Reactions of Fe(III), Co(II) and Cu(II) Ions with 2-Salicylidene-4-aminophenyl Benzimidazole

M. Chandrakala[1,2]

[1]Department of Chemistry, Bangalore Institute of Technology, K.R. Road, Bengaluru-560004, India
[2]Department of Chemistry, V.V. Pura College of Science, K.R. Road, Bengaluru-560004, India

Corresponding author: E-mail: mchandrakala.kum@gmail.com

Reactions of Fe(III), Co(II) and Cu(II) ions with 2-salicylidene-4-aminophenyl benzimidazole (LH; SAPbzlH) in ethanol/acetone produced complexes of the formulae $[FeCl(L)_2]_2 \cdot 2H_2O$; $[FeBr_2(LH)_2]Br$; $[MCl(L)]_2 \cdot 0.5H_2O$ (M = Co, Cu), $[M(L)H_2O]_2Br_2 \cdot nH_2O$ (M = Co, n = 0 ; M = Cu, n = 2); $[Co(LH)_2]n$. The metal complexes were characterized by elemental analysis, molar conductance, IR, Far-IR, MS, AAS and TGA. The chloro complex of iron(III) is dimeric with dichloro bridge whereas the bromo complex is monomeric, the metal ion having an octahedral environment. The chloro complexes of Co(II) and Cu(II) are dimeric with bridging Schiff base and terminal halides, the metal ion being in a square planar environment. The bromo complexes of Co(II) and Cu(II) are dimeric with bridging Schiff base and terminal water molecule, the metal ion being in a square planar environment. Molar conductance measurements of the bromo complexes in DMSO has revealed 1:2 electrolytic behaviour. Cobalt acetate and perchlorate with SAPbzlH yielded polymeric complexes with ligand bridging. The magnetic susceptibility data have suggested tetrahedral environment around the metal ion.

Keywords: 2-Salicylidene-4-aminophenyl benzimidazole, Fe(III), Co(II), Cu(II) complexes.

INTRODUCTION

Investigations on benzimidazole derivatives and their transition metal complexes are of considerable interest owing to their analytical, biological and biochemical significance [1-4]. The coordination of benzimidazole derivatives to metal ions depend on various factors like solvent, stoichiometry, temperature and pH of the media [5-7]. Such factors play significant roles on the composition and geometry of the resulting complexes. In this communication, we report the results of the reactions of iron, cobalt and copper halides with 2-salicylidene-4-aminophenyl benzimidazole (SAPbzlH; LH **I**; LH = (N-N-OH)). Which would function as monodentate or bridging ligand.
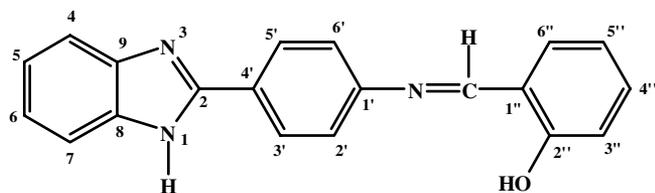
I; SAPbzlH; LH = (N-N-OH)

EXPERIMENTAL

The conductivity measurements of the complexes in DMSO at room temperature were made on a digital conductivity meter (Elico model-180). Elemental analyses were carried out using Elementer Vario EI 111 and Carlo Erba-1108 instruments. The IR spectra of the complexes (KBr medium) were recorded on a Nicolet-impact-400D spectrometer in the range 4000-400 cm⁻¹. The Far-IR spectra of the complexes in polyethylene powder were recorded in the range 700-50 cm⁻¹ using Bruker optical spectrometer IFF 66 V/S.

The metal content was determined by atomic absorption spectrometer ECIL model-4139. Electronic spectra of SAPbzlH and its metal complexes were recorded in the range 200-600 nm on a Elico SL 159 UV-visible spectrophotometer in DMSO. Mass spectra of SAPbzlH and metal complexes were recorded on a ESI, esquine 300 plus, Bruker Daltionics instrument. Room temperature Magnetic moment measurements were carried out by Gouy method using $Hg[Co(SCN)_4]$ as the calibrant. ESR spectra of chloro and bromo complexes of copper(II) in the solid state at room temperature were recorded using a Bruker

EMX X-band instrument with DPPH as the reference. Thermogravimetric analysis of the metal complexes were carried out from ambient temperature up to 1000 °C under nitrogen atmosphere at heating rate of 20 °C min^{-1}.

