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Spectral and Lattice Parameters of Transition Metal Complexes of Polydentate Schiff Bases Derived from 3-Formyl 4-Hydroxy Coumarin and 4-Amino phenol/2-Amino benzoic acid

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Metal(II) complexes of type $M(L^1)_2 \cdot nH_2O$ and $M(L^2)_2 \cdot nH_2O$ [where M = Mn(II), Co(II), Ni(II), Cu(II), L^1 = Schiff base derived from 3-formyl-4-hydroxy coumarin and 4-amino phenol, L^2 = Schiff base derived from 3-formyl-4-hydroxy coumarin and 2-amino benzoic acid, n = 0,1,2] have been prepared and characterized by different physico-chemical methods like, IR, ESR, NMR, X-ray, UV-Vis, etc. Molar conductivity measurements indicate that the complexes are non-electrolytic in nature. Magnetic measurements and electronic spectra indicate that some complexes exhibit octahedral geometry and others exhibit square-planar geometry. The analytical data indicate that metal to ligand stoichiometry in $M(L^1)$ complexes are 1 : 2 and $M(L^2)$ complexes are 1 : 1.

Key Words: Transition metal complexes, Polydentate, Schiff Bases.

INTRODUCTION

Transition metal compounds containing the Schiff base ligands have been of interest for many years. These complexes play an important role in the developing of coordination chemistry related to catalysis and enzymatic reactions, magnetism and molecular architectures[1–3]. Schiff bases and its transitional complexes have been used as anticancer, anti-tubercular, antibacterial, antifungal, hypotensive and hypothermic reagents[4, 5]. Schiff bases derived from coumarin and its metal complexes have been found to be exhibiting antibiotic, antibacterial, antifungal, anticoagulation and plant regulating activities[6, 7]. In this paper we describe the synthesis, characterization and crystal lattice parameters of transition metal complexes of Schiff bases derived from 3-formyl-4-hydroxy coumarin and 4- aminophenol (HL^1) or 2-amino benzoic acid (H_2L^2) with Mn(II), Co(II), Ni(II) and Cu(II) ions.

EXPERIMENTAL

All chemicals used for the synthesis were of AR grade. 4-Hydroxy coumarin was obtained from Fluka Ltd. Triethyl orthoformate, 4-aminophenol, 2-amino benzoic acid and metal salts were obtained from S.D. Fine Chemicals. Distilled solvents were used throughout the experiment.

Synthesis of Schiff bases: 3-Formyl-4-hydroxy coumarin was synthesized according to the method reported in literature[8]. The Schiff bases were prepared by refluxing 3-formyl-4-hydroxy coumarin (3.8 g, 20 mmol) with 4-aminophenol (2.18 g, 20 mmol)/2-amino benzoic acid (2.74 g, 20 mmol), in ethanol for 3 h. The resulting solution was concentrated and then cooled. The solids formed were filtered off, washed with water and then with ethanol and dried in an oven. The Schiff bases were recrystallized from ethanol. m.p. is 265°C and 275°C respectively.

Synthesis of metal complexes: The metal complexes were synthesized by mixing hot ethanolic solution of ligands with hot ethanolic solution of metal salts, in the ratio of 1 : 2 for ligand HL^1 and 1 : 1 for ligand H_2L^2. The resulting mixture was refluxed for 3 h on a water bath and cooled. The pH of the solutions was adjusted in the range 6.5–8 by adding alcoholic ammonia. The reaction mixture was digested for 30 min. The metal complexes obtained were filtered, washed with water and then with hot ethanol and dried in an oven.

The melting points of all the complexes were determined by open capillary method. Elemental analysis was carried out in the Micro-analytical Lab, University of Mumbai. The metal content of all the metal complexes was determined by standard method. The complexes were examined for solubility using various solvents. Molar conductivities of ligands and complexes were recorded using 1×10^{-3} M solutions in DMF on Toshniwal TSM-15 conductivity meter. The electronic absorption spectra of ligand and complexes were recorded in the UV-Vis region using DMF as solvent on UV-Vis 2100 spectrometer 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 using $Hg[Co(NCS)_4]$ as reference. Thermogravimetric analyses were carried out on Perkin-Elmer instruments, Pyris Diamond TG/DTA analyzer in static nitrogen atmosphere with a heating rate of 10°C per min. ^1H NMR spectrum of ligand was recorded using Bruker spectrospin at 400 MHz. X-ray diffraction spectra were recorded on X-ray diffractometer supplied by M/s Philips, Holland.

