

## SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF Co (II), Ni (II) AND Cu (II) WITH 1-HYDROXYL-2, 3-DIPHENYL-6-AMINO-MERCAPTO-1, 4, 5-TRIAZA-1, 3-HEXADIENE (HL)

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A number of binuclear metal complexes of the type  $[ML_2(H_2O)_2]X_2$  where HL = 1-hydroxy-2,3-diphenyl-6-amino-6-mercapto-1,4,5-triaza-1,3-hexadiene, M = Co(II), Ni(II) and Cu(II), X = Cl, Br, NO<sub>3</sub>, ClO<sub>4</sub> have been synthesized and characterized by elemental analyses, magnetic susceptibility, infrared and electronic spectral data.

**Key words:** Metal complex, Schiff base ligand, Transition metal

### Introduction

Transition metal complexes with Schiff bases have been widely studied compounds in the past years, (West 1968), since they are becoming increasingly important as biochemical, analytical and antimicrobial reagents; Schiff bases derived from a large number of carbonyl compounds and amines have been studied, however, those derived from 1,2-diphenyl-1-hydroxyiminoethane-2-one have received scanty attention (Rai *et al* 1990; 1995). They are expected to be potentially polydentate ligands capable of forming annulated metal chelate rings.

In the present investigation, we report the preparation and characterization of a few homobinuclear metal complexes with a NNSO donor Schiff base, 1-hydroxy-2,3-diphenyl-6-amino-6-mercapto-1,4,5-triaza-1,3-hexadiene.

### Experimental

All the chemicals used were BDH or E. Merck reagents except 1,2-diphenylethane-1,2-dione which was obtained from Aldrich. 1,2-diphenyl-1-hydroxyiminoethane-2-one, (m.p 138°C; temp 140°C). The Schiff base, 1-hydroxy-2,3-diphenyl-6-amino-6-mercapto-1,4,5-triaza-1,3-hexadiene (HL) was prepared by refluxing equimolar quantities of thiosemicarbazide and 1,2-diphenyl-1-hydroxyiminoethane-2-one in ethanolic medium for 6 h. It was cooled overnight in a refrigerator, filtered, washed with ethanol, dried over fused CaCl<sub>2</sub> and analysed. An in situ method was adopted for the preparation of the complexes.

In a typical reaction, 1,2-diphenyl-1-hydroxyiminoethane-2-one thiosemicarbazide and CuCl<sub>2</sub>·2H<sub>2</sub>O were mixed together in the molar ratio 1:1:1 in an ethanolic medium and refluxed for 4 h. The solution was cooled at room temperature when colored precipitates formed. The product was filtered, washed

with ethanol and dried over fused CaCl<sub>2</sub>. Other complexes were prepared in an identical manner by taking appropriate metal salts. Metal, sulphur and halogen contents of the complexes were determined by standard methods (Vogel 1978). C, H and N were estimated using a KLV-CHN microanalyser. IR spectra in KBr pellets were recorded on Perkin-Elmer 398 Spectrometer. Reflectance spectra were recorded on a Beckman 35 Double Beam Spectrometer. Magnetic susceptibilities were measured on a Gouy Balance using Hg[Co-(CNS)<sub>4</sub>] as the calibrant (Table 1).

### Results and Discussion

The infrared spectrum of the ligand shows strong and broad bands in the range 3050-3300 cm<sup>-1</sup> and centered at 3200 cm<sup>-1</sup> which may be assigned to the combined mode of  $\nu_{N-H}$ ,  $\nu_{S-H}$  and  $\nu_{O-H}$ . The broadness of the band suggests the presence of strong intramolecular hydrogen bonding. On the basis of these results, the ligand is expected to exist in different tautomers consisting of thio-keto and thiol forms in addition to the hydrogen bonded structure.

It also showed a very weak band at 2510 cm<sup>-1</sup> and a medium intensity band in the region 1250-1350 cm<sup>-1</sup> assignable to  $\nu_{S-H}$  and  $\nu_{C-S}$  respectively, supporting the above proposed structure of the ligand in the tautomeric forms. A strong band at 740 cm<sup>-1</sup> might be due to phenyl ring vibrations.

The ligand also exhibits at 1635 cm<sup>-1</sup> and 450 cm<sup>-1</sup> assignable to  $\nu_{C=N}$  of azomethine and oxime groups respectively (Nakamoto Kazuo 1997). The infrared spectra of all the complexes are highly complicated and exhibit an identical pattern. Attempts have been made to identify some important bands which furnish vital informations about the most probable mode of coordination of the ligand.

