

## Isolation and Spectroscopic Characterization of some Schiff Base Complexes

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**ABSTRACT:** Five Schiff base complexes of Co(II), Ni(II), Cu(II), Cr(III) and La(III) ions with a Schiff base derived from the reaction of 2-hydroxyacetophenone and ethylenediamine were isolated and characterized by several physicochemical analyses, such as, CHN elemental analysis, molar conductivity, thermogravimetric analysis, spectroscopic techniques (IR, electronic and e.p.r). The CHN elemental analyses showed the formation of the complexes. The molar conductivity measurements revealed the existence of non-electrolytic nature. The thermogravimetric analysis data exhibited the presence of water molecules with different ratios. The infrared spectra showed the complexation sites which bonded to the metal ions. The electronic spectra suggested the geometrical structures of the complexes. The electron paramagnetic resonance spectra of the complexes confirmed the data which obtained from previous analyses.

**Keywords:** Isolation; Spectroscopic Characterization; Schiff base Complexes and Physicochemical Techniques.

**INTRODUCTION:** The coordination trends of several compounds behave as ligands and their geometrical structures produced after chelation with transition metal ions and its biological applications have been reported<sup>1</sup>. The Schiff bases derived from aldehydes and diamines (especially, ethylenediamine), have proved to be the source of versatile ligands for many transition metals, including vanadium(IV)<sup>2</sup>. The Schiff base (Reaction of ethylenediamine and 3-hydroxyl-4-nitrobenzaldehyde) complexes with Co(II), Ni(II), Ni(II) and Zn(II) ions have been synthesized and investigated based on some physicochemical tools. Also their antibacterial, antifungal and DNA binding were reported<sup>3</sup>. Hamil et al.<sup>4</sup> Synthesis some complexes with a Schiff base derived from 2-hydroxyacetophenone and hydrazine. The complexes were characterized by using several physicochemical tools and an octahedral geometry was confirmed for all the complexes. The trivalent complexes of chromium, ruthenium and molybdenum with 2-hydroxyacetophenonepropylimine have been isolated and studied by using several physicochemical tools<sup>5</sup>.

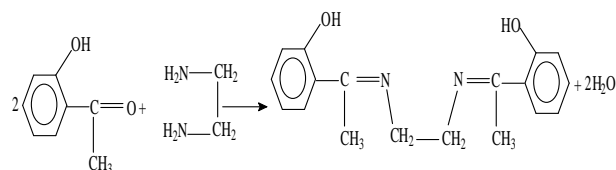
This study aims to isolate and characterize five Schiff base complexes derived from 2-hydroxyl-

acetophenone and ethylenediamine with some divalent and trivalent metal ions.

**MATERIAL AND METHODS:** All chemicals and solvents used in this investigation were of Analar Grade (BDH/Aldrich). They include; 2-hydroxyacetophenone, ethylenediamine, metal salts CoCl<sub>2</sub>.6H<sub>2</sub>O, NiCl<sub>2</sub>.6H<sub>2</sub>O, CuSO<sub>4</sub>.5H<sub>2</sub>O, CrCl<sub>3</sub>.6H<sub>2</sub>O, LaCl<sub>3</sub>.7H<sub>2</sub>O, absolute ethanol and dimethyl formamide (DMF). The CHN elemental analyses were done by using 2400 elemental analyzer. The molar conductance measurements were performed on a BC 3020 Professional Benchtop Conductivity Meter. The thermogravimetric analyses of the complexes were achieved using Shimadzu thermal analyzer (Japan). The weight loss of the sample was measured from ambient temperature up to 1000°C in a rate of 10°C/min. The infrared spectra were recorded as KBr disc on a Perkin-Elmer 1430 IR Spectrophotometer. The electronic spectra were recorded on a Unicam Model UV-2 Spectrophotometer. The EPR spectra were recorded by using EMX ESR spectrometer (Bruker) 1998 Y. All analyses were done at Microanalytical center, Cairo University, Giza, Egypt.

