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Cobalt(II), Nickel(II) and Copper(II) Complexes with 2-Hydroxyimino-4,5-Diaza-3-phenyl-6-Amino-6-Mercapto-3-Hexene

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Some homo-binuclear metal complexes of the type $[(HAPAME)M(H_2O)_2]_2X_2$, where HAPAME is a Schiff's base ligand obtained by the condensation of thiosemicarbazide with 1-phenyl-1,2-propanedione-2-oxime, M = copper(II), nickel(II) and cobalt(II) and $X = Cl^-$, Br^-, OAc^-, NO_3^- or ClO_4^- have been isolated. Infrared spectra of the complexes suggest that the ligand coordinates of the metal ion through both of its imine nitrogen, oxime oxygen and thionyl sulphur. Reflectance spectra of the complexes indicate octahedral geometry around the metal ions.

INTRODUCTION

Metal chelates of oximes have been reported to be biologically active[1, 2] and semiconducting materials[3, 4]. The Schiff bases derived from thiosemicarbazide and ketoxime have received scanty attention[5]. They are expected to be potentially polydentate ligands capable of forming annulated metal chelate rings. As a part of our studies in the field[6], we report here the preparation and characterisation of a few homo-binuclear metal complexes with a NNSO donor Schiff base, 2-hydroxyimino-4,5-diaza-3-phenyl-6-amino-6-mercapto-3-hexene (HAPAME).

EXPERIMENTAL

All the chemicals used were of analytical grade. Solvents were used without further purification.

Preparation of the Schiff Base (HAPAME)

The Schiff base, 2-hydroxyimino-4,5-diaza-3-phenyl-6-amino-6-mercapto-3-hexene (HAPAME) was prepared by refluxing equimolar concentrations of thiosemicarbazide and 1-phenyl-1,2-propanedione-2-oxime in ethanolic medium for 4 h. When the reaction was complete, the volume of the mixture was reduced to half. On cooling the solution overnight in a refrigerator raw silky crystals separated out. The crystals were filtered and washed several times with cold ethanol. It was dried over fused $CaCl_2$ and analysed (m.p. = 212 ± 2°C; yield = 75%).

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Preparation of the Complexes

The complexes were prepared by adopting two different methods: (1) directly by reacting metal(II) salts with the Schiff base, and (2) by template process. However, in both the cases complexes of the same stoichiometry were isolated. In the present communication, we report the preparation of the complexes through template method as the yield is higher in this method as compared to the traditional method.

In a typical reaction, $CuCl_2 \cdot 2H_2O$ (165 mg; 1 mmole), thiosemicarbazide (90 mg; 1 mmole) and 1-phenyl-1,2-propanedione-2-oxime (160 mg; 1 mmole) were taken together in 23 mL of ethanol. The resulting mixture was refluxed for 3–4 h. On cooling the solution to room temperature, coloured precipitates started separating out. The precipitates were filtered, washed several times with ethanol and finally dried over fused $CaCl_2$. Other complexes were prepared in an identical manner by taking appropriate metal salts. Metal, sulphur and halogen contents of the complexes were determined by adopting standard methods[7].

RESULTS AND DISCUSSION

The analytical data of the ligand and the complexes are recorded in Table-1. All the complexes are highly coloured and have high melting points (> 250°C). They are quite stable at room temperatures and can be stored for a long period without decomposition. All the complexes are insoluble in common organic solvents. However, freshly prepared complexes are highly soluble in DMF and dioxane. The copper(II) complexes are decomposed by hot dilute acids or alkalies to black CuS suggesting the presence of Cu–S bond in the complexes[8]. All the complexes have high molar conductance values in dioxane at room temperature suggesting them to be electrolytes.

Infrared Spectra

The ligand is expected to exist in different tautomeric forms consisting of thioketo and thiol forms as shown in Fig. 1 in addition to the hydrogen bridged structure.