A strong and broad band scanning over 3300-3450 cm<sup>-1</sup> may

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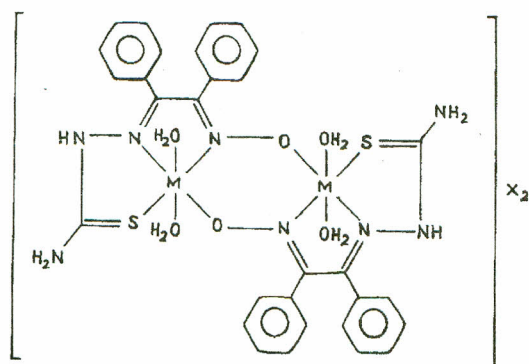
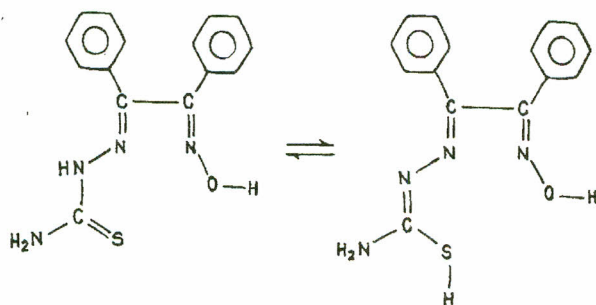
**Table 1**  
Analytical data of the ligand and its complexes with Co (II) Ni(II) and Cu(II)

Complexes	$\mu_{\text{eff}}$ in B.M	Colour	M.P. in °C	Calculated (Found)					
				C	H	N	S	X	M
$\text{C}_{15}\text{H}_{14}\text{N}_4\text{OS}$	-	Raw silk	230	60.40 (60.40)	4.69 (4.73)	18.70 (18.78)	10.73 (10.72)	--	--
$[\text{Co}(\text{C}_{15}\text{H}_{13}\text{N}_4\text{OS})(\text{H}_2\text{O})_2]\text{Cl}_2$	4.86	Brown	275	42.00 (42.10)	3.26 (4.00)	13.06 (13.10)	7.46 (7.50)	8.28 (8.29)	13.76 (13.78)
$[\text{Co}(\text{C}_{15}\text{H}_{13}\text{N}_4\text{OS})(\text{H}_2\text{O})\text{Br}_2$	4.92	Grey	275	38.05 (18.14)	2.95 (3.63)	11.83 (11.86)	6.76 (6.99)	16.91 (16.92)	12.47 (12.48)
$[\text{Co}(\text{C}_{15}\text{H}_{13}\text{N}_4\text{OS})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$	4.89	Grey	275	36.54 (36.63)	2.84 (3.48)	11.37 (11.39)	6.49 (6.52)	20.23 (20.22)	11.98 (11.97)
$[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_4\text{OS})(\text{H}_2\text{O})_2]\text{Cl}_2$	2.91	Grey	260	42.05 (42.24)	3.27 (4.00)	13.08 (13.10)	7.41 (7.50)	8.29 (8.29)	13.71 (13.73)
$[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_4\text{OS})(\text{H}_2\text{O})_2]\text{Br}_2$	2.90	Grey	270	38.09 (38.17)	2.96 (3.63)	11.85 (11.87)	6.77 (6.98)	16.93 (16.93)	12.42 (12.44)
$[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_4\text{OS})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$	2.86	Red	270	42.00 (42.10)	3.26 (4.00)	13.06 (13.10)	7.46 (7.50)	8.28 (8.29)	13.76 (13.78)
$[\text{Cu}(\text{C}_{15}\text{H}_{13}\text{N}_4\text{OS})(\text{H}_2\text{O})_2]\text{Cl}_2$	1.65	Mimosa	272	41.57 (41.66)	3.23 (3.46)	12.93 (12.96)	7.39 (7.40)	8.19 (8.20)	14.66 (14.69)
$[\text{Cu}(\text{C}_{15}\text{H}_{13}\text{N}_4\text{OS})(\text{H}_2\text{O})_2(\text{NO}_3)_2$	1.56	Green	270	39.17 (39.25)	3.04 (3.73)	15.23 (15.26)	6.96 (6.97)	-	13.81 (13.84)

**Table 2**  
Spectral data of the complexes

Complexes	Band position in $\text{cm}^{-1}$	Transition	$10D_q$	B	C	$F_4$	$F_2$
			$\text{cm}^{-1}$				
$[\text{Co}(\text{C}_{15}\text{H}_{13}\text{N}_4\text{OS})(\text{H}_2\text{O})_2]\text{Cl}_2$	11050	${}^4T_{1g} \rightarrow {}^4T_{2g}$	12300	805.7	3810	110.2	1122
	13770	${}^4T_{1g} \rightarrow {}^4T_{2g}$					
	17470	${}^4T_{1g} \rightarrow {}^4T_{2g}$ (P)					
	26580	CT					
$[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_4\text{OS})(\text{H}_2\text{O})_2]\text{Cl}_2$	12928	${}^3T_{1g} \rightarrow {}^3T_{2g}$	12928	815	3560	106.5	1250
	17830	${}^3A_{2g} \rightarrow {}^3T_{1g}$					
	20640	${}^3T_{2g} \rightarrow {}^3T_{2g}$					
$[\text{Ni}(\text{C}_{15}\text{H}_{13}\text{N}_4\text{OS})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$	11956	${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P)	11956	845.5	3950	121.7	1468
	15317	${}^3T_{2g} \rightarrow {}^3T_{2g}$ (P)					
	20060	${}^3A_{2g} \rightarrow {}^3T_{1g}$					
	28700	${}^3A_{2g} \rightarrow {}^3T_{2g}$ (B)					
$[\text{Cu}(\text{C}_{15}\text{H}_{13}\text{N}_4\text{OS})(\text{H}_2\text{O})_2]\text{Cl}_2$	11050	${}^2E_g \rightarrow {}^2T_{2g}$	15800	--	--	--	--
	26100	CT					