The chemicals used for the reaction were of Merck make. The solvents were distilled prior to their use.

Reactions of iron(III) salts with 2-salicylidene-4-aminophenyl benzimidazole [FeCl(L)$_2$]$_2$·2H$_2$O, [FeBr$_2$(LH)$_2$]Br; (LH= SAPbzlH): To an acetone solution (7.5 mL) of iron halide (0.60 mmol) as chloride (0.08 g)/bromide (0.14 g) was added SAPbzlH (0.38 g; 1.20 mmol) in acetone (7.5 mL) and the mixture was refluxed for about 6 h on a steam-bath, during which a coloured solid separated. The solid was washed with acetone and dried in vacuum.

Reactions of cobalt(II) salts with 2-salicylidene-4-aminophenyl benzimidazole [CoCl(L)]$_2$·0.5H$_2$O, [Co(L)H$_2$O]$_2$Br$_2$, [Co(LH)$_2$]$_n$; (LH = SAPbzlH): To an ethanolic solution (7.5 mL) of cobalt salt (0.60 mmol) as chloride (0.143 g)/bromide (0.131 g)/acetate (0.149 g)/perchlorate (0.155 g) was added SAPbzlH (0.38 g; 1.20 mmol) in ethanol (7.5 mL) and the resultant solution was refluxed for about 6 h on a steam-bath and on cooling the mixture a coloured solid separated and the solid was washed with ethanol and dried in vacuum.

Reactions of copper(II) salts with 2-salicylidene-4-aminophenyl benzimidazole [CuCl(L)]$_2$·0.5H$_2$O, [Cu(L)H$_2$O]$_2$Br$_2$· 2H$_2$O; (LH = SAPbzlH): To an ethanolic solution (7.5 mL) of copper halide (0.60 mmol) as chloride (0.16 g)/bromide (0.22 g) was added SAPbzlH (0.38 g; 1.20 mmol) in ethanol (7.5 mL) and the mixture was refluxed for about 6 h on a steam-bath. The mixture was left for overnight during which coloured solid separated. The solid was washed with ethanol and dried in vacuum.

RESULTS AND DISCUSSION

The analytical data of complexes are presented in Table-1. The molar conductance data in DMSO has revealed [FeCl(L)$_2$]$_2$· 2H$_2$O as non-electrolyte, [FeBr$_2$(LH)$_2$]Br as 1:1 electrolyte, [CoCl(L)]$_2$·0.5H$_2$O and [Co(LH)$_2$]$_n$ as non-electrolyte and [Co(L)H$_2$O]$_2$Br$_2$ as 1:2 electrolyte. [CuCl(L)]$_2$·0.5H$_2$O) as non-electrolyte and [Cu(L)H$_2$O]$_2$Br$_2$·2H$_2$O as 1:2 electrolyte [8].

Infrared and Far IR spectral studies: The IR spectrum of the Schiff base (Table-2), SAPbzlH showed a band in the range 3450-3300 cm^{-1} and due to ν(OH) and ν(NH) [9,10]. The spectrum also displayed multiple peaks in the range 3050-2660 cm^{-1} and these are assigned to ν(CH) of the phenyl and methine groups. Two bands at 1600 and 1618 cm^{-1} are ascribed to ν(N=CH) and ν(C=C), respectively. A peak at 1572 cm^{-1} is assigned to ν(N=C) of the imidazole ring. A band at 1276 cm^{-1} is attributed to ν(C-O) of the phenolic group.

A comparison of the IR spectra of the complexes with that of SAPbzlH revealed minor shifts in the positions of the bands. The ν(C-O) of the phenolic group has shown a marginal shift towards higher wavenumber region, suggesting weak coordination of oxygen to the metal ion. A peak observed at 1600 cm^{-1} in the spectrum of Schiff base due to ν(N=CH) has shifted to lower wavenumber by 15-16 cm^{-1} in the spectra of the complexes, indicating the coordination of the imine nitrogen to the metal ion [11,12]. IR bands observed in the range 3700-3300 cm^{-1} are attributed to coordinated/lattice water molecules in the complexes. In the Far-IR spectrum of the chloro complex of iron a broad band observed at 370 cm^{-1} is assigned to ν(Fe-Cl(b)); (b = bridging) and other bands at 311 and 231 cm^{-1} are assigned to ν(Fe-N) and ν(Fe-O), respectively [13]. In the case of the chloro complex of cobalt, a broad bands observed at 337, 323 cm^{-1} are assigned to ν(Co-Cl(t)); (t = terminal) and other bands at 291 and 225 cm^{-1} assigned to both ν(Co-N) and ν(Co-O), respectively. In the spectrum of chloro complex of copper, a broad band observed at 350, 325 cm^{-1} is assigned to ν[Cu-Cl(t)]; (t = terminal) further, other bands observed at 284 and 229 cm^{-1} are assigned to ν(Cu-N) and ν(Cu-O), respectively [13].