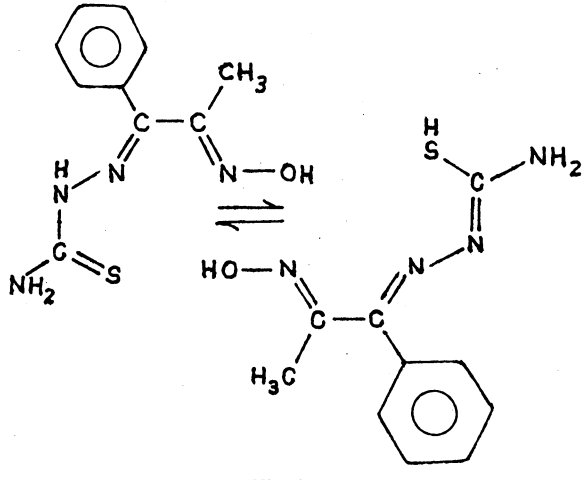

Fig. 1

TABLE-1
ANALYTICAL DATA OF THE METAL COMPLEXES OF HAPAME

Complexes (Colour)	m.p. (°C)	% Analysis, Found (Calcd.)				μ_{eff} in B.M.
		M	N	C	H	
1. HAPAME (Raw silk)	> 210	—	23.62 (23.72)	51.02 (50.84)	5.02 (5.08)	—
2. $[Cu(HAPAME)(H_2O)_2]_2Cl_2$ (Green)	> 250	17.15 (17.12)	15.02 (15.09)	32.38 (32.34)	4.35 (4.31)	1.70
3. $[Cu(HAPAME)(H_2O)_2]_2(OAc)_2$ (Green)	> 250	16.12 (16.05)	14.23 (14.16)	36.38 (36.40)	4.03 (4.04)	1.65
4. $[Cu(HAPAME)(H_2O)_2]_2(NO_3)_2$ (Green)	> 250	15.91 (15.97)	17.58 (17.61)	30.21 (30.18)	4.05 (4.02)	1.62
5. $[Cu(HAPAME)(H_2O)_2]_2Br_2$ (Brown)	> 250	15.30 (15.28)	13.43 (13.47)	28.91 (29.88)	3.78 (3.85)	1.64
6. $[Cu(HAPAME)(H_2O)_2]_2(ClO_4)_2$ (Green)	> 250	14.65 (14.60)	12.91 (12.87)	27.42 (27.58)	3.91 (3.67)	1.65
7. $[Ni(HAPAME)(H_2O)_2]_2Cl_2$ (Green)	> 250	16.15 (16.09)	15.31 (15.28)	32.76 (32.74)	4.39 (4.36)	2.95
8. $[Ni(HAPAME)(H_2O)_2]_2(OAc)_2$ (Green)	> 250	15.18 (15.12)	14.28 (14.35)	36.81 (36.92)	4.14 (4.10)	2.94
9. $[Ni(HAPAME)(H_2O)_2]_2Br_2$ (Green)	> 250	14.32 (14.35)	13.59 (13.62)	29.21 (29.19)	3.83 (3.89)	2.96
10. $[Ni(HAPAME)(H_2O)_2]_2(ClO_4)_2$ (Red)	> 250	13.72 (13.70)	13.02 (13.00)	27.86 (27.87)	3.70 (3.71)	2.92
11. $Co(HAPAME)(H_2O)_2]_2Cl_2$ (Brown)	> 250	16.02 (16.09)	15.31 (15.28)	32.79 (32.74)	4.32 (4.36)	4.91
12. $[Co(HAPAME)(H_2O)_2]_2Br_2$ (Green)	> 250	14.33 (14.35)	13.61 (13.62)	29.22 (29.19)	3.91 (3.89)	4.97
13. $[Co(HAPAME)(H_2O)_2]_2(ClO_4)_2$ (Green)	> 250	13.73 (13.70)	12.98 (13.00)	27.91 (27.87)	3.73 (3.71)	4.93