**Preparation of complexes:** These complexes were formed by adding the synthesized Schiff base (<sup>5</sup>); L (2.96 gm; 0.01 mole) in 50 cm<sup>3</sup> ethanol to CoCl<sub>2</sub>.6H<sub>2</sub>O, NiCl<sub>2</sub>.6H<sub>2</sub>O, CuSO<sub>4</sub>.5H<sub>2</sub>O, CrCl<sub>3</sub>.6H<sub>2</sub>O and LaCl<sub>3</sub>.7H<sub>2</sub>O (2.3793, 2.3769, 2.4968, 2.6650 and 3.7137 gm). The mixtures were stirred for three hours. Few drops of ammonia solution were added to establish the pH equal to 8 until the complexes isolated. The isolated complexes were filtered, recrystallized and finally kept in desiccators over silica gel. The obtained complexes have melting points >250<sup>0</sup>C and their yields are in the range of 74-92%

**RESULTS AND DISCUSSION:** The reaction of ethylenediamine with 2-hydroxyacetophenone gives one product which is a Schiff base of chemical structure shown below:



**Physical properties, CHN elemental analysis and molar conductivity:** The synthesized Schiff base is soluble in alcohols, DMF and DMSO solvents, but not in water. Whereas, its complexes with Co(II), Ni(II), Cu(II), Cr(III) and La(III) are not soluble in water and alcohols, but soluble in DMF or DMSO solvents. The Schiff base and its complexes are stable in air and their CHN elemental analysis data confirm the formation of the Schiff base and its complexes have a ratio of 1:1 and 2:1 [M:L]. The complexes are non-electrolytes as the molar conductivity values are found to be in the range of 5.66-29.80 Ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>.<sup>6</sup> The CHN elemental analysis data and the molar conductivity of the complexes are listed in table 1.

**Table 1: Some physical properties, CHN elemental analysis and molar conductivity**

Complexes	Color	M.Wt.	M.P., <sup>0</sup> C	Found (calc.) %				Λ
				C%	H%	N%	Cl%	
[CoL1(H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	Green	407.33	237.2	53.73(53.08)	5.44 (5.94)	6.93 (6.88)	-	16.30
[NiL1(H <sub>2</sub> O) <sub>2</sub> ]	Orange	389.07	298.7	55.09 (55.57)	5.88 (5.70)	7.76 (7.20)	-	5.66
[Cr <sub>2</sub> L1OCl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ] 2H <sub>2</sub> O	Green	593.01	239.8	35.42(36.24)	5.12(5.10)	4.77(4.72)	12.13(11.95)	29.80
[CuL1(H <sub>2</sub> O) <sub>2</sub> ]H <sub>2</sub> O	Violet	411.94	209.2	52.18(52.48)	5.83(5.87)	6.28(6.80)	-	21.50
[LaL1 Cl (H <sub>2</sub> O)] H <sub>2</sub> O	Yellow	504.74	274.4	42.18(42.83)	4.56(4.39)	5.20(5.55)	7.33(7.02)	12.64

**Thermogravimetric analysis:** The thermogravimetric analysis data of the complexes were measured from the ambient temperature up to 800<sup>0</sup>C using a heating rate of 10<sup>0</sup>C/min. The thermogram of the complexes show the weight-losses in the range of 4.16-6.38% which are in a good agreement with the calculated values, indicating the existence of one or two hydrated water molecules at 38-179 <sup>0</sup>C. Meanwhile, at the temperatures of 179-441 <sup>0</sup>C, the values in the range of 4.18-12.89% which are closed to the theoretical values corresponding to the presence of 1, 2, or 4 coordinated water molecules in the complexes. At tempera-

tures of 295-620 <sup>0</sup>C (Table 2 and figures 1-5), the Schiff base (free ligand) decomposes as carbonate or oxalate ion. The metal oxides (CoO, NiO, Cr<sub>2</sub>O<sub>3</sub>, CuO and La<sub>2</sub>O<sub>3</sub>) appeared at the end of the curves as stable states >620 <sup>0</sup>C.<sup>7</sup> The following pattern illustrates the decomposition process of the complexes at different temperatures:

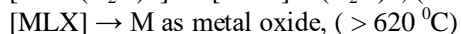
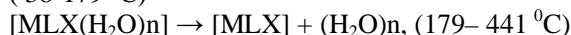
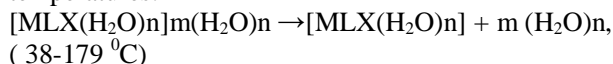


Table 2: Thermogravimetric analysis data of some complexes.