Electronic and magnetic susceptibility studies: The electronic spectrum of SAPbzlH (Table-3) in DMSO exhibited

TABLE-1
PHYSICAL AND ANALYTICAL DATA OF METAL COMPLEXES

S. No.	Compound	Colour	m.p. (°C)	Elemental analysis (%): Found (calcd.)			
				C	H	N	M
1	[FeCl(L)$_2$]$_2$·2H$_2$O	Brown	> 250	65.11 (65.45)	4.76 (4.09)	11.77 (11.45)	7.91 (7.62)
2	[FeBr$_2$(LH)$_2$]Br	Brown	> 250	52.25 (52.08)	4.46 (3.25)	9.96 (9.11)	5.64 (6.05)
3	[CoCl(L)]$_2$·0.5H$_2$O	Green	> 250	58.62 (58.41)	3.72 (3.52)	10.38 (10.22)	14.49 (14.33)
4	[Co(L)H$_2$O]$_2$Br$_2$	Green	> 250	52.19 (51.21)	3.67 (3.41)	9.13 (8.96)	13.69 (12.57)
5	[Co(LH)$_2$]$_n$	Pink	> 250	69.46 (69.37)	4.20 (4.19)	12.29 (12.14)	8.60 (8.51)
6	[CuCl(L)]$_2$·0.5H$_2$O	Olive green	> 250	57.76 (57.76)	3.70 (3.48)	10.35 (10.10)	15.87 (15.29)
7	[Cu(L)H$_2$O]$_2$Br$_2$·2H$_2$O	Olive green	> 250	48.30 (48.83)	3.35 (3.66)	8.43 (8.54)	13.43 (12.92)

TABLE-2
IR AND FAR-IR SPECTRAL DATA (cm^{-1}) OF SAPbzlH AND ITS METAL COMPLEXES

Compound	ν(OH/NH)	ν(N=C)	ν(C=C)	ν(N=CH)	ν(C-O)	ν(M-X(b))	ν(M-N)	ν(M-O)
SAPbzlH	3450-3300	1572	1618	1600	1276	–	–	–
[FeCl(L)$_2$]$_2$·2H$_2$O	3550-3000	1570	1618	1585	1298	370	311	231
[FeBr$_2$(L)$_2$]Br	3550-3300	1597	1620	1584	1307	–	–	–
[CoCl(L)]$_2$·0.5H$_2$O	3550-3350	1535	1604	1585	1284	337, 323	291	225
[Co(L)H$_2$O]$_2$Br$_2$	3764-3573	1537	1602	1582	1282	–	–	–
[Co(LH)$_2$]$_n$	3500-3300	1531	1577	1600	1276	–	–	–
[CuCl(L)]$_2$·0.5H$_2$O	3550-3300	1539	1614	1580	1282	350, 325	284	229
[Cu(L)H$_2$O]$_2$Br$_2$·2H$_2$O	3700-3300	1533	1602	1587	1284	–	–	–