RESULTS AND DISCUSSION

Analytical parameters of the ligands and complexes are given in Table-1. All complexes are coloured, stable in air and decompose at higher temperature. The elemental analysis of the metal complexes suggests 1 : 2 metal to ligand stoichiometry for ligand $H(L^1)$ and 1 : 1 metal to ligand stoichiometry for ligand $H_2(L^2)$. The complexes were soluble in DMF, DMSO, THF, etc. The molar conductivity of 1×10^{-3} solution of metal complexes in DMF falls in the range of 3×10^{-3} to 8×10^{-3} ohm^{-1} cm^2 mol^{-1}. The low conductance value of the metal complexes indicates their non-electrolytic nature.

The magnetic moments of the Mn(II) complexes are 5.43 and 4.95 B.M. which suggest high spin octahedral or tetrahedral complexes, respectively. The electronic absorption spectra of MnL^1 shows bands at 15740 and 25570 cm^{-1} that are due to *d-d* transitions in octahedral environment[9]. The complexes MnL^1 and MnL^2 show bands at 33003 and 29627 cm^{-1} respectively that are assigned to charge transfer transition. The CoL^1 and CoL^2 show bands at 14705, 23752 and 11248, 22988 cm^{-1}, which are assigned to *d-d* transition in octahedral and square-planar geometry respectively[10, 11]. The bands at 32573 and 29850 cm^{-1} are due to charge transfer transition. The magnetic moments of these complexes are 4.44 and 1.85 B.M, which are in agreement with the octahedral and square-planar structures. The NiL^1

TABLE-1

ANALYTICAL AND PHYSICAL DATA OF COMPOUNDS

Compounds/Empirical formulae	m.w.	Colour	m.p. (°C)	Molar cond. (ohm^{-1} cm^2 mol^{-1})	Stoichio-metry	Elemental analysis (%), Found (Calcd.)				Maagnetic moment $\mu_{eff.}$ (B.M.)
						C	H	N	M	
HL^1 $C_{16}H_{11}NO_4$	281.00	Green	265	3.40	–	67.69 (68.32)	3.65 (3.90)	4.55 (4.90)	–	–
$Mn(L^1)_2 \cdot 2H_2O$ $Mn \cdot C_{32}H_{20}N_2O_8 \cdot 2H_2O$	650.94	Light brown	> 300	4.15	1:2	59.55 (58.99)	3.84 (3.69)	4.48 (4.30)	9.09 (8.93)	5.43
$Co(L^1)_2 \cdot 2H_2O$ $Co \cdot C_{32}H_{20}N_2O_8 \cdot 2H_2O$	654.93	Pale green	> 300	3.95	1:2	59.82 (58.43)	3.41 (3.66)	4.15 (4.28)	9.34 (8.99)	4.44
$Ni(L^1)_2 \cdot 2H_2O$ $Ni \cdot C_{32}H_{20}N_2O_8 \cdot 2H_2O$	654.71	Brown	> 300	4.25	1:2	59.85 (59.43)	3.48 (3.66)	4.58 (4.28)	9.31 (8.96)	2.76
$Cu(L^1)_2$ $Cu \cdot C_{32}H_{20}N_2O_8$	623.54	Brown	> 300	4.40	1:2	61.12 (61.58)	3.48 (3.20)	4.25 (4.44)	10.59 (10.14)	1.76
HL^2 $C_{17}H_{11}NO_5$	309.00	Yellow	275	4.85	–	66.52 (66.01)	3.85 (3.56)	4.78 (4.53)	–	–
$Mn(L^2) \cdot H_2O$ $Mn \cdot C_{17}H_9NO_5 \cdot H_2O$	379.94	Off white	> 300	6.58	1:1	53.89 (53.68)	2.87 (2.36)	3.98 (3.68)	14.68 (14.38)	4.95
$Co(L^1) \cdot H_2O$ $Co \cdot C_{17}H_9NO_5 \cdot H_2O$	383.93	Light brown	> 300	7.51	1:1	52.34 (52.89)	2.51 (2.33)	3.82 (3.63)	15.80 (15.28)	1.85
$Ni(L^2) \cdot H_2O$ $Ni \cdot C_{17}H_9NO_5 \cdot H_2O$	383.71	Green	> 300	8.24	1:1	52.34 (52.89)	2.10 (2.33)	3.43 (3.62)	15.48 (15.22)	Diamagnetic
$Cu(L^2) \cdot H_2O$ $Cu \cdot C_{17}H_9NO_5 \cdot H_2O$	388.54	Green	> 300	5.68	1:1	52.88 (52.30)	2.10 (2.32)	3.89 (3.60)	17.12 (16.35)	1.89

complex shows bands at 15220, 21551 and 31948 cm^{-1}. The first two bands are assigned to *d-d* transitions and the third is due to charge transfer transition in octahedral geometry[10]. The NiL^2 complex shows bands at 14084, 27472 and 34965 cm^{-1}, which are assigned to *d-d* and charge transfer transitions respectively in square-planar geometry[12]. The Cu(II) complexes show absorption bands at around 21000 and 27000 cm^{-1}, which are assigned to *d-d* transition and charge transfer transition respectively in square-planar environment[13].