Complexes	Hydrated water weight loss%	No. of water molecule	Temp. °C	Coordinated water weight loss%	No. of water molecules	Temp. °C	Temp. °C of Schiff base decomposition	Metal oxide weight loss%	Temp. °C
[CoL1(H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	4.51 <b>(4.42)</b>	1	42-144	8.99 <b>(8.84)</b>	2	145-302	303-644	18.79 <b>(18.40)</b>	>645
[NiL1(H <sub>2</sub> O) <sub>2</sub> ]	-	-	-	9.83 <b>(9.25)</b>	2	354-441	476-539	18.97 <b>(19.20)</b>	>616
[Cr <sub>2</sub> L1OCl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ]2 H <sub>2</sub> O	6.38 <b>(6.05)</b>	2	38-179	12.89 <b>(12.10)</b>	4	179-295	295-548	25.92 <b>(25.54)</b>	>548
[CuL1(H <sub>2</sub> O) <sub>2</sub> ](H <sub>2</sub> O)	4.16 <b>(4.37)</b>	1	75-132	9.12 <b>(8.74)</b>	2	273-383	459-670	19.73 <b>(19.31)</b>	>670
[LaL1 Cl (H <sub>2</sub> O) <sub>2</sub> ].H <sub>2</sub> O	4.18 <b>(3.56)</b>	1	79-138	4.18 <b>(4.78)</b>	1	252-310	310-610	64.11 <b>(64.55)</b>	>610

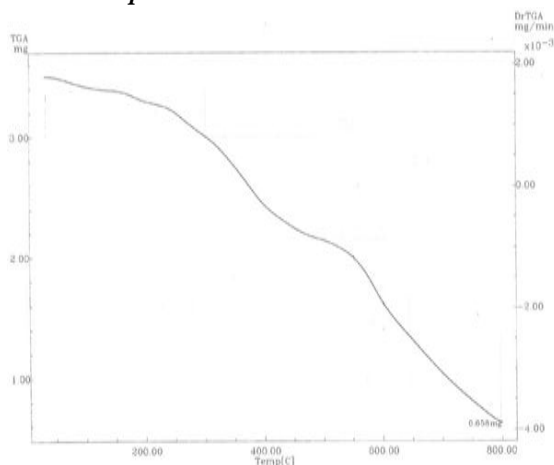
**Bold= Experimental value**

Figure 1: Thermogravimetric analysis of Co-L1 complex.

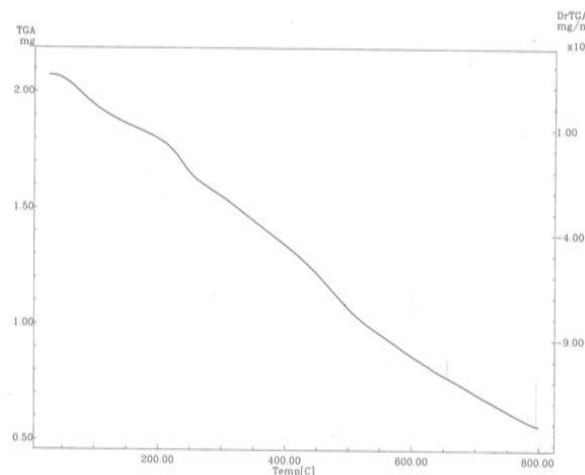
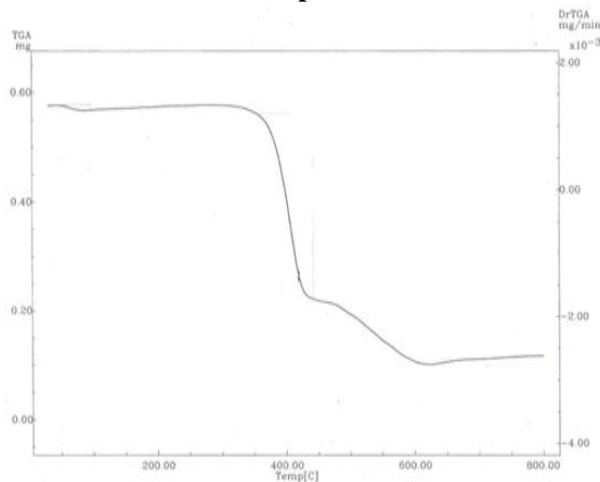
Figure 3: Thermogravimetric analysis of Cr<sub>2</sub>-L1 complex.

Figure 2: Thermogravimetric analysis of Ni-L1 complex.