TABLE-3
ELECTRONIC SPECTRAL DATA AND MAGNETIC MOMENTS OF SAPbzlH AND METAL COMPLEXES

Compound	λ, nm (cm^{-1})	Transition	μ_{eff} (BM)
SAPbzlH	297 (33,670) –379 (26,385), 414 (24,154)	$\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$	–
[FeCl(L)$_2$]$_2$·2H$_2$O	522 (19,157)	$^2T_{1g} \xrightarrow{d-d} {}^2T_{1g}$	2.72 (Oh)
[FeBr$_2$(L)$_2$]Br	520 (19,230)	$^2T_{1g} \xrightarrow{d-d} {}^2T_{1g}$	2.68 (Oh)
[CoCl(L)]$_2$. 0.5H$_2$O	594 (16,835)	$^4A_{2g} \xrightarrow{d-d} {}^4T_{1g}(P)$	2.87 (sq.p)
	647 (15,444)	$^4A_{2g} \longrightarrow {}^4T_{1g}(F)$	
[Co(L)H$_2$O]$_2$Br$_2$	596 (16,708)	$^4A_{2g} \xrightarrow{d-d} {}^4T_{1g}(P)$	2.27 (sq.p)
	666 (15,021)	$^4A_{2g} \longrightarrow {}^4T_{1g}(F)$	
[Co(LH$_2$)]$_n$	919 (10,881)	$^4A_2 \xrightarrow{d-d} {}^4T_1$	4.52 (Td)
	531 (18,832)	$^4A_2 \longrightarrow {}^4T_1(P)$	
[CuCl(L)]$_2$·0.5H$_2$O	718 (13,927)	$^2B_{1g} \xrightarrow{d-d} {}^2A_{1g}$	1.85 (sq. p)
[Cu(L)H$_2$O]$_2$Br$_2$·2H$_2$O	721 (13,869)	$^2B_{1g} \xrightarrow{d-d} {}^2A_{1g}$	1.72 (sq. p)

three bands at 297 (33,670), 379 (26,385) and at 414 nm (24,154 cm^{-1}). These are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The electronic spectra of complexes **1** and **2** (Figs. 