



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

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### ABSTRACT

The Fe(III) and Cr(III) complexes of Schiff base derived from acetoacetanilide and ethylenediamine, [MXL(H<sub>2</sub>O)]. LH<sub>2</sub> = acetoacetanilidoethylenediamine M = Fe<sup>3+</sup> or Cr<sup>3+</sup> and X = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NCS<sup>-</sup>, OAc<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 enolisable 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 the respective DTA curve in the temperature region where the TGA curves indicates loss in weight.

**Key words:** Ethylenediamine, Acetoacetanilide, Schiff base complexes.

### INTRODUCTION

Schiff bases are the compounds containing azomethine group (-HC=N) formed by condensation of primary amine and carbonyl compounds. They are important class of compounds which are considered to be the best candidates for coordination with metal ions<sup>1</sup>. The field of Schiff base complexes is fast developing because of the wide variety of possible structures for the ligands, depending on the aldehyde and

amine used. It is important to use amines containing at least two nitrogen atoms, since they produce quite stable complexes with transition metals<sup>2</sup>. The majority of Schiff bases usually act as multidentate N-N and N-O donors with the formation of mono or polynuclear complexes<sup>3</sup>. Recently, there has been a considerable interest in the chemistry of Schiff base compounds and their metal complexes due to their biological and analytical activities<sup>4</sup>. Schiff bases possess excellent characteristics, structural similarities with natural biological substances,

relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural properties<sup>5</sup>. The design, synthesis and characterization of iron complexes with Schiff base ligands play a relevant role in the coordination chemistry of iron due to their importance as synthetic models for the iron-containing enzymes, oxidation catalysts and stable molecular materials based on temperature, pressure or light induced spin-crossover behaviour<sup>6</sup>.

In this paper, the synthesis and characterisation of a Schiff base derived from acetoacetanilide and 1,2-diaminoethane and its complexes with trivalent metal ions like Fe(III) and Cr(III) are described.

## EXPERIMENTAL

Transition metal salts, acetoacetanilide, 1,2-diaminoethane and other reagents were AR grade. Solvents such as ethanol, methanol and acetone were purified by standard procedures<sup>7</sup>. C, H and N were estimated by using Elemental analyzer, Elementar Vario EL III. The IR spectra of the Schiff base and its metal complexes were recorded on a Shimadzu FT Infrared spectrophotometer in the 4000-400  $\text{cm}^{-1}$  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 susceptibility measurements of the complexes in the solid state were determined by Gouy balance. Thermal decomposition studies were recorded in a static nitrogen atmosphere with a heating rate of 10 $^{\circ}$ C/min, using Diamond TG/DTA Thermogravimetric / Differential thermal Analyser.

### Synthesis of the ligand

1,2-diaminoethane (0.01M, 0.67mL) was added drop wise to acetoacetanilide solution in acetone (0.02M, 3.55g). The above solution was refluxed for 2 hours and kept over night in an ice bath. The pale yellow solid formed was filtered and washed several times with ethanol and recrystallised from ethanol.

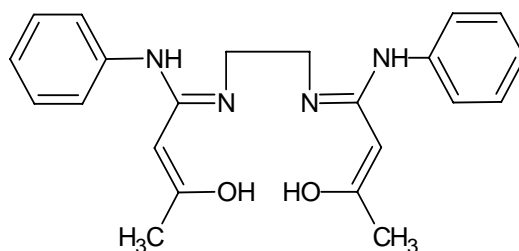


Fig. 1: Acetoacetanilidoethylenediamine

### Synthesis of Complexes

The Ligand (0.01M, 3.78g) in 20mL aqueous methanol was added to metal salt solution (0.01M) in 20mL methanol with stirring. Reflux for 3 hours, concentrated to one third and cooled to 0 $^{\circ}$ C. The resulting complex was filtered, washed with ethanol and dried.

## RESULTS AND DISCUSSION

### Characterization of metal complexes

All the complexes are found to be stable in air and 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 for Schiff base ligand LH<sub>2</sub> (acetoacetanilidoethylenediamine) and its chelates are in good agreement with the molecular formulae. The molar electrical conductivities of the complexes in DMF and DMSO are respectively in the range 12.6 -18.2 and 14.8 - 20.5  $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ . The low molar conductance values indicates that the complexes are non-electrolytes<sup>8,9</sup>. The formulation of the complexes were based on IR, NMR and electronic spectral data, molar conductivity values, magnetic susceptibilities and elemental analyses which were in close agreement with the values calculated for the assigned molecular formula. The obtained data exhibit the formation of the complexes in the ratio of 1:1[M:L]. The stoichiometric ratio of the Schiff base complexes shows the formula of the type [M(L)(H<sub>2</sub>O)X] where M represent Fe<sup>3+</sup> and Cr<sup>3+</sup> and X represent 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>.