IR spectra of ligands show bands at around 1680 cm^{-1} assigned to ν(C═O) vibration of chromone. The ligands show bands at around 1645 cm^{-1} due to ν(C═N) of azomethine group[14]. The lowering of the ν(C═N) vibration of the azomethine group to the extent of 30–40 cm^{-1} in all complexes indicates the participation of the azomethine nitrogen in complexation. In all complexes the phenolic ν(C—O) absorption band appears 15–30 cm^{-1} lower than the corresponding ligands. This suggests the bonding of the phenolic oxygen to the metal ions. The additional bands at 570 and 430 cm^{-1} are assigned to ν(M—N) and ν(M—O) respectively. All complexes show a broad absorption band at around 3300 cm^{-1} due to coordinated water molecule.

The TGA analysis of the complexes confirms the presence of coordinated water molecule. All complexes have either one or two water molecules coordinated to the metal, except CuL^1 complex.

DMSO-d_6 was used as a deuterated solvent to measure the ^1H NMR spectrum of the ligand. ^1H NMR spectrum of ligand L^1 shows mutiplet at 6.85–8.75 ppm, which is due to aromatic protons. A singlet at 9.83 ppm is due to azomethine proton. A singlet at 13.54 ppm is assigned to phenolic proton. ^1H NMR spectrum of L^2 ligand shows mutiplet signal due to aromatic proton at 7.18–8.30 ppm. A singlet at 8.93 ppm is due to azomethine proton. Two singlets at 13.77 and 14.53 ppm are assigned to —COOH and phenolic proton respectively.

ESR spectra of the Cu(II) complexes were recorded and $g^{\parallel}$ and $g^{\perp}$ values were in the range of 1.96 and 1.93 respectively, indicating overall symmetry to be square-planar[11]. The absence of the half field signal at 1600 G, corresponding to Ms = ± 2 transition, ruling out any Cu—Cu interaction in ESR spectrum[15]. Therefore, the complexes exist as mononuclear. The g_{av} value less than 2.3 indicates the covalent character of the metal-ligand bond in these complexes. For the observed g value, it is evident that the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital[16]. In the axial spectra the g-values are related with exchange interaction coupling constant (G) by the expression $G = g^{\parallel} - 2/(g^{\perp} - 2)$. According to Hathaway[17, 18] if G value is larger than four, the exchange interaction is negligible because the local tetragonal axes are aligned parallel or are slightly misaligned. If the value of G is less than four, the exchange interaction is considerable and the local tetragonal axes are misaligned. For the present two copper complexes, the G values are 2.38 and 1.74, which suggests that the exchange interaction is considerable and the local tetragonal axes are misaligned.

The crystal lattice parameters of the complexes Mn(II), Co(II), Ni(II) and Cu(II) are found out by X-ray powder diffraction method. The X-ray diffractograms of complexes were recorded in the range of 5–60° 2θ value. The major refluxes and the corresponding *d*-values were obtained. An independent indexing for each of these refluxes was carried out by least-square method. The Miller indices (h, k, l) were calculated and refined using Back-Cal Program by computational method.

The lattice parameters of the MnL^1 complex are a = 16.5614 Å, b = 21.6801 Å, c = 26.4796 Å, α = 90°, β = 58.7891°, γ = 90° with cell volume 9507 $Å^3$. The standard deviation in lattice parameters for Mn(II) complex observed is 0.1785%. The complex is crystallized with 8 molecules (Z) per unit cell. The calculated density of complex (1.0630) is well in agreement with observed density (0.9283). The crystal system and space group of the complex are monoclinic and $P_{2/m}$.