The spectrum of the ligand exhibits strong and broad bands in the range 3400–3100 cm^{-1} and centred at 3280 cm^{-1}, which may be assigned to the combined mode of ν(NH), ν(SH) and ν(OH). The broadness of the band suggests the presence of strong intramolecular hydrogen bonding. These results are consistent with the above proposed structure[9]. The ligand molecule contains NCSH and HNCS units. Therefore, one should expect thioamide bands in its IR spectra[10]. The spectrum of the ligand shows a very weak band *ca.* 2525 cm^{-1} and a strong band at *ca.* 755 cm^{-1} assignable to ν(S—H) and ν(C=S) respectively, thus suggesting the existence of the ligand in tautomeric forms. The bands 1650 cm^{-1} and 960 cm^{-1} are assigned to ν(C=N) and ν(N—O) respectively. In addition to these bands, a band of medium intensity 1030 cm^{-1} may be assigned to ν(N—N)[11].

The spectra of all the complexes exhibit an identical pattern and are highly

complex. Attempts have been made to identify some important bands which furnish vital information about the most probable mode of coordination of the ligand. A strong and broad band scanning over 3500–3400 cm^{-1} can be assigned to the combined mode of ν(N—H), ν(S—H) and ν(O—H) (of water molecules) vibration. The weak band due to ν(S—H) at 2500 cm^{-1} disappears in the complexes. The ligand band due to ν(C=N) is shifted to higher frequency region indicating the participation of the azomethine nitrogens in the complexation. The ν(N—O) band in the complexes appears at *ca.* 915 cm^{-1} showing red shift as compared to the ligand. The shifts of these bands suggest wider delocalisation of the electronic charge in the newly formed chelate rings on account of coordination of both nitrogen and oxygen atoms of the oxime group to the metal centre. The ν(C=S) band at *ca.* 750 cm^{-1} in the ligand experiences a downward shift[12] in the metal complex and appears at *ca.* 710 cm^{-1}, suggesting the participation in coordination of the sulphur atom in the thioketo form in the complexes.

The coordination of NO_3^- group is generally ascertained by the appearance of bands[13] *ca.* 1200 and 1020 cm^{-1} and that of ClO_4^- group[14] by bands in the region 1280 (ν_8), 1110 (ν_6) and 1005 (nu_1) cm^{-1} respectively. Since no such bands are observed in the metal complexes, it may be concluded that the anionic groups are not coordinated to the metal ion. This observation is in accordance with the high molar conductance values of the complexes in dioxane.

In the far infrared region, new additional bands 460–430 cm^{-1} and 425–410 cm^{-1} are observed. They may be assigned to ν(M–N) and ν(M—S) vibrations respectively[15–17]. Thus IR spectral data lead us to believe that the ligand behaves as a tetradentate ligand coordinating through both of its imine nitrogens, thionyl sulphur and oxime-oxygen. Further, considering the ligand to be planar and that the four potential donor atoms cannot coordinate to the same metal ion, a binuclear structure with coordinating water molecules, as shown in Fig. 2, has been proposed.