### IR Spectra

The assignment of the characteristic IR frequencies for the Schiff base ligand and their

resulting complexes are discussed as follows. Both the ligand and the complexes show an intense peak at  $\sim 3100\text{ cm}^{-1}$  which is a characteristic feature of N-H stretching frequency indicating the existence of an  $-\text{NH}$  group<sup>10,11,12</sup>. The  $-\text{OH}$  stretching and bending vibrational frequencies of the acetoacetanilide moiety of the ligand appearing in the region of  $\sim 3300\text{ cm}^{-1}$  and  $\sim 1327\text{ cm}^{-1}$  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  $-\text{OH}$  group<sup>12</sup>. Appearance of a broad band around  $3400\text{ cm}^{-1}$  region was observed in the spectra of complexes indicating the presence of coordinated water molecules<sup>13</sup>. The bands in the region of  $650-730$  and  $500-620\text{ cm}^{-1}$  are also assigned to coordinated water molecules<sup>14</sup>. A notable peak appears around  $\sim 1591\text{ cm}^{-1}$  in the IR spectrum of the free ligand is caused by  $\text{C}=\text{N}$  stretching within the ligand. The shifting of this band to lower frequency region in metal complexes happens because within the metal ligand complexes the  $\text{C}=\text{N}$  group becomes conjugated with other ligand groups. Conjugations

along with the metal-ligand  $\pi$  bonding are responsible for the shift peak frequency between the independent ligand and the metal complexes<sup>15</sup>. The low frequency skeletal vibrations due to M-O and M-N stretching provide direct evidence for the complexation. This is because a large dipole moment change is involved in the vibration of M-O bond in comparison to that of M-N bond<sup>16</sup>. Present study of the complexes  $\nu(\text{M}-\text{N})$  vibrations occur in the region  $500-600\text{ cm}^{-1}$  and  $\nu(\text{M}-\text{O})$  occur in the region  $400-500\text{ cm}^{-1}$  have been assigned<sup>17</sup>.

In the nitrate complex the absence of the  $\nu_3$  band of ionic nitrate  $\sim 1360\text{ cm}^{-1}$  and the occurrence of two strong bands around  $1467$  and  $1290\text{ cm}^{-1}$  are attributed to  $\nu_4$  and  $\nu_1$  stretching vibrations respectively of the coordinated nitrate ion of  $\text{C}_{2v}$  symmetry<sup>18,19</sup>. If  $\nu_4-\nu_1$  difference is taken as an approximate measure of covalence of nitrate groups a value of  $\sim 180\text{ cm}^{-1}$  for the complexes under study suggest a strong covalent nature of the nitrate in the complexes<sup>20</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  $22\text{ cm}^{-1}$  in Fe(III) complex and  $19\text{ cm}^{-1}$  in Cr(III) complex as combination

**Table 1: Elemental and other physico-chemical data of the ligand and its complexes**

Compound	M.P <sup>o</sup> C	Colour	Found (Calcd.) %					$\mu_{\text{eff}}$
			M	C	H	N	C/I/S	
$\text{C}_{22}\text{H}_{26}\text{N}_4\text{O}_2$ [LH <sub>2</sub> ]	182	Pale yellow	-	68.58 (69.12)	7.26 (7.35)	14.02 (14.43)	-	
[Fe L (Cl) H <sub>2</sub> O]	218	Yellowish brown	11.53 (11.50)	54.05 (54.40)	5.43 (5.39)	11.25 (11.53)	6.98 (7.30)	5.80
[FeL(NO <sub>3</sub> )H <sub>2</sub> O]	246	Reddish brown	10.87 (10.90)	52.28 (51.58)	5.18 (5.12)	13.26 (13.67)	-	5.73
[FeL(AcO)H <sub>2</sub> O]	240	Reddish yellow	10.28 (10.96)	57.11 (56.59)	5.98 (5.74)	11.66 (11.71)	-	5.82
[FeL(NCS)H <sub>2</sub> O]	250	Reddish brown	10.34 (10.98)	55.12 (54.34)	5.20 (5.15)	13.82 (13.78)	6.91 (6.13)	5.40
[FeL(ClO <sub>4</sub> )H <sub>2</sub> O]	242	Brownish black	10.58 (10.16)	50.28 (48.06)	5.10 (4.97)	9.48 (10.11)	6.21 (6.45)	5.82
[CrL (Cl)H <sub>2</sub> O]	238	Greenish black	10.05 (10.79)	53.15 (54.83)	5.52 (5.44)	11.24 (11.62)	6.80 (7.36)	3.78
[CrL(NO <sub>3</sub> )H <sub>2</sub> O]	274	Greenish Black	10.30 (10.23)	50.12 (51.97)	5.05 (5.15)	13.58 (13.77)	-	3.84

frequencies  $\nu_1 + \nu_4$  in the 1800-1700  $\text{cm}^{-1}$  region supports the monodentate nitrate coordination.