1 and 2) exhibited absorption bands at 522, 520 nm and these were assigned to $^2T_{1g} \rightarrow {}^2T_{1g}$ (*d-d*) transition arising from octahedral environment around iron [14]. Complexes **3**, **4** and **5** exhibited absorption bands at around 594, 647 nm for the chloro (Fig. 3) 596, 666, 1013 nm for the bromo (Fig. 4, 4a) and 531, 919 nm for polymeric (Fig. 5) types. The bands were assigned to *d-d* transitions; $^4A_{2g} \rightarrow {}^4T_{1g}(P)$, $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ arising from square planar [15,16] geometry for the chloro and bromo complexes and tetrahedral [17,18] geometry $^4A_2 \rightarrow {}^4T_1$, $^4A_2 \rightarrow {}^4T_1(P)$ for the polymeric complex. Copper complexes **6** and **7** (Figs. 6 and 7) exhibited absorption bands at 718 and 721 nm. The bands were assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ (*d-d*) transition arising from the square planar environment around divalent copper [19,20].
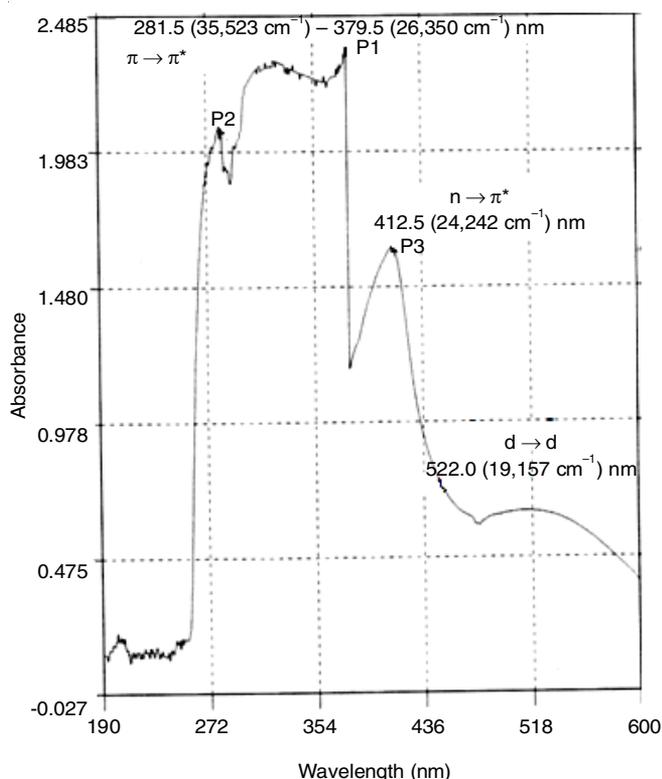
Fig. 1. Electronic absorption spectrum of [FeCl(L)$_2$]$_2$·2H$_2$O complex
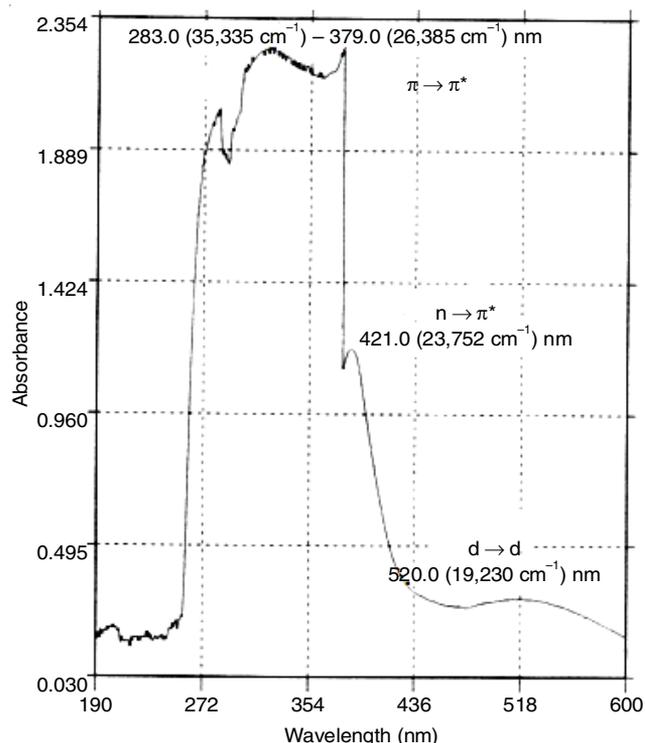
Fig. 2. Electronic absorption spectrum of [FeBr$_2$(LH)$_2$]Br complex

