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Synthesis and Characterization of Some Transition Metal Complexes Derived from 4-Hydroxy Coumarin and 4-Aminophenol

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Metal(II) complexes of the type $ML_2{\cdot}nB$ [Mn(II), Co(II), Ni(II) and Cu(II), L = Schiff base derived from 3-formyl-4-hydroxy coumarin and 4-aminophenol, B = H_2O, n = 0, 1, 2, . . .] have been prepared and characterized by elemental analysis, molar conductance, IR, electronic and magnetic susceptibility studies. Molar conductivity measurements indicate that the complexes are non-electro- lytic in nature. The analytical data indicate that the metal to ligand ratio in all complexes is 1 : 2. IR spectra show that the Schiff base behaves as a bidentate ON donor system.

Key Words: Synthesis, Transition metal complexes, 4-Hydroxy coumarin, 4-Aminophenol.

INTRODUCTION

There has been considerable interest among inorganic chemists in studying the structural, magnetic and biological properties of transition metal complexes derived from Schiff bases[1–4]. Imines are an important class of ligands in coordination chemistry and have various applications in analytical chemistry and in catalysis[5, 6]. They also exhibit antifungal, antibacterial and other biological properties[7, 8]. Schiff bases derived from coumarin and also its transition metal complexes are reported to be potential biochemical and analytical reagents[9, 10]. They exhibit antibacterial, antifungal and anti-inflammatory properties[11–13]. The dimer of 4-hydroxy coumarin is a good anticoagulating agent[14]. Literature survey reveals that comparatively lesser work has been done on the metal complexes of Schiff base derived from 3-formyl-4-hydroxy coumarin and 4-aminophenol. The present paper therefore deals with the study of complexes derived from the above Schiff base and Mn(II), Co(II), Ni(II) and Cu(II) metal ions. These metal complexes are characterized by various spectral techniques.

EXPERIMENTAL

All the chemicals used for the synthesis were of LR grade. 4-hydroxy coumarin was obtained from Fluka Ltd. Triethylorthoformate, 4-aminophenol and metal salts were obtained from S.D. Fine Chem. and Loba Chemie. Distilled solvents were used throughout the experiment.

Synthesis of Schiff Base: 3-Formyl-4-hydroxy coumarin was synnthesized according to the method reported in literature[15]. The Schiff base was prepared by refluxing 3-formyl-4-hydroxy coumarin with 4-aminophenol (1 : 1) in ethanol for

3 h. On pouring the reaction mixture into crushed ice, green precipitate was formed. The precipitate was separated, washed with water and dried in an oven at 60°C. The Schiff base was recrystallized from ethanol. Its purity was checked by TLC. m.p. 265°C, yield 65%.

Synthesis of Metal Complexes: The metal complexes were synthesized by mixing hot ethanolic solution of ligand with hot ethanolic solution of metal salts (2 : 1). The pH of the solution was adjusted to 6.5–7.5 by adding alcoholic NH_3. The reaction mixture was refluxed for 2–3 h. The metal complexes obtained were filtered, washed with water followed by hot ethanol and dried in an oven at 60°C.

The melting points of all complexes were determined by open capillary method. The elemental analysis was carried out in the Micro-analytical Lab, University of Mumbai. The metal content for all metal complexes were determined as reported in the literature[16]. The complexes were examined for solubility using various polar and nonpolar solvents. Molar conductivity of ligand and metal complexes was recorded using 1×10^{-3} M solution in DMF on Toshniwal TSM-15 conductivity meter. The electronic absorption spectra of ligand and complexes were recorded in the UV-Visible region using DMSO as solvent on UV-Visible 2100 spectrophotometer supplied by M/s Shimadzu Corporation. IR spectra were recorded using KBr pellets on FTIR-4200 supplied by M/s Shimadzu Corporation. Magnetic susceptibility measurements were made on Gouy's balance. The experimental results are summarized in Tables 1 and 2.