The IR spectrum of the acetate complex showed bands in the region 1603  $\text{cm}^{-1}$  and 1437  $\text{cm}^{-1}$  which correspond to asymmetric stretching vibration  $\nu_{(\text{COO})_{\text{as}}}$  and symmetric stretching vibration  $\nu_{(\text{COO})_{\text{s}}}$ . The separation of 166  $\text{cm}^{-1}$  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 2058  $\text{cm}^{-1}$  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 820  $\text{cm}^{-1}$  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 468  $\text{cm}^{-1}$ <sup>25</sup>.

The perchlorate complex of Fe(III) exhibit a strong band near 1128  $\text{cm}^{-1}$  and another medium band around 1040  $\text{cm}^{-1}$ . These are assigned to  $\nu_4$ , and  $\nu_1$  of monodentate perchlorate, group. Similarly, two bands of medium intensity, occurring around 640 and 632  $\text{cm}^{-1}$  are attributed respectively to the  $\nu_3$ , and  $\nu_5$  of coordinated perchlorate group. The weak band observed near 930  $\text{cm}^{-1}$  can be assigned as  $\nu_2$  band of coordinated perchlorate group<sup>26,27</sup>. The  $\nu_6$  vibration expected around 472  $\text{cm}^{-1}$  for coordinated perchlorate couldnot be located since the metal-ligand stretching frequency is also expected in this region. The position of bands in the

region 1118  $\text{cm}^{-1}$  and 640  $\text{cm}^{-1}$  and the magnitude of separation between them suggest the monodentate nature for the coordinated perchlorate group in the complex<sup>28</sup>.

### <sup>1</sup>H NMR Spectra

The <sup>1</sup>H NMR Spectrum of the Schiff base in DMSO shows the following signals. The multiplet signals around 7.56—7.16 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 3.35—2.97 ppm and 1.9—1.74 ppm are assigned to methylenic protons of ethylenediamine moiety<sup>9</sup>. The presence of the singlet at 9.156 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.

### Electronic Spectra and magnetic susceptibility

The high spin Fe(III) complexes with  $d^5$  configuration have the ground state  ${}^6A_{1g}$  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 337 - 492 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  ${}^6A_{1g} \rightarrow {}^4T_{2g}$  transitions of Fe(III) ion in an octahedral field<sup>9</sup>. The electronic spectra of Cr(III) complexes show bands at around 564 ,457 and 341 nm which may be attributed to  ${}^4A_{2g} \rightarrow {}^4T_{2g}(F)$ ,  ${}^4A_{2g} \rightarrow {}^4T_{1g}(F)$ ,  ${}^4A_{2g} \rightarrow {}^4T_{1g}(P)$ , transitions, respectively, indicating an octahedral geometry around Cr(III)<sup>17,32</sup> ions

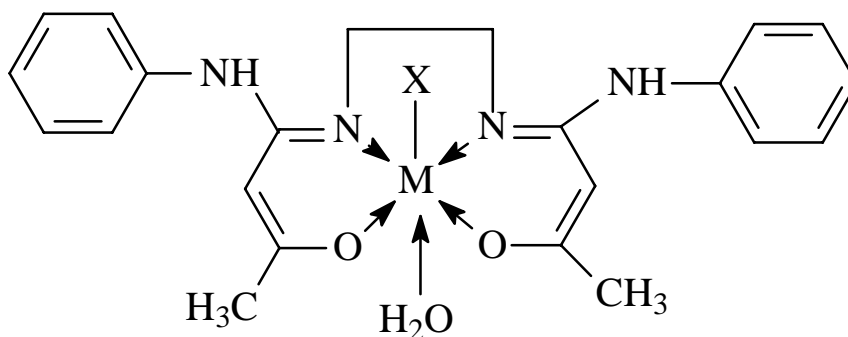


Fig. 2:  $M = \text{Fe}^{3+}$  or  $\text{Cr}^{3+}$  and  $X = \text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{NCS}^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{ClO}_4^-$

High spin complexes of Fe(III) are formed with weak or moderately strong ligands. The ground state term  ${}^6S$  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 3.68—3.73 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>

#### Thermal studies

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 a 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 where the TGA curves indicate 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 in the coordination sphere (weight loss, found: 3.9 to 4.1%, calculated: 3.3 to 3.7%). 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 may be proposed for all the synthesized complexes.

