



## Synthesis, Characterization and Spectral Studies of Fe(III) and Cr(III) Schiff base Complexes with Acetoacetanilidepropylenediamine

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The Fe(III) and Cr(III) complexes of Schiff base derived from acetoacetanilide and propylenediamine, [MXL(H<sub>2</sub>O)], where LH<sub>2</sub> = acetoacetanilidepropylenediamine, M = Fe<sup>3+</sup> or Cr<sup>3+</sup> and X = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NCS<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup> or ClO<sub>4</sub><sup>-</sup>, have been synthesized in alcohol and characterized by elemental analysis, electrical conductance in non-aqueous solvents, infrared and electronic spectra as well as magnetic susceptibility measurements. In these complexes, ligand LH<sub>2</sub> acts as dibasic tetradentate ligand coordinating through the two azomethine nitrogen atoms and the two enolizable carbonyl group of acetoacetanilide moiety. The molar conductance of the complexes in DMF and DMSO are in the range of non-electrolytes. The electronic spectra and molar magnetic moment of the complexes show a distorted octahedral environment around the metal ion. Presence of water coordination in the complexes is confirmed by the endothermic bands observed in DTA curve in the temperature region where the TGA curves indicates loss in weight.

**Key Words:** Propylenediamine, Acetoacetanilide, Schiff base complex.

### INTRODUCTION

Schiff bases or imines have the general formula RN = CHR', where the R and R' are alkyl, aryl, cycloalkyl or heterocyclic groups. They are formed by condensation reaction that occurs when aldehydes and some ketones react with primary amines. They play an important role in inorganic chemistry, as they easily form stable complexes with most transition metal ions<sup>1</sup>. Over the last three decades, there has been a dramatic growth of interest in inorganic complexes based materials that exhibit unusual properties<sup>2</sup>. Schiff bases derived from an amine and aldehyde/ketone are an important class of ligand that coordinate to metal ion *via* azomethine nitrogen and have been studied extensively<sup>3</sup>. The chelating Schiff base ligands derived from diamines and various carbonyl compounds, encompass a highly remarkable class of compounds having a wide range of applications in catalytic<sup>4</sup>, synthetic<sup>5</sup>, analytical<sup>6</sup>, clinical<sup>7</sup> and biochemical areas<sup>8</sup> and they possess considerable physiological activities<sup>9</sup>. A lot of amine complex compounds have been synthesized and their properties (carcinogenic and optical) and biological activities are established<sup>10</sup>.

In this paper, the synthesis and characterization of a Schiff base (Fig. 1) derived from acetoacetanilide and 1,3-diaminopropane and its complexes with Fe(III) and Cr(III) are described.

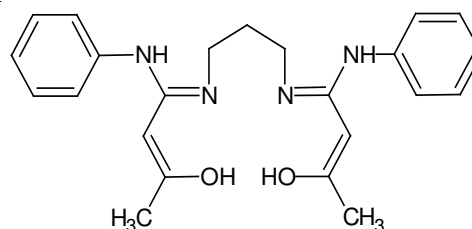


Fig. 1. Structure of the ligand

### EXPERIMENTAL

Transition metal salts, acetoacetanilide, 1,3-diaminopropane and other reagents were AR grade. Solvents such as ethanol, methanol and acetone were purified by standard procedures<sup>11</sup>. C, H and N were estimated by using elemental analyzer, elemental Vario EL III. The IR spectra of the Schiff base and its metal complexes were recorded on a FTIR Shimadzu spectrophotometer in the 4000-400 cm<sup>-1</sup> region in KBr powder. The electronic spectra of the complexes were recorded in HPLC grade DMF and DMSO on a Shimadzu spectrophotometer in the region of 800-200 nm. Molar conductivity measurements were recorded on systronic conductivity meter type 304. Magnetic measurements of the complexes were performed on a Magway MSB Mk 1 susceptibility balance at room temperature. Thermal decomposition studies