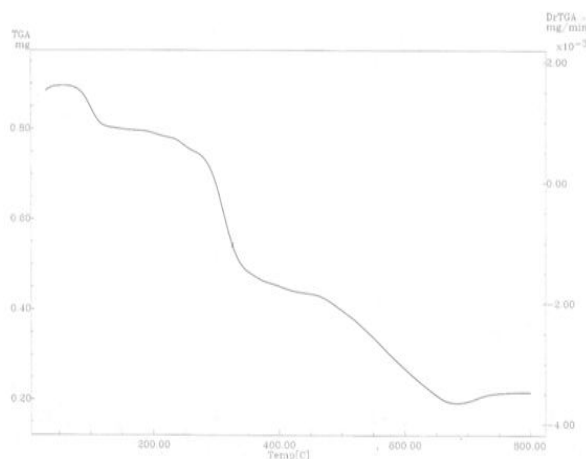
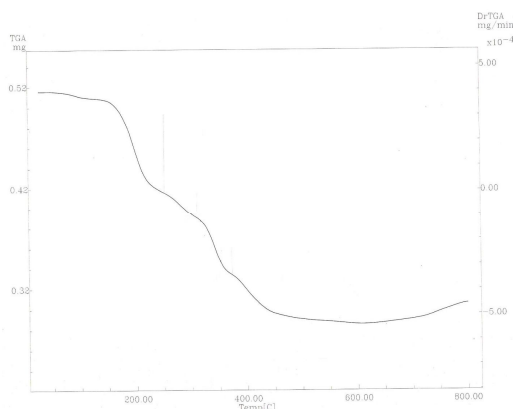
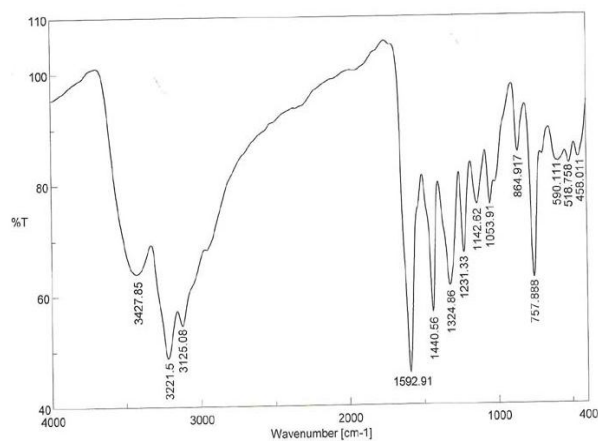


Figure 4: Thermogravimetric analysis of Cu-L1 complex.