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#### REFERENCES

1. S.T. Ha, et al. *Am. J. Applied Sci.*, **7**: 214 (2010)
2. M. Sekerci C. Alkan C. *Inorganic, Metal-Organic Chemistry*, **29**: 168 (1999).
3. Eid A. Abdalrazaq, Omar M. Al-Ramadane and Khansa S. Al-Numa. *Am. J. Applied Sci.*, **7**: 628 (2010)
4. S.S. Al-Shihry, *Sci. J. King Faisal University*, **6**: 77 (2010)
5. Sheikh Aadil Abbas et al. *The Biol-E-J. Life Sci.* **1**: 37 (2010)
6. Fahmideh Shabani, Lotf Ali Saghatforeoush and Shahriar Ghammamy. *Bull. Chem. Soc. Ethiop.*, **2**: 193 (2010).
7. D. D. Perrin. W. L., Armarego, D. R. Perrin. *Purification of Laboratory Chemicals*, Pergamon: (Oxford, U K). (1980).
8. W.J. Geary, *Coord. chem Rev.*, **7**(1): 82 (1971)
9. M. Mohapatra., V. Chakravorty, and K.C. Dash. *Polyhedron* **8**: 509 (1989)
10. N. Raman, Y. Pitchikani Raja, Kundaisamy, *Indian Acad. Sci.*, **113**: 183 (2001).
11. Sulekh Chandra, Amit Kumar Sharma,

- J. Indian Chem. Soc.*, **86**: 690 (2009).
12. Sarika R.Yaul, Amit.R.Yaul, Gaurav B. Pathe, S. Anand, *American-Eurasian J. of Scientific Research.*, **4**: 229 (2009).
  13. B. Jezowska, J. Lisowski and P. Chmielewski, *Polyhedron.*, **7**: 337 (1988).
  14. Gajendrakumar, Dharmendra Kumar, C.P. Singh, Amit Kumar, V.B. Rana, *J. Serb. Chem. Soc.*, **75**; 629 (2010).
  15. J. Woollins, *Inorganic Experiments*: 2<sup>nd</sup> Edn: Weinheim; Wiley-VCH, (2008)
  16. N. Revanasiddappa, T. Suresh, and Syed khasim. *E- journal of chemistry*. **5**: 395 (2008)
  17. F.M. Morad, M M EL.ajaily, S. Ben Gweirif., *J. of Sci and its Applications.*, **1**: 72 (2007)
  18. R.E. Heter, Grossman Well. *Inorganic Chemistry*. **5**: 1308 (1966)
  19. N.M. Karayannis, C.M. Mikulski, L.L. Pytlewski, M.M. Labes. *Inorganic Chemistry.*, **13**: 1146 (1974).
  20. C.C Addison, N. Logan, S.C. Wallwork, C.D. Garner. *Quarterly Reviews of the Chemical Society*. **25**: 289 (1971)
  21. A.B.P. Lever, E. Mantovani, B.S. Ramaswamy *Can. J. Chem.*, **49**: 1957 (1971)
  22. J.R. Ferraro. *J. of Molecular Spectroscopy*. **4**: 99-105 (1960).
  23. Ram K. Agarwal, Deepak Sharma, Lakshman Singh, Himanshu Agarwal. *Bioinorganic Chemistry and Applications.*, **1**(2006)
  24. K. Nakamoto, *IR and Raman Spectra of inorganic and coordination compounds*. Wiley, New York. (1997).
  25. R., K. Agarwal, R.K Garg, S.S.S. Indhu. *J. Iranian Chemical Society*. **2**: 203 (2005).
  26. A. E. Wickenden, R. A. Krause *Inorg. Chem.*, **4**: 404 (1965).
  27. M.L. Hari Kumaran Nair, L. Shamla L. *J. Indian Chem. Soc.*, **86**: 913 (2009).
  28. C. G. Radhakrishnan Namboori, G. Krishnan. *Asian. J. Chem.*, **16**: 1455 (2004).
  29. Ajaykumar D. Kulkarni, Sangamesh A. Patil, Prema S. Badami. *Int. J. Electrochem. Sci.*, **4**: 717 (2009)
  30. Raafat M. Issa, Abdulla M. Khedr, Helen Rizk., *Journal of the Chinese Chemical Society*. **55**: 875-884 (2008).
  31. C.K. Jorgenson., "Absorption spectra and Chemical bonding in Complexes" Addison Wesley (1962).
  32. R.K. Dubey, et al, *Indian J. Chem., Sec. A.*, **47**: 1210 (2008)
  33. Y. Prashanthi, Shiva Raj. *J. Sci. Res.*, **2**: 114-126 (2010).