TABLE-1  
ELEMENTAL AND OTHER PHYSICO-CHEMICAL DATA OF THE LIGAND AND ITS COMPLEXES

| Compound   | m.p.<br>(°C) | Colour          | Found (calcd.) (%) |               |             |               |             | $\mu_{\text{eff}}$ |
|--|--------------|-----------------|--------------------|---------------|-------------|---------------|-------------|--------------------|
|  |              |                 | M                  | C             | H           | N             | Cl/S        |                    |
| C <sub>23</sub> H <sub>28</sub> N <sub>4</sub> O <sub>2</sub> [LH <sub>2</sub> ] | 184          | Pale yellow     | -                  | 70.50 (70.41) | 7.36 (7.14) | 14.06 (14.29) | -           | -                  |
| [FeL(Cl)H <sub>2</sub> O]  | 258          | Yellowish brown | 10.93 (11.18)      | 55.05 (55.23) | 5.83 (5.61) | 11.07 (11.22) | 6.82 (7.10) | 5.45               |
| [FeL(NO <sub>3</sub> )H <sub>2</sub> O]  | 278          | Reddish brown   | 10.37 (10.62)      | 52.28 (52.48) | 5.12 (5.32) | 13.05 (13.31) | -           | 5.93               |
| [FeL(AcO)H <sub>2</sub> O]   | 246          | Reddish yellow  | 10.43 (10.68)      | 57.15 (57.38) | 6.33 (5.93) | 10.66 (10.71) | -           | 5.78               |
| [FeL(NCS)H <sub>2</sub> O]   | 252          | Reddish brown   | 11.34 (10.70)      | 55.54 (55.19) | 5.14 (5.37) | 13.22 (13.41) | 5.91 (6.13) | 5.6                |
| [FeL(ClO <sub>4</sub> )H <sub>2</sub> O]   | 202          | Brownish black  | 11.13 (9.91)       | 50.09 (49.35) | 4.70 (4.97) | 9.54 (9.94)   | 6.04 (6.29) | 5.88               |
| [CrL (Cl)H <sub>2</sub> O]   | 256          | Greenish black  | 10.78 (10.48)      | 55.92 (55.70) | 5.5 (5.69)  | 12.06 (11.30) | 6.8 (7.15)  | 3.82               |
| [CrL(NO <sub>3</sub> )H <sub>2</sub> O]  | 268          | Greenish black  | 10.30 (9.95)       | 54.2 (52.87)  | 5.28 (5.40) | 13.52 (13.40) | -           | 3.86               |

were recorded in a static nitrogen atmosphere with a heating rate of 10 °C/min, using diamond TG/DTA (thermogravimetric/differential thermal analyzer).

**Synthesis of the ligand:** 1,3-Diaminopropane (0.01 M, 0.833 mL) was added drop wise to acetoacetanilide solution in acetone (0.02 M, 3.548 g). The above solution was refluxed for 2 h and kept over night in an ice bath. The pale yellow solid formed was filtered and washed several times with ethanol and recrystallized from ethanol.

**Synthesis of complexes:** The ligand (0.01 M, 3.928 g) in 20 mL aqueous methanol was added to metal salt solution (0.01 M) in 20 mL methanol with stirring. Reflux for 3 h, concentrated to one third and cooled to 0 °C. The resulting complex was filtered, washed with ethanol and dried.

## RESULTS AND DISCUSSION

All the complexes are stable at room temperature and are non-hygroscopic. On heating, they decompose at high temperatures. The complexes are insoluble in water, but are soluble in DMF and DMSO. The elemental analysis data shown in Table-1 for Schiff base ligand LH<sub>2</sub> (acetoacetanilidepropylenediamine) and its chelates are found to be consistent with the expected results. The molar electrical conductivities of the complexes in DMF and DMSO are respectively in the range 16.5-22.2 and 5.6-20.8 ohm<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>. The low molar conductance values indicates that the complexes are non-electrolytes<sup>12</sup>. The stoichiometric ratio of the Schiff base complexes shows the formula of the type [M(L)(H<sub>2</sub>O)X], where M = Fe<sup>3+</sup> and Cr<sup>3+</sup> and X = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NCS<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup> or ClO<sub>4</sub><sup>-</sup>.

The IR spectrum of the free ligand was compared with the spectrum of the complex in order to study the binding mode of Schiff base to the metal salt. Both the ligand and the complexes show an intense peak at *ca.* 3160 cm<sup>-1</sup>, which is a characteristic feature of N-H stretching frequency indicating the existence of an -NH group<sup>13</sup>.

