

# Physicochemical studies and X-ray powder diffraction of new homodinuclear Schiff base complexes

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## ABSTRACT

Homodinuclear mixed ligand complexes of Mn(II) and Fe(II) metal ions with Schiff base ligand (LH) (formed from p-amino azobenzene and 7-methoxy-3- hydroxyl coumarin) in molar ratio (1:1) and some amines (anthranilic acid or L-alanine and o-phenylene diamine) have been prepared and characterized by different physico-chemical methods . The structures of the ligand and its complexes have been investigated by X-ray powder diffraction (from which the general formulae  $[M_2(LH)_2(anH)_2Cl_2]Cl_2$ ,  $[M_2(LH)_2(al)_2Cl_2]$ ,  $[M_2(LH)_2(O)_2Cl_2]Cl_2$ ,  $K_2[M_2(L)_2(A)_2Cl_2]$  and  $[M_2(L)_2(O)_2Cl_2]$  have been suggested in neutral and basic medium respectively, where anH=anthranilic acid, aLH=L-alanine, O=o-phenylene diamine; an, al= deprotonated forms, A=anH or aLH, M=Mn(II) or Fe(II). The study suggested that the complexes had octahedral geometries forming dinuclear complexes (dimer).

**Keywords:** Homodinuclear complexes, X-ray powder diffraction, Mixed ligand complexes, Mn (II) and Fe(II) complexes .

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## INTRODUCTION

Mixed ligands chelates containing the azomethine group  $-C=N-$ , have a wide application in the field of chemistry and medicine, with the development of variety of techniques for the analysis of and identification (1-4) . The mixed ligand complexes have been of considerable importance in the field of metalloenzymes and other biological activities(5). Ainscough and coworkers prepared a variety of N-O bidentates containing the phenolate and N-heterocycle in attempt to model the specific Fe-binding sites of iocaferrin and trans- ferrin(6). Some earlier workers have reported the chemotherapeutic value of coumarin and its Schiff base.

Some earlier workers have reported the chemotherapeutic value of coumarin and its Schiff base. Our investigation concentrates on the preparation of mixed-ligand complexes besides coumarin containing two bidentate groups, amino and carboxylate groups with different basicity. These ligands have wide applications in medicine and chemistry. For example phenylenediamine and derivatives have been used in micro determination for H<sub>2</sub>S by calorimetric method (7). The aim of the present work is to prepare new mixed-ligand complexes by interacting Mn (II) and Fe(II) chlorides with the above mentioned ligand to establish their geometrical structures. The structures of the ligands are shown in Figure 1.

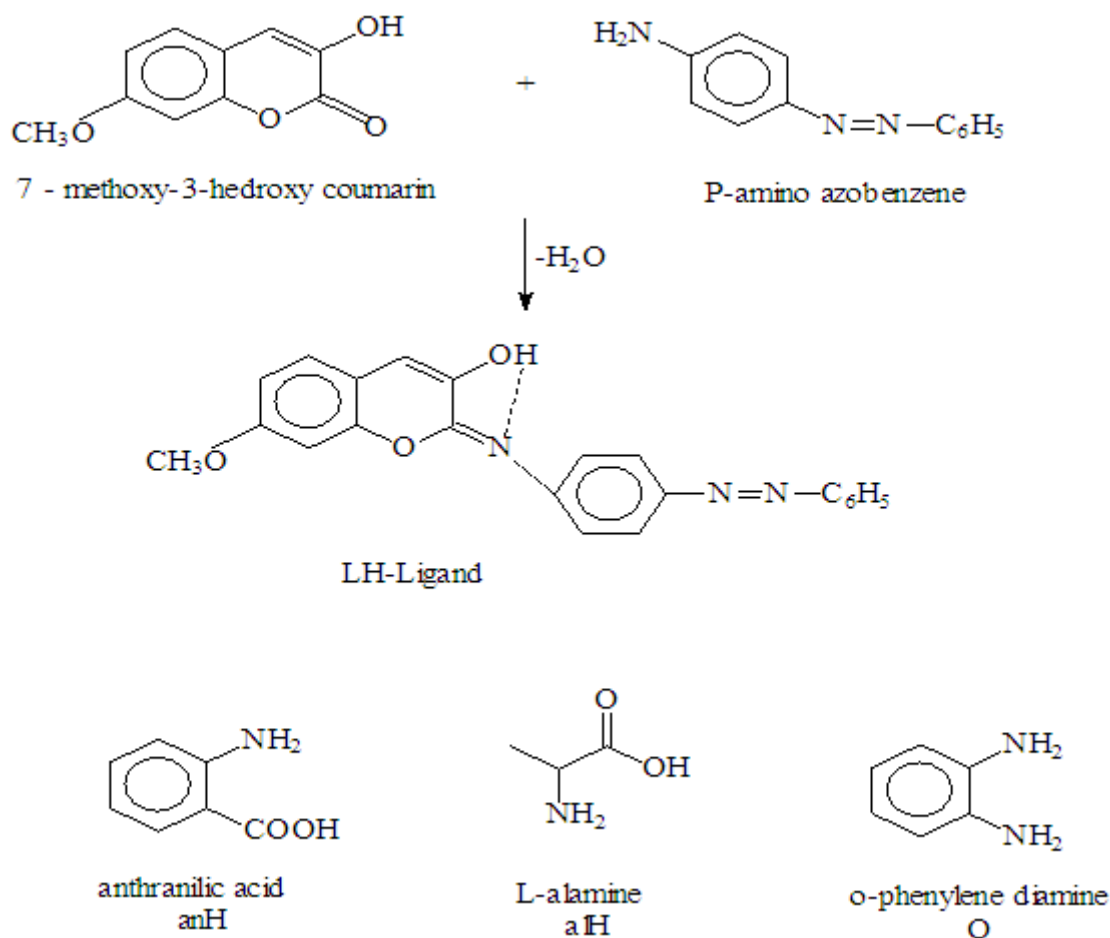


Figure (1): Structure of the ligands

## EXPERIMENTAL

All chemicals used in this study have been supplied (Fluka, BDH or Aldrich).

### 1. Preparation of the First ligand LH (Schiff base)

An ethanolic solution of 7-methoxy-3- hydroxyl coumarin (0.03 mole, 5.79g) and has been added to an ethanolic solution of p-amino azobenzene (0.03 mole, 5.91g) and refluxed for about 1 hr. The for about 1 hr. The resulting solution has been concentrated and the precipitate has been separated by filtration, washed with distilled water and recrystallize from ethanol (m.p.197°).

### 2. Preparation of the complexes

In neutral medium: in ethanolic solution of 0.01 mole of manganese or iron chloride ( $MnCl_2 \cdot 4H_2O$ , 1.98g or  $FeCl_2 \cdot 4H_2O$  1.99g ,respectively)has been treated with ethanolic solution of 3.72g 0.01 mole of the first ligand LH. The resulted metal-ligand solution has been refluxed for half hour