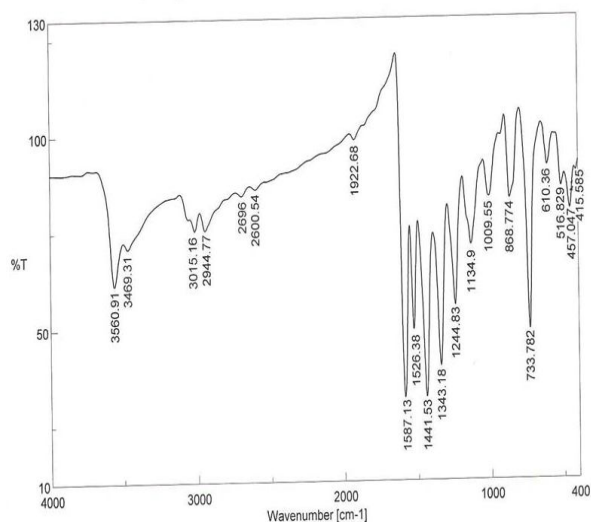


**Figure 5: Thermogravimetric analysis of La-L1 complex.**

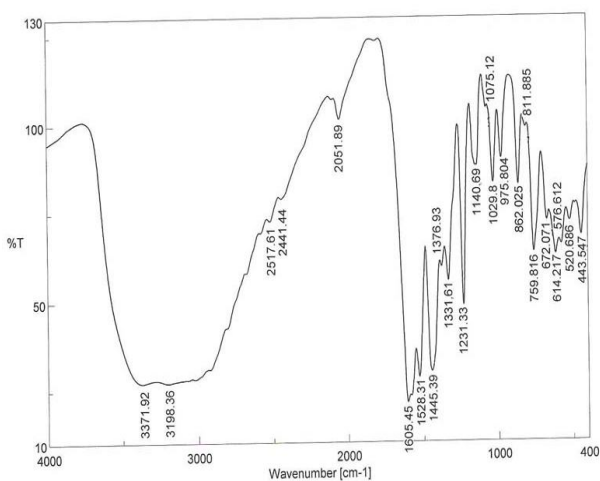
**Infrared Spectra:** The infrared band assignments ( $\text{cm}^{-1}$ ) of the Schiff base and its complexes are listed in table 3 and their spectra are shown in figures (6-10). The spectra of the Schiff base displays a band at  $1610 \text{ cm}^{-1}$  which belongs to  $-\text{C}=\text{N}$ , another band at  $3422 \text{ cm}^{-1}$  is attributed to  $-\text{OH}$  group, and the band corresponds to  $-\text{C}-\text{OH}$  was found at  $1292 \text{ cm}^{-1}$ . The spectra of the complexes show bands in the range of  $1587\text{--}1608 \text{ cm}^{-1}$  which are shifted to lower frequencies during complex formation compared with the free Schiff base indicating the involvement of the azomethine group via nitrogen atom in bonding with the metal ions <sup>(8)</sup> Thus the bands appeared in the range of  $483\text{--}576$  and  $415\text{--}458 \text{ cm}^{-1}$  are corresponding to the existence of  $\nu\text{M}-\text{O}$  and  $\nu\text{M}-\text{N}$  vibrations. The appearance of these bands which are not present in the free Schiff base confirm the participation of azomethine and hydroxyl groups in chelation through nitrogen and oxygen atoms.<sup>9</sup> The same spectra exhibit bands in the range of  $3320\text{--}3560 \text{ cm}^{-1}$  due to the presence of water molecules in the complexes.<sup>10</sup>



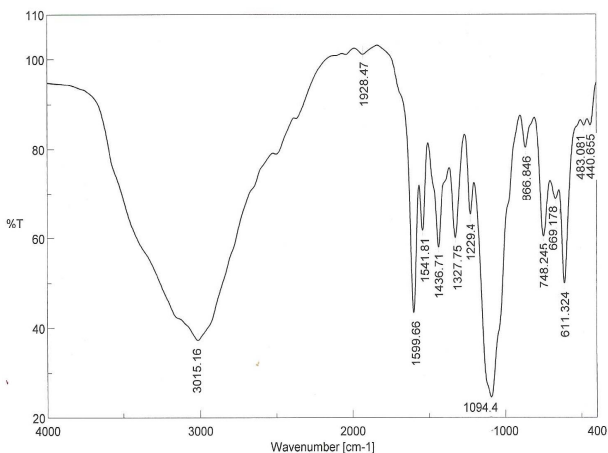
**Figure 6: IR spectrum of Co-L1 complex.**



**Figure 7: IR spectrum of Ni-L1 complex.**



**Figure 8: IR spectrum of  $\text{Cr}_2\text{-L1}$  complex.**



**Figure 9: IR spectrum of Cu-L1 complex.**

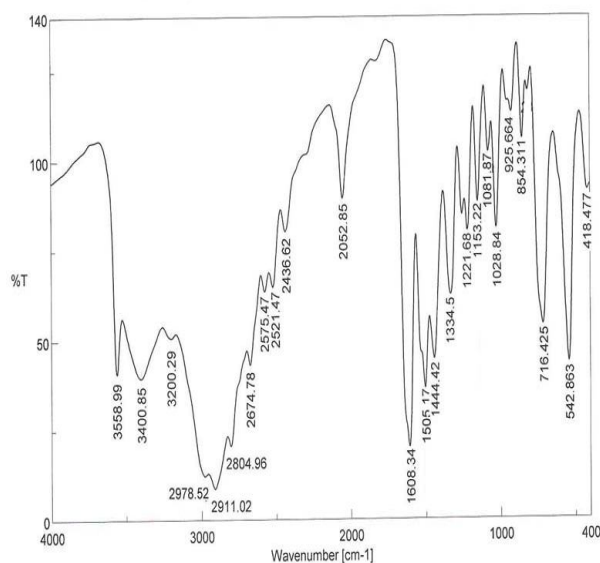


Figure 10: IR spectrum of La-L1 complex.