The -OH stretching and bending vibrational frequencies of the acetoacetanilide moiety of the ligand appearing in the region of 3306 cm<sup>-1</sup> and 1310 cm<sup>-1</sup> respectively indicate that the enolic carbonyl group is not involved in the reaction and only the imide carbonyl group participates in the condensation. The disappearance of these two peaks in the spectra of all the complexes indicates that the chelation takes place *via* the enolic -OH group<sup>14</sup>. Appearance of a broad band around 3400 cm<sup>-1</sup> region was observed in the spectra of complexes indicating the presence of coordinated water molecules. The bands in the region of 868-741 and 650-583 cm<sup>-1</sup> are also assigned to

coordinated water molecules<sup>15</sup>. The IR spectrum of the free ligand shows a strong band at *ca.* 1631 cm<sup>-1</sup> assignable to the presence of azomethine group. The observation of this band confirms the formation of azomethine linkage and shifting of this band to lower frequency region after complexation indicating the coordination of nitrogen atoms of two azomethine nitrogens to empty *d* orbitals<sup>16</sup>. The bonding through O and N is further supported by the appearance of new bands in the region 560-520 and 460-440 cm<sup>-1</sup>, which may be assigned to  $\nu(\text{M-O})$  and  $\nu(\text{M-N})$  vibrations respectively<sup>17,18</sup>.

In the spectrum of nitrate complexes the absence of the  $\nu_3$  band of ionic nitrate at 1360 cm<sup>-1</sup> and the occurrence of two strong bands around 1408 and 1258 cm<sup>-1</sup> due to the split  $\nu_3$  mode in the lower symmetry indicate a coordinated nitrate group<sup>19,20</sup>. If the  $\nu_4$ - $\nu_1$  difference is taken as an approximate measure of covalence of nitrate groups a value of *ca.* 150 cm<sup>-1</sup> for the complexes under study suggest a strong covalency nature of the nitrate in the complexes<sup>21</sup>. To identify the monodentate or bidentate nature, we applied the lever separation method<sup>21-23</sup>. In the present nitrate complexes a separation of 21 cm<sup>-1</sup> in Fe(III) complex and 19 cm<sup>-1</sup> in Cr(III) complex as combination frequencies  $\nu_1 + \nu_4$  in the 1800-1700 cm<sup>-1</sup> region supports the monodentate nitrate coordination.

The IR spectrum of the Fe(III) acetate complex showed bands in the region 1680 cm<sup>-1</sup> and 1450 cm<sup>-1</sup>, which correspond to asymmetric stretching vibration  $\nu(\text{COO}^-)_{\text{as}}$  and symmetric stretching vibration  $\nu(\text{COO}^-)_{\text{s}}$ . The separation of 230 cm<sup>-1</sup> between these two bands and their positions indicates the monodentate nature of the acetate ion<sup>18,24</sup>.

In the Fe(III) thiocyanate complex the C-N stretching frequency appears in 2039 cm<sup>-1</sup> region, which lies on the boarder line for distinguishing between S and N bonding in the thiocyanate. Although the high relative intensity of the band in this case suggest that the thiocyanate group is N bonded. The (C-S) bond identified in 840-780 cm<sup>-1</sup> region further confirms that the thiocyanate group is N-bonded. The  $\delta(\text{N-C-S})$  ( $\nu_2$ ) is also identified in this complex at 470 cm<sup>-1</sup><sup>25</sup>.

The perchlorate complex of Fe(III) exhibit a strong band near 1140 cm<sup>-1</sup> and another medium band around 1040 cm<sup>-1</sup>. These are assigned to  $\nu_4$  and  $\nu_1$  of monodentate perchlorate group. Similarly, two bands of medium intensity, occurring around 645 and 635 cm<sup>-1</sup> are attributed respectively to the  $\nu_3$  and  $\nu_5$  of coordinated perchlorate group. The weak band observed near 945 cm<sup>-1</sup> can be assigned as  $\nu_2$  band of coordinated perchlorate group<sup>26,27</sup>. The  $\nu_6$  vibration expected around 480 cm<sup>-1</sup> for coordinated perchlorate could not be located since

the metal-ligand stretching frequency is also expected in this region. The position of bands in the region  $1140\text{ cm}^{-1}$  and  $645\text{ cm}^{-1}$  and the magnitude of separation between them suggest the monodentate nature for the coordinated perchlorate group in the complex<sup>28</sup>.