The solid state magnetic moments of iron(III) complexes (**1** and **2**) under ambient condition are in the range of 2.72-2.68 BM and the values are closer to low spin octahedral environment around the metal ion [21]. The magnetic moments of cobalt(II) complexes are in the range of 2.27-2.87 BM for **3** and **4** and 4.52 BM for **5**; the values suggest square planar [22,23] (for **3**, **4**) and tetrahedral [24,25] (for **5**) environments around the metal ion. The magnetic moments of copper(II) complexes (**6** and **7**) are in the range 1.72-1.85 BM, implying a square planar environment [26].

Mass spectral analysis: The mass spectrum of iron(III) complex **1**, exhibited a large number of peaks, some of them being higher than those of the molecular ion peaks. The peaks latter may be due to the association of fragmented species formed in the spectrum are three of the prominent peaks observed at *m/z*, 726, 314 and 210 are assigned to fragmented species, [FeCl(L)$_2$·0.5H$_2$O], [L+H]$^+$ and [4-APBzlH+H]$^+$,
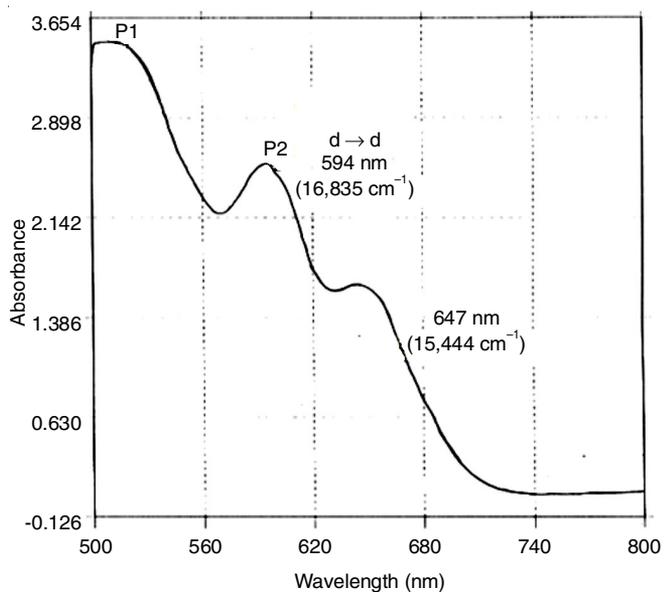
Fig. 3. Electronic spectrum of [CoCl(L)]$_2$·0.5H$_2$O complex
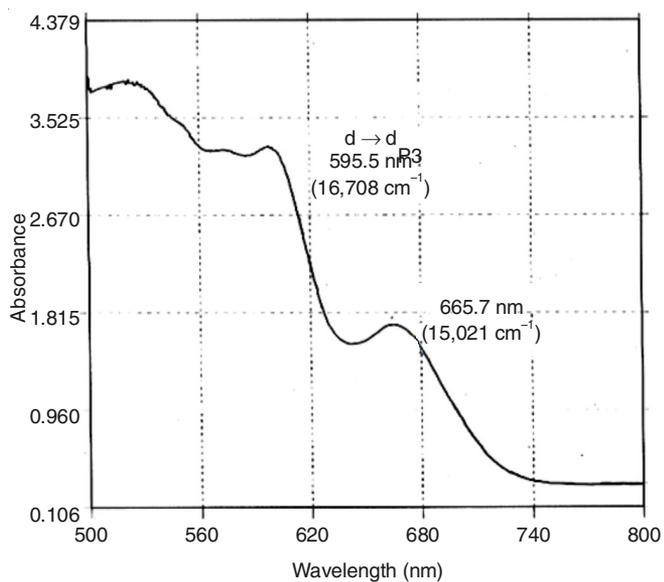
Fig. 4. Electronic spectrum of [CoBr(L)(H$_2$O)]$_2$ complex
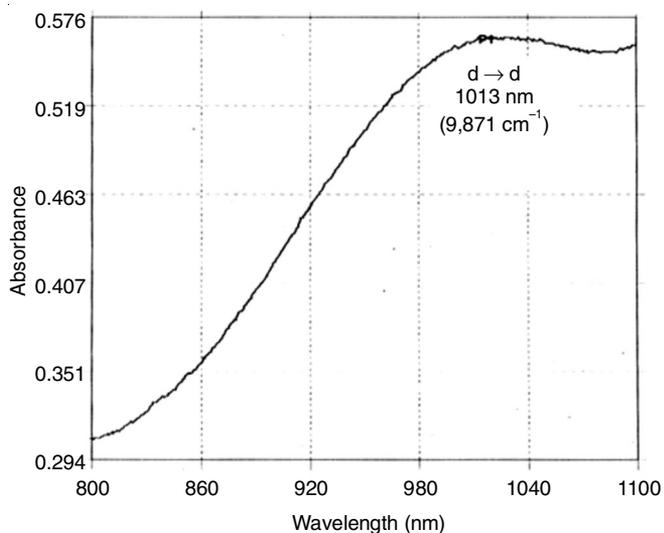
Fig. 4a. Expanded region of electronic spectrum of [CoBr(L)(H$_2$O)]$_2$ complex
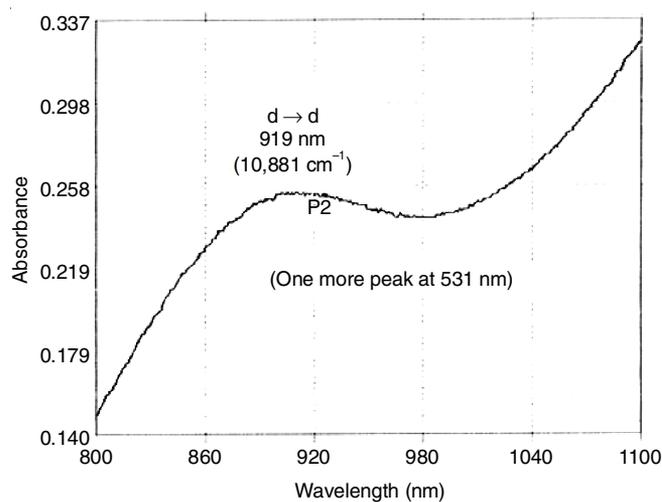
Fig. 5. Electronic spectrum of [Co(LH)$_2$]$_n$ complex
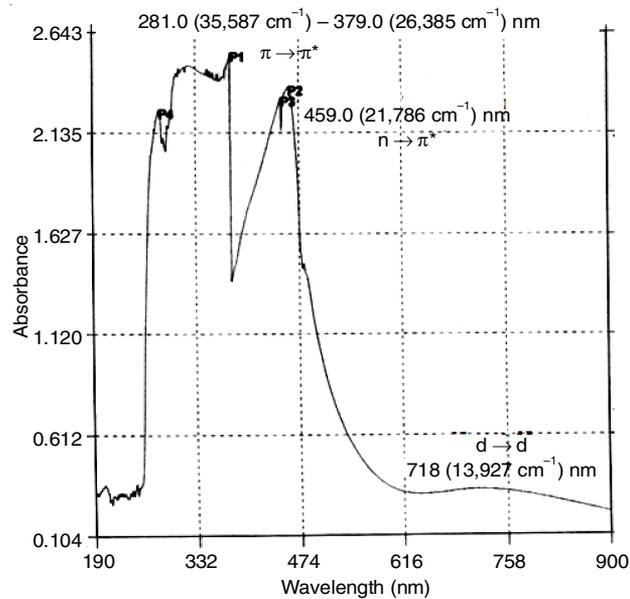
Fig. 6. Electronic spectrum of [CuCl(L)]$_2$·0.5H$_2$O complex
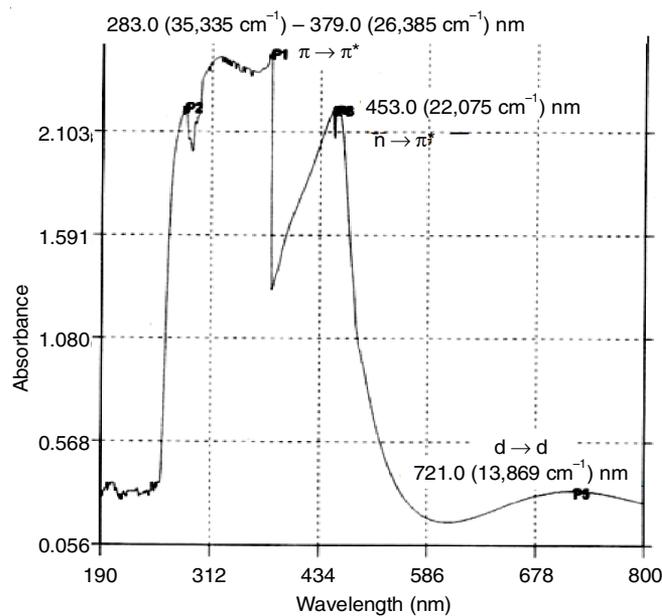
Fig. 7. Electronic spectrum of [Cu(L)H$_2$O]$_2$Br$_2$·2H$_2$O complex