CT-Charge Transfer Band

(M=Co(II), Ni(II), Cu (II) and X =  $\bar{\text{Cl}}$ ,  $\bar{\text{Br}}$ ,  $\bar{\text{NO}}_3$ ,  $\bar{\text{ClO}}_4$ )

Thio-keto and thiol form

be assigned to the combined mode of  $\nu_{\text{N-H}}$ ,  $\nu_{\text{S-H}}$  and  $\nu_{\text{O-H}}$  (of water molecule) vibration. The band at  $2500 \text{ cm}^{-1}$  due to  $\nu_{\text{S-H}}$  disappears in the complexes. The high frequency  $\nu_{\text{C=N}}$  bands are shifted to a lower frequency region and the low frequency  $\nu_{\text{C=N}}$  bands suffer a blue shift which can be attributed to the variation in electronic environment due to co-ordination of azomethine and oxime nitrogen with the metal ions. (Rai *et al* 1979). The  $\nu_{\text{N-O}}$  band appears at  $930 \text{ cm}^{-1}$ , suggesting the co-ordination of oxygen atom of the oxime group to the metal centre.

The  $\nu_{\text{C=S}}$  band in the region  $1250\text{-}1350 \text{ cm}^{-1}$  in the ligand undergoes a downward shift indicating participation of the sulphur atom in the thio-keto form in the co-ordination.

I.R. spectra also indicate  $\bar{\text{NO}}_3$  and  $\bar{\text{Cl}}_4$  groups to be uncoordinated which is in accordance with the high molar conductivity values in the range  $220\text{-}230 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  for the complexes in dioxane Rai *et al* (1979).

In the far infra-red region, new additional bands at  $460\text{-}430 \text{ cm}^{-1}$  and  $425\text{-}410 \text{ cm}^{-1}$  are observed which may be assigned to  $\nu_{\text{M-N}}$  and  $\nu_{\text{M-S}}$  vibrations respectively. Thus I.R. spectral data led us to suggest that the ligand, HL behaves as a tetradentate ligand coordinating through its azomethine N, oxime N, thionyl S and oxime O. Further considering the ligand to be planar and that the four potential donor atoms can not coordi-

nate to the same metal ion, a binuclear structure with coordinating water molecules has been proposed.

a) *Thermal analysis.* Since I.R. spectra of the complexes indicated the presence of water molecules, thermal analyses were undertaken to ascertain the nature of the water molecules. The thermogram of all the complexes have an identical pattern. In case of copper (II) complexes, for example, there was no loss upto  $200^\circ\text{C}$  suggesting the absence of lattice water. The first weight loss was observed at about  $220^\circ\text{C}$  supported by an exothermic peak at the same temperature. The weight loss occurs in a single step and corresponds to the loss of four water molecule. Thus, the water molecules may be considered to be coordinated to the metal centre. (Rai and Sharma 1995).

b) *Magnetic moment and electronic spectra.* The magnetic moments and electronic spectral data of representative complexes are recorded in Table-2. A metal complex with different anions displays an identical spectral pattern suggesting the same chemical environment around the metal ion. The spectra of some of the representative complexes are discussed here. The cobalt (II) complex  $[\text{CoL}(\text{H}_2\text{O})_2]_2\text{X}_2$  possesses magnetic moment in the range 4.86-4.92 B.M. which are expected values for high spin octahedral cobalt (II) complexes. The complex  $[\text{CoL}(\text{H}_2\text{O})_2]_2\text{Cl}_2$  exhibits three ligand field bands at  $11050$ ,  $13770$  and  $17470 \text{ cm}^{-1}$  and may be assigned to the  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ ,  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$  and  ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$  transitions respectively. The high frequency band observed at  $26800 \text{ cm}^{-1}$  may be due to charge transfer. (Satpathy *et al* 1991).

The reflectance spectrum of the nickel (II) complex,  $[\text{NiL}(\text{H}_2\text{O})_2]_2\text{Cl}_2$  displays three ligand field bands. The bands at  $129280$ ,  $17830$  and  $20640 \text{ cm}^{-1}$  have been assigned to the  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ ,  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$  transitions respectively in an approximately octahedral field. The high frequency band at  $25360 \text{ cm}^{-1}$  corresponds to charge transfer. The magnetic moments are in the range 2.85 - 2.95 B.M., which are almost equal to the spin only value due to quenching of orbital angular momentum.

The copper (II) complexes  $[\text{CuL}(\text{H}_2\text{O})_2]_2\text{X}_2$  show a single band which lies in the range  $15800\text{-}20900 \text{ cm}^{-1}$  and may be assigned to the transition  ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ . Another band at  $26100 \text{ cm}^{-1}$  may be due to charge transfer.

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