The  $^1\text{H NMR}$  spectrum of the Schiff base in DMSO shows the following signals. The multiplet signals around 7.5-7.8 ppm are ascribed to aromatic protons<sup>9,29</sup>. The signals observed at 2.5 ppm are due to methyl protons. The signals in the range 3.30-2.9 ppm and 1.9-1.74 ppm are assigned to methylenic protons of propane diamine moiety<sup>9</sup>. The presence of the singlet at 9.158 ppm due to -OH group indicates a high contribution of enolic structure. The absence of this signal in the complexes indicate the loss of the -OH proton due to complexation<sup>16,30</sup>. Thus the NMR results further supports the IR inferences.

Less information is available on the electronic spectra of high spin octahedral complexes of Fe(III). However the spectral features of Fe(III) ion in an octahedral environment are in accordance with the theoretical expectations. The high spin Fe(III) complexes with  $d^5$  configuration have the ground state  $^6\text{A}_{1g}$  and all the  $d-d$  transitions are spin and laporte forbidden<sup>31</sup>. The electronic spectra of Fe(III) complexes showed bands within the range 320-490 nm. It is not possible to identify the type of the  $d-d$  transition. The weak bands in the range 421-402 nm, assigned to the spin and parity forbidden  $^6\text{A}_{1g} \rightarrow ^4\text{T}_{2g}$  transitions of Fe(III) ion in an octahedral field<sup>9</sup>. The electronic spectra of Cr(III) complexes show bands at around 590, 420 and 340 nm, which may be attributed to  $^4\text{A}_{2g} \rightarrow ^4\text{T}_{2g}(\text{F})$ ,  $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}(\text{F})$ ,  $^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}(\text{P})$ , transitions, respectively, indicating an octahedral geometry around Cr(III)<sup>17,32</sup> ions.

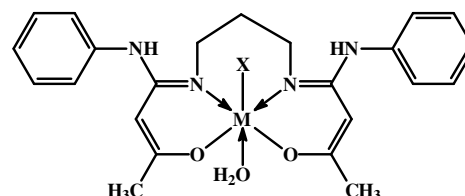
High spin complexes of Fe(III) are formed with weak or moderately strong ligands. The ground state term  $^6\text{S}$  of free Fe(III) ion is not split by the presence of any ligand field. Therefore the magnetic moments of high spin complexes are found to be very close to the spin only value 5.92 BM. The magnetic moment values observed for Cr(III) complex correspond to three unpaired electrons. The magnetic moments of 3.82-3.86 BM is slightly less than the spin only value 3.88 BM as is generally the case with octahedral complexes due to very small spin orbit coupling constant of Cr(III)<sup>9</sup>.

In metal complexes, water molecules may present as lattice water and/or coordinated water. Lattice water is lost at lower temperature regions between 60-120 °C whereas the loss of coordinated water requires 150 °C or above 150 °C. The thermogram above this temperature is horizontal and the final product of decomposition corresponds to their metal oxides. Presence of water molecules is further confirmed by the endothermic bands observed in the respective DTA curve in the temperature region, whereas the TGA curves indicates loss in weight. In addition to the endothermic bands, the DTA curves of complexes also show exothermic bands. These bands appeared at higher temperatures which represent phase transition, oxidation and/or decomposition of the compound<sup>33</sup>. The TGA and DTA curves are obtained at a heating rate of 10 °C/min in nitrogen atmosphere over a temperature range of 50 to 900 °C. The thermogram of the complexes show weight loss between 100-200 °C corresponding to the presence of one water molecule from the coordination sphere (weight loss found 3.4 % to 4.2 %. Calculated 3.2 % to 3.9 %). The organic moiety

decomposes further with increasing temperature. The complete decomposition of ligand occurs at 550-700 °C and finally the horizontal nature of the thermogram above this temperature suggests the formation of final decomposition products corresponding to the metal oxide<sup>18,34</sup>.

## Conclusion

Based on various studies, such as elemental analysis, conductance measurements and magnetic susceptibilities, as well as IR, NMR and electronic spectral studies, a distorted octahedral geometry around the metal ions may be proposed for all the synthesized complexes (Fig. 2).



M = Fe<sup>3+</sup> or Cr<sup>3+</sup> and X = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NCS<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup> or ClO<sub>4</sub><sup>-</sup>

Fig. 2. Structure of metal-complexes

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