respectively. In the case of cobalt complexes, the peaks observed at m/z, 824, 624 and 437 are assigned to fragmentation species $[CoCl(L)]_2 \cdot 0.5H_2O$, $[Co_2Cl(L-H)]_{1.5} + 3H]^+$ and $[Co_2L \cdot 0.5H_2O-2H]^+$, 979, 907, 684, 627 and 437 to $Co_2L_2(H_2O)_2Br_2 \cdot 3H_2O + 5H$, $Co_2 L_2(H_2O)_2Br_2 \cdot 2H_2O + 6H$, $[CoL_2 + 1H]^+$, $[L_2 + 3H]^+$ and $[Co_2 L \cdot 0.5H_2O-2H]^+$ and 689, 527 and 367 to $[Co(LH)_2]_n$, $[Co(LH)_{1.5}]^+$, $[Co(LH) \cdot H_2O]^+$. For the copper chloro complex, two prominent peaks observed at m/z, 872, 624 and 314 are attributed to fragmented species $[CuCl(L-H)]_2 \cdot 2.5H_2O-4H$, $[Cu_2Cl(L-H)_{1.5}-6H]^+$, $[(L-H)+2H]^+$. The remaining may be due to the association of fragments produced during ionization.

ESR spectral analysis: The observed g values for the copper chloro (Fig. 8) and bromo (Fig. 9) are more than the free electron value, implying covalent character in metal-ligand bonds [27].
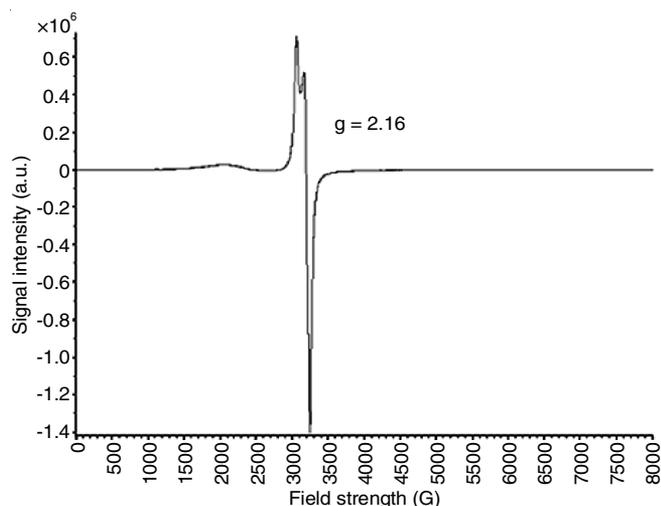
Fig. 8. ESR spectrum of $[CuCl(L)]_2 \cdot 0.5H_2O$ complex
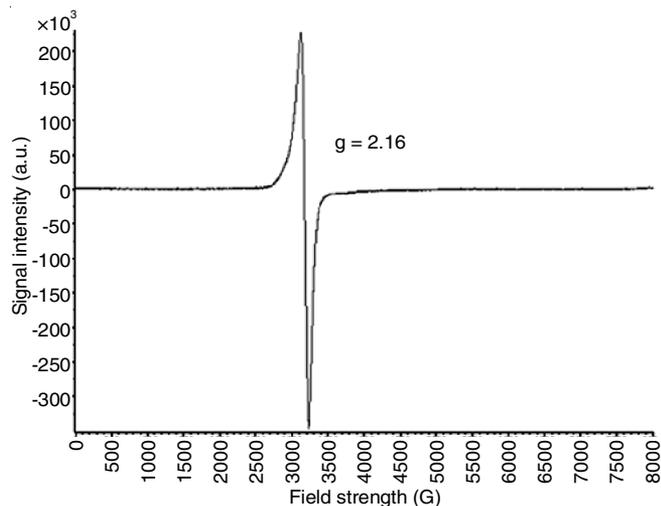
Fig. 9. ESR spectrum of $[CuBr(L)H_2O]_2 \cdot 2H_2O$ complex

Thermogravimetric analysis (TGA): Thermogravimetric analysis of the complexes was carried out under nitrogen atmosphere at a heating rate of 20 °C min^{-1} from ambient temperature up to 1000 °C. The molecular formula of the complex deduced from elemental analysis indicate the presence of lattice water. In case of the iron(III) chloro complex there is a significant weight loss below 120 °C suggesting the presence of lattice water molecules. In case of the cobalt(II) bromo

complex there is a significant weight loss above 400 °C suggesting the presence of coordinated water molecules.

Conclusion

Based on the analytical and spectroscopic studies the following structures have been proposed for the complexes (**II-VI**).
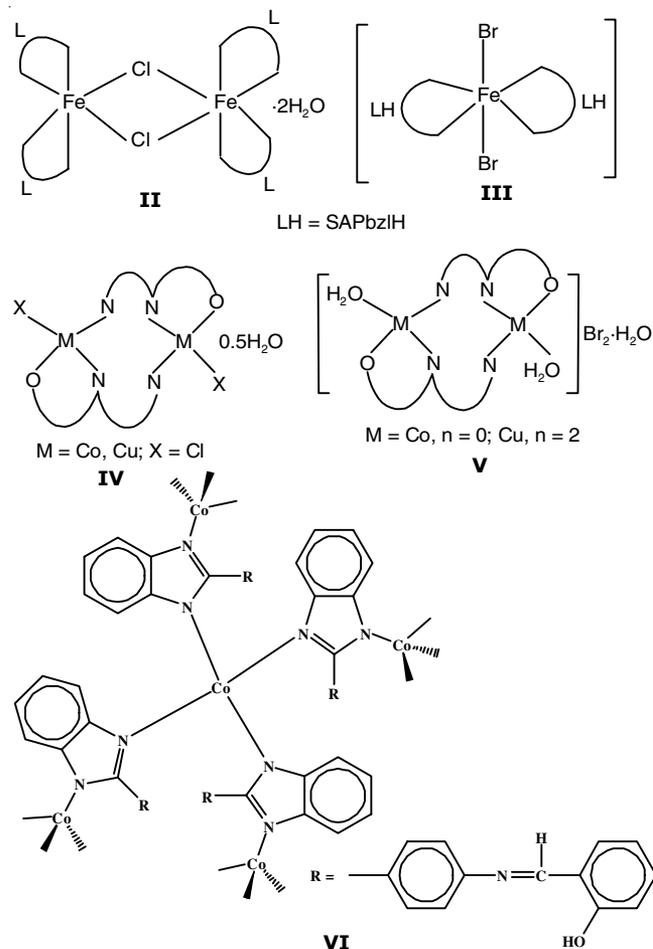
CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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