**Electronic Spectra and Magnetic Moment:** The electronic spectra of the Schiff base and its complexes are shown in figures (11-15) and their electronic spectral data (nm) are listed in table 3. The electronic spectrum of the Schiff base shows bands at 250 and 300 nm attributed to  $\pi \rightarrow \pi^*$  (phenyl ring) and  $n \rightarrow \pi^*$  (C=N and -OH). The magnetic moment value of the Co(II) complex (3.88 B.M) and the spectrum of the same complex which exhibits three bands at 520, 550 and 610 nm belongs to  ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ ,  ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$  transition support the presence of an octahedral geometry.<sup>(11)</sup> Whereas, the spectrum of Ni(II) complex shows two bands at 620 and 710 nm assigned to  ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$   ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$  transition. The magnetic moment (2.92 B.M) and the intensity of the bands confirm the existence of an octahedral structure.<sup>12</sup> The electronic spectrum of Cu(II) complex displays two bands at 620 and 680 nm which could be due to  ${}^2E_g \rightarrow {}^2T_{2g}$  transition. The nature of the bands and the magnetic moment (1.84 B.M) support the existence of an octahedral geometry.<sup>13</sup> The electronic spectral data of Cr(III) complex of the formula  $[Cr_2L1OCl_2(H_2O)_4] 2H_2O$  exhibits two bands at 540 and 630 nm analogous to  ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$  and  ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$  transition. Both the magnetic moment of the complex (3.77 B.M) and its bands intensity suggest the presence of an octahedral structure.<sup>14</sup> Based on the diamagnetic character and the electronic spectrum of La(III) complex (Table 3), an octahedral structure was proposed for the complex.<sup>15</sup>

Table 3: Infrared, electronic and paramagnetic resonance spectral data of some complexes.

Complexes	$\nu$ OH (H <sub>2</sub> O)	$\nu$ C=N	$\nu$ M-O	$\nu$ M-N	nm
[CoL1(H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	3427	1592	518	458	520, 550, 610
[NiL1 (H <sub>2</sub> O) <sub>2</sub> ]	3560	1587	516	415	690, 710
[Cr <sub>2</sub> L1OCl <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ] 2H <sub>2</sub> O	3371	1605	576	443	540, 630
[CuL1 (H <sub>2</sub> O) <sub>2</sub> ] H <sub>2</sub> O	3320	1599	483	440	620, 680
[LaL1 Cl (H <sub>2</sub> O)] H <sub>2</sub> O	3558	1608	542	418	550

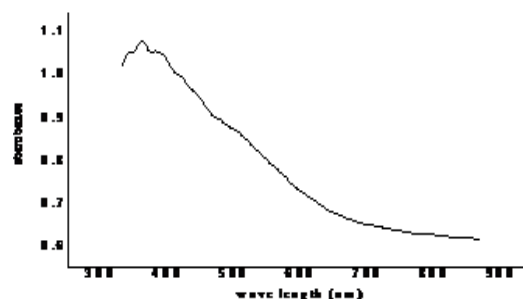


Figure 11: Electronic spectrum of Co-L1 complex.

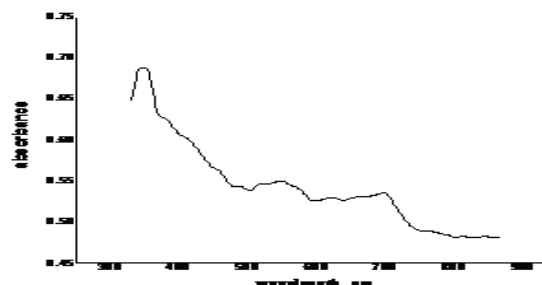


Figure 12: Electronic spectrum of NiL1 complex.

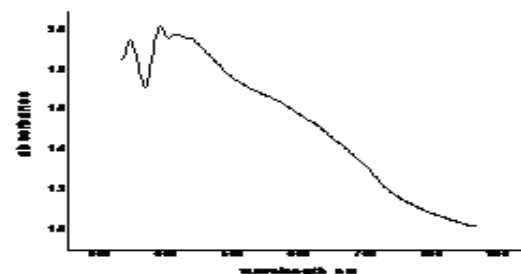


Figure 13: Electronic spectrum of Cr<sub>2</sub>.L1 complex.

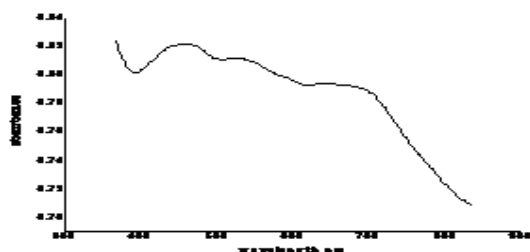


Figure 14: Electronic spectrum of Cu-L1 complex.