TABLE-1
ANALYTICAL DATA OF LIGAND AND METAL COMPLEXES

Ligand/ complexes (Colour)	m.w.	m.p. (°C)	Stoichiometry	Molar cond. (1×10^{-3}) (ohm^{-1} cm^2 mol^{-1})	Elemental analysis (%), Found (Calcd.)				$\mu_{eff.}$ (B.M.)
					C	H	N	M	
$C_{16}H_{11}O_4N$ (Green)	281	265	—	3.40	67.69 (68.32)	3.55 (3.90)	4.55 (4.90)	—	—
$CuC_{32}H_{20}O_8N_2$ (Light brown)	623	> 300	1 : 2	4.15	61.12 (61.58)	3.48 (3.20)	4.25 (4.44)	10.59 (10.19)	1.76
$NiC_{32}H_{20}O_8N_2{\cdot}2H_2O$ (Pale green)	655	> 300	1 : 2	3.95	59.32 (58.65)	3.52 (3.60)	4.58 (4.27)	9.31 (8.96)	2.76
$CoC_{32}H_{20}O_8N_2{\cdot}2H_2O$ (Brown)	654	> 300	1 : 2	4.25	57.82 (58.43)	3.41 (3.66)	4.15 (4.28)	9.34 (8.99)	4.44
$MnC_{32}H_{20}O_8N_2{\cdot}2H_2O$ (Brown)	651	> 300	1 : 2	4.40	59.55 (58.99)	3.84 (3.68)	4.48 (4.30)	9.09 (8.43)	5.43

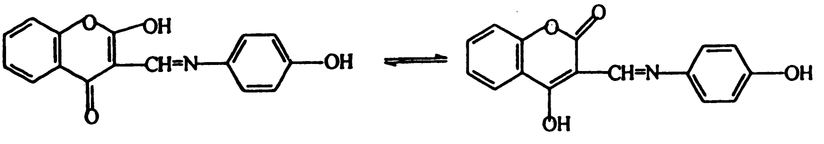
RESULTS AND DISCUSSION

Analytical parameters of ligand and complexes are given in Table-1. All the complexes are coloured, stable in air and decompose at higher temperature (> 300°C). The elemental analysis of metal complexes suggests 1 : 2 ($ML_2{\cdot}nH_2O$, n = 0, 1, 2, . . .) metal to ligand stoichiometry. The complexes are soluble in DMSO, DMF and THF, while they are sparingly soluble in solvents like ethanol, methanol, chloroform, ethyl acetate, ether, etc. The molar conductivity value of 1×10^{-3} M solution of metal complexes in DMF falls in the range 3×10^{-3} to 6×10^{-3} ohm^{-1} cm^{2} mol^{-1}. This value indicates their non-electrolytic behaviour[17, 18].

TABLE-2
UV-VISIBLE AND IR SPECTRAL DATA OF LIGAND AND METAL COMPLEXES

Ligand/ complexes	IR spectral data (cm^{-1})						Electronic spectral data (cm^{-1}) (ε = dm^3 mol^{-1} cm^{-1} × 10^4)			
	ν(OH)	ν(C=O)	ν(C=N)	ν(C–O)	ν(M–N)	ν(M–O)	Assignment for d-d transition			Charge transfer
$C_{16}H_{11}O_4N$	3300	1685	1640	1470	—	—	—	26143 (0.21)	38240 (0.12)	40650 (0.07)
$CuC_{32}H_{20}O_8N_2$	3400	1685	1610	1420	520	460	21880 (0.31)	26809 (0.78)	32362 (2.50)	38240 (4.30)
$NiC_{32}H_{20}O_8N_2 \cdot 2H_2O$	3400	1670	1610	1440	520	470	21550 (0.20)	—	31897 (2.80)	38087 (5.15)
$CoC_{32}H_{20}O_8N_2 \cdot 2H_2O$	3400	1670	1610	1440	540	470	23200 (1.40)	—	32520 (3.50)	38240 (5.04)
$MnC_{32}H_{20}O_8N_2 \cdot 2H_2O$	3400	1680	1610	1440	520	470	23557 (1.40)	—	33000 (4.60)	38314 (7.20)

IR spectrum of ligand shows strong band in the region 3300–3200 cm^{-1} which is assigned to hydrogen bonded ν(OH) stretching vibration[19]. The spectra of complexes exhibit a broad absorption band in the region of 3200–3400 cm^{-1} with weak intensities attributed to —(OH) group of the co-ordinated water molecule[21]. It can be confirmed by TGA analysis. 4-hydroxy coumarin is known to exhibit tautomerism[14] and the present ligand can exist in the tautomeric (a) chromone and (b) lactone forms.