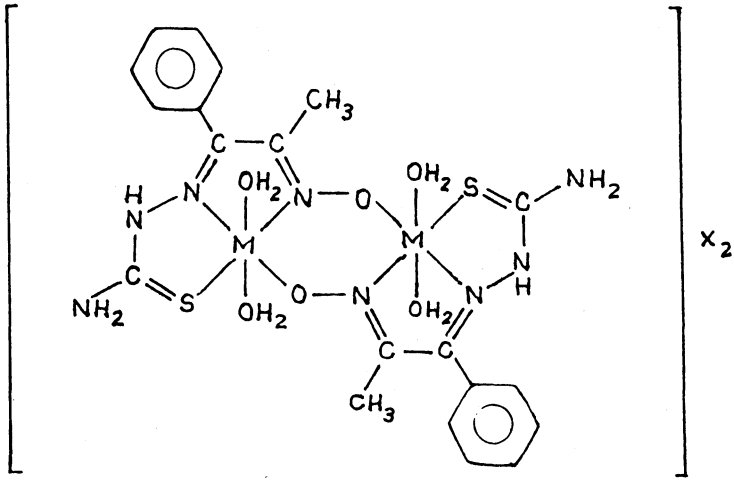

Fig. 2

Thermal Analyses

Since IR spectra of the complexes indicated the presence of water molecules, thermal analyses were undertaken to ascertain the nature of the water molecules. The thermograms of all the complexes showed an identical pattern. In case of copper(II) for example, there was no mass loss up to 200°C suggesting the absence of lattice water. The first weight loss was observed at about 220°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 molecules. Thus, the water molecules may be considered to be coordinated to the metal centre. After the first weight loss, the complex becomes stable upto 350°C, after which it starts decomposing slowly to its corresponding metal oxides.

Electronic Spectra and Magnetic Properties:

The magnetic moment values and electronic spectral data of the complexes are recorded in Tables 1 and 2 respectively. 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.

TABLE-2
MAGNETIC AND SPECTRAL DATA OF THE METAL COMPLEXES

Complexes	Band Position (cm^{-1})	Assignments	10 D_q	B	C	F_4	F_2	β
[Cu(HAPAME)	20850	$^2E_g \rightarrow {}^2T_{2g}$	—	—	—	—	—	—
$(H_2O)_2]_2Cl_2$	35000	CT						
[Ni(HAPAME)	13000	$^3A_{2g} \rightarrow {}^3T_{1g}$	992.5	770.1	3625	103.8	1287.2	0.73
$(H_2O)_2]_2Cl_2$	17800	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$						
	20500							
	25400	CT						
[Ni(HAPAME)	12000	$^3A_{2g} \rightarrow {}^3T_{1g}$	1130	862.5	4050	116.8	1445	0.82
$(H_2O)_2]_2(ClO_4)_2$	15350	$^3A_{2g} \rightarrow {}^3T_{1g}(D)$						
	20000							
	28500	CT						
[Co(HAPAME)	11200	$^4T_g \rightarrow {}^4A_{2g}$	730.2	811.2	3750	107.5	1150.8	0.82
$(H_2O)_2]_2Cl_2$	13800	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$						
	26800	T						

The electronic spectra of cobalt(II) complexes exhibit three bands. The ligand field bands 13,800 cm^{-1} and 17,500 cm^{-1} may be assigned to the $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively. The high frequency band observed at 27,000 cm^{-1} may be due to charge-transfer. The

magnetic moment of the complexes are in the range 4.91 to 4.97 B.M. which are expected for high spin octahedral cobalt(II) complexes[18].

The reflectance spectra of the nickel(II) complexes display three ligand field bands. The bands 12,498 and 20.660 cm^{-1} has been assigned to $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions respectively in an approximately octahedral field[19]. The high frequency band corresponds to charge-transfer. The magnetic moment values of the complexes are in the range 2.91 to 2.96 B.M. which are slightly lower than the spin-only value. The lowering of the magnetic moment may be due to partial quenching of the orbital moment. The electronic spectra of the copper(II) complexes show a single band spreading in the region *ca.* 21,000–16,000 cm^{-1} and another band 26,000 cm^{-1}. The former band correspond to $^2E_g \rightarrow {}^2T_g$ transition and the latter to charge-transfer respectively.

The nephelauxetic ratios (β) calculated for cobalt(II) and nickel(II) complexes are less than unity. It indicates partial covalency in metal-ligand bonds. The crystal field splitting energy (Dq), the Racah parameters (B and C) and Shortly-Condon parameters F_2 and F_4 calculated for cobalt(II) and nickel(II) complexes are in close agreement with the values obtained for their known octahedral complexes[5].

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