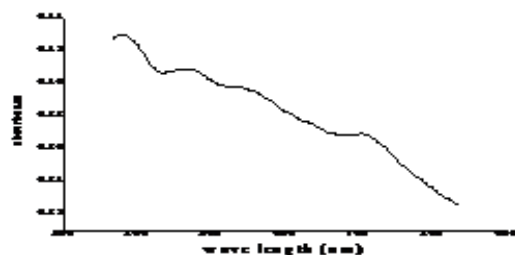
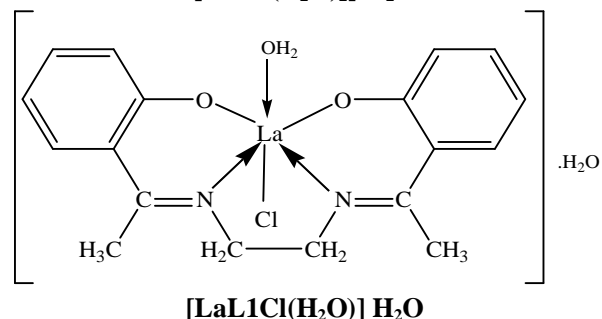
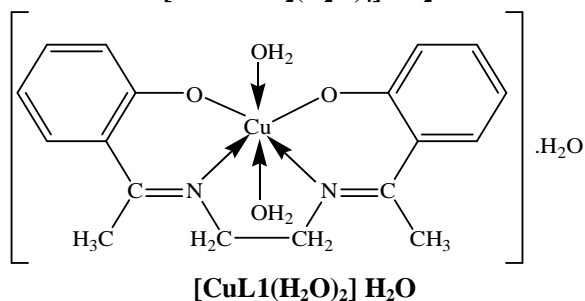
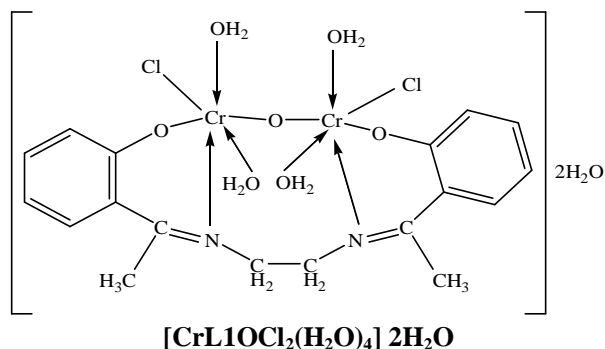
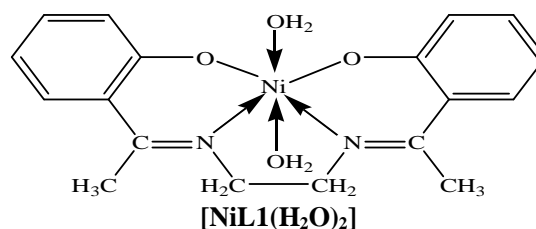
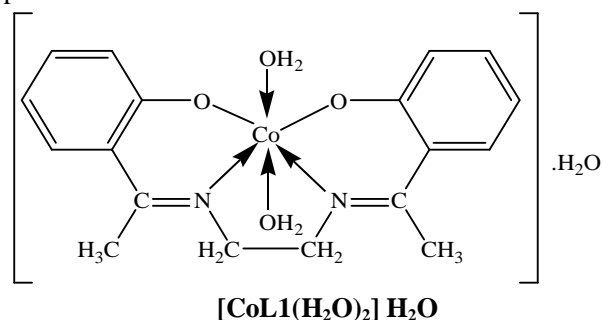


Figure 15: Electronic spectrum of La-L1 complex.

**Electron Paramagnetic Resonance Spectra of the Complexes:** The e. p. r spectra of the complexes were recorded at ambient temperature and the observed g values of the complexes at 2.00217, 1.98521, 1.98479 and 0.00000, respectively, are different from the ideal value (2.0023), this difference is in agreement with the covalent character of the metal- ligand bond.<sup>(16)</sup> The present deviation of these values compared to the ideal value supports the existence of an octahedral geometry around the metal ions.<sup>17</sup>

**CONCLUSION:** On the basis of CHN elemental analysis data, molar conductivity, thermogravimetric analysis and some spectroscopic techniques (Infrared, electronic and electron paramagnetic resonance spectra) of the Schiff base complexes under investigation, octahedral structures were suggested for all complexes.



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