0.01M ligand were mixed together with 2 ml of α- picoline. The mixture was refluxed on water bath for one and half hour at low temperature. On cooling the solid separated out. The solid complex so obtained in each case was filtered, washed several times with hot water and finally with alcohol. It was dried in desiccator over anhydrous calcium chloride. The ligand and metal complexes were analyzed for C, H, N, S and metal. Molar conductance of metal complexes was determined. For this 10^{-3}M solution in DMSO was used. Magnetic susceptibility and μ_{eff} of metal complexes were determined by Gouy's balance method[9].

RESULTS AND DISCUSSION

The analytical data given in table: 1 show 1:2 (M:L) stoichiometric composition of metal complexes. Low values of molar conductance of all the complexes indicate their non-electrolytic nature. A weak band at 2560 cm^{-1} in IR spectrum of free ligand (L) is assigned to í (SH) stretching vibration. Disappearance of this band in IR spectra of complexes indicates the deprotonation of mercapto group and coordination to metal ions through deprotonated mercapto sulphur[10]. A strong band appearing at 2850cm^{-1} in IR spectrum of free ligand may be assignable to H-bonded phenolic –OH group, which remains unaltered in the spectra of complexes indicating its non-participation in complexation.[11]A band at 1628 cm^{-1} in the IR spectrum of free ligand is assigned to azomethine group. Blue shift (15-24 cm^{-1}) of this band in the IR spectra of metal complexes is indicative of coordination through azomethine nitrogen of ligand.[12] Three bands at 2910 cm^{-1}, at 3050 cm^{-1} and at 1456 cm^{-1} appearing in the IR spectra of metal complexes are assignable to ν_{CH} of methyl group aromatic, ν_{CH} and $\nu_{C=N}$ of α-picoline molecules respctively.[13-15] A band at 755 cm^{-1} is appeared in the IR spectra of metal complexes. This may be due to coordinated α-picoline to metal ions in complexs.[16-19] The non-ligand band at 315cm^{-1}and 265cm^{-1} in spectrum of Ni- complex are assignable to í (M-N) and í (M-S) respectively. The non-ligand band at 320cm^{-1}and 270cm^{-1} in spectrum of Co-complex are assignable to ν (M-N) and ν (M-S) respectively. The non-ligand band at 320cm^{-1} and 280cm^{-1} in spectrum of Fe- complex are assignable to ν (M-N) and ν (M-S) respectively. Study of IR spectra of metal complexes reveals that the ligand has been found to be coordinated though thiol sulphur and azomethine nitrogen, so the chelates may be called to be heterochelates.

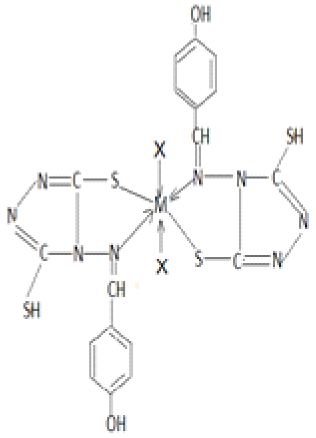
Magnetic moment (μ_{eff}) value of Ni (II) complex is 2.80 B.M. which is in the better agreement with octahedral Ni(II) complexes.[20-22]

Table 1:

Compound	**%M Calc (Found)**	**%C Calc (Found)**	**%H Calc (Found)**	**%N Calc (Found)**	**%S Calc (Found)**	**μ_{eff} (B.M.)**	**Conductivity moh cm^{-1} mole^{-1}**
LH	—	42.86	3.18	22.22	25.40		
	(—)	(42.89)	(3.20)	(22.25)	(25.37)		
FeiL$_2$(α-pico)$_2$]	7.50	48.40	3.76	18.82	17.21	5.25	16.5
	(7.55)	(48.48)	(3.79)	(18.80)	(17.19)		
[CoL$_2$(α-pico)$_2$]	7.89	48.20	3.75	18.74	17.14	2.60	16.0
	(7.92)	(48.25)	(3.73)	(18.77)	(17.12)		
[NiL$_2$(α-pico)$_2$]	7.86	48.21	3.75	18.75	17.14	2.80	15.5
	(7.90)	(48.24)	(3.79)	(18.72)	(17.10)		

LH = 4-(p-hydroxylbenzalidimino)-3,5-dimercapto-1,2,4-triazole α-pico =α- Picolene, Calc = Calculated

Considering the above facts the structure of complexes is proposed as follow:



M=Fe, Ni, Co X=α- picoline

Magnetic moment (μ_{eff}) for Co (II) complex is determined and found to be 2.60 B.M. at room temperature . This μ_{eff} value is intermediate between those of low-spin octahedral or planar and high-spin octahedral Co (II) complexes. This anomalous value of magnetic moment for Co (II) complex may be attributed to spin state equilibrium between high spin and low spin species. Magnetic moment (μ_{eff}) for Fe(II) complex is determined and found to be 5.25 B.M. which is slightly greater than that of the value of spin free octahedral Fe(II) complexes. This may be attributed to appreciable contribution from triply degenerate ground state term, i.e., $^5T_{2g}$. This value of μ_{eff} of Fe (II) complex is in good agreement with the reported values for spin free octahedral Fe (II) complexes.[23-25]

The electronic spectra of Ni(II) complex exhibits three bands at 11280cm^{-1}, 16840cm^{-1} and 26190cm^{-1} which are assignable to the transition $^3A_{2g}(F)\rightarrow{}^3T_{2g}(F)(\nu_1)$, $^3A_{2g}(F)\rightarrow{}^3T_{1g}(F)(\nu_2)$ and $^3A_{2g}(F)\rightarrow{}^3T_{1g}(P)(\nu_3)$ respective -ly. The various crystal field parameters of Ni (II) complex, viz, 10Dq, B and â were calculated. The value of 10Dq, B and â are found to be 11290cm^{-1}, 616.4cm^{-1} and 0.59 respectively. The values of different crystal field parameters are in good agreement with reported values of octahedral Ni(II) complexes.[26-29] The electronic spectra of Co(II) complex exhibits three bands at 9755cm^{-1}, 17310cm^{-1} and 23515cm^{-1} which are assigned to the transition $^4T_{1g}(F)\rightarrow{}^4T_{2g}(F)(\nu_1)$, $^4T_{1g}(F)\rightarrow{}^4A_{2g}(F)(\nu_2)$ and $^4T_{1g}(F)\rightarrow{}^4T_{1g}(P)(\nu_3)$ respectively. The various crystal field parameters of Co (II) complex, viz, 10Dq and B are calculated. The value of 10Dq and B are found to be 7555cm,$^{-1}$ and 1266cm^{-1} respectively. The values of different crystal field parameters are in good agreement with reported values for octahedral Co(II) complexes.[30-33] A broad band having shoulder at 11810cm^{-1} is appeared in electronic spectrum of Fe(II) complex. The spectral band is assigned to $^5T_{2g}$'!^5E_g transition. Shoulder in electronic band is indicative of the distortion from octahedral symmetry. Thus Fe complex has distorted octahedral symmetry. [34-37]

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