The lattice parameters of the CoL^1 complex are: a = 17.8247 Å, b = 18.1637 Å, c = 47.8745 Å, α = 90°, β = 88.7918°, γ = 90°. The crystal system and space groups of the complex are monoclinic and $P_{2/m}$. The volume of the complex is 15496 $Å^3$. The standard deviation is 0.0199% and the complex crystallizes with 16 molecules per unit cell. This may be due to the larger volume of the complex. The calculated density (1.1225) is well in accordance with the observed (1.0788) value.

The lattice parameters of the NiL^1 complex are: a = 16.5286 Å, b = 21.7624 Å, c = 26.3731 Å, α = 90°, β = 58.8711°, γ = 90°. The standard deviation of the parameters observed is 0.0093%. The volume of the complex is 8120 $Å^3$. The complex crystallizes with 8 (Z) molecules in the unit cell. The calculated and observed densities are 1.2190 and 1.0698 respectively. The crystal system and space group of the NiL^1 complex are monoclinic and $P_{2/m}$. On the other hand, NiL^2 complex crystallizes in orthorhombic system and the cell parameters are a = 17.6152 Å, β = 21.5858 Å, c = 40.8610 Å and α, β, γ = 90°. The cell volume is 15537 $Å^3$ and number of molecules per unit cell is 8. The calculated and observed densities are 1.3118 and 1.1860 respectively.

The lattice parameters of the CuL^1 complex are a = 165788 Å , b = 21.8443 Å, c = 26.3538 Å, α = 90°, β = 58.8378°, γ = 90° with unit cell volume 8137 $Å^3$. The standard deviation is 1.5121%. The value of Z = 8 molecules per unit cell. The calculated (1.0167) and observed (1.2020) densities agree well. The lattice parameters of the CuL^2 complex are a = 17.95721 Å, b = 20.7190 Å, c = 40.4434 Å. α = 90°, β = 90°, γ = 90°. The complex crystallizes with 32 molecules per unit volume. This value is in accordance with the high cell volume 15233 Å .The crystal systems of the complex are monoclinic and orthorhombic.

On the basis of analytical data, magnetic measurements and spectral data, a possible structure for complexes $M(L^1)_2$ [M = Mn, Co, Ni] is octahedral (Fig. 1a) and $M(L^1)_2$, [M = Cu] is square-planar (Fig. 1b). $M(L^2)$ complexes exhibit square-planar geometry (Fig. 1c).

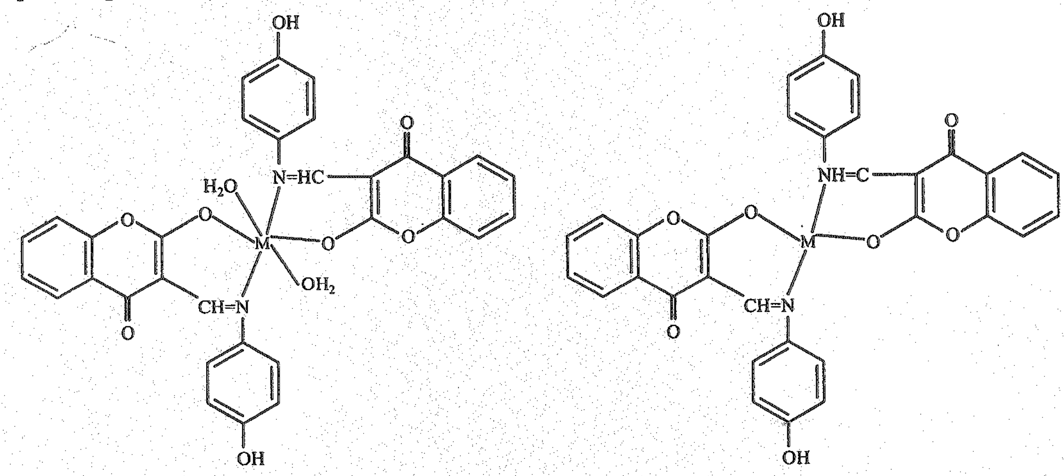
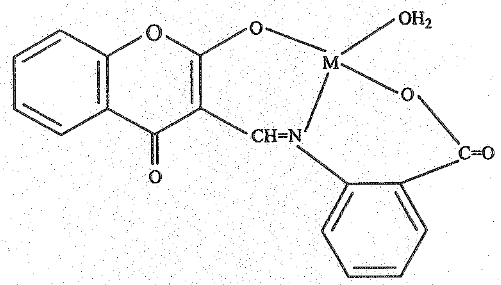


Fig. 1. (a) $M(L^1)_2 \cdot 2H_2O$ (M = Mn, Co, Ni) (b) M = Cu



(c) $[M(L^2)\cdot H_2O]$

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