(a) (b)

IR band for ν(C=O) in chromone form generally appears in the range 1680–1650 cm^{-1}, while that for ν(C=O) in lactone form appears in the range 1720–1700 cm^{-1}.[20] IR spectrum of ligand shows an intense band at 1685 cm^{-1}, which is assigned to ν(C=O) of chromone[19].

IR spectrum of ligand shows a strong band at 1540 cm^{-1}, which is assigned to ν(C=N) azomethine. The lowering of ν(C=N) azomethine group to the extent of 30 cm^{-1} in all complexes indicates the participation of azomethine nitrogen in complexation[23]. The ligand exhibits ν(C—O) stretching vibration at 1470 cm^{-1}. In the metal complexes, ν(C—O) phenolic absorption band appears at 1440–1420 cm^{-1}, which is 20–40 cm^{-1} lower than the corresponding ν(C—O) vibration of the free ligand. This indicates bonding of phenolic oxygen to the metal ion[22]. The additional bands around 530 and 480 cm^{-1} are assigned to ν(M—N) and ν(M—O) modes respectively[20–24]. The changes in the IR spectra of complexes indicate the formation of metal chelates.

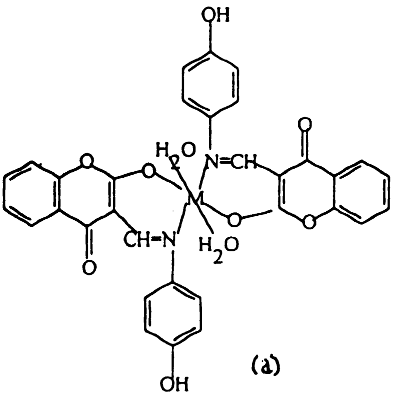
The magnetic moment value of Mn(II) complex is 5.43 B.M. which is slightly lower than the spin only value of 5.92 B.M. This may be due to the presence of magnetic exchange and small traces of Mn(III) species[26]. The electronic spectrum of Mn(II) complex shows three absorption bands in the region 23557, 33000 and 38315 cm^{-1} which are assigned to $^6A_{1g} \rightarrow {}^4T_{2g}$, $^6A_{1g} \rightarrow {}^4E_g$ and charge transfer transition respectively, indicating octahedral geometry[25, 26].

The magnetic moment of Co(II) complex is 4.44 B.M. suggesting high spin octahedral configuration[20]. The abnormal value may be due to orbital contribution. The Co(II) complex exhibits three bands, each at 23200, 32520 and 38240 cm^{-1}. These bands can be assigned to $^4T_{1g} \rightarrow {}^4A_{2g}$, $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ and charge transfer transition respectively, which are in accordance with octahedral geometry[19, 25].

The observed room temperature magnetic moment value of Ni(II) complex in 2.76 B.M., which is close to the value required for high spin octahedral complex[28]. The electronic spectrum of Ni(II) complex shows three bands in the region 21550, 31897 and 38087 cm^{-1}, which can be assigned to the transition of $^3A_{2g} \rightarrow {}^3T_{1g}(F)$, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ and charge transfer spectra respectively, which are observed in octahedral geometry[18, 25].

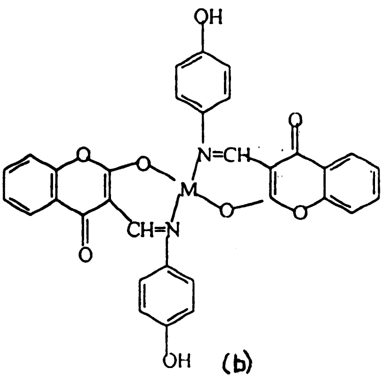
The observed room temperature magnetic moment of Cu(II) complex is 1.76 B.M., which is a characteristic of square-planar monomeric arrangement[29]. The electronic spectrum of Cu(II) complex shows four absorption bands, each at 21880, 26809, 32362 and 38240 cm^{-1}. The first two bands can be assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions respectively, while the last two bands may be attributed to charge transfer transition[30].

On the basis of magnetic susceptibility measurements, analytical and spectral data, Mn(II), Co(II) and Ni(II) complexes exhibit octahedral structure (a), while Cu(II) complex exhibits a square-planar structure (b).



(a)

M—Ni, Co, Mn



(b)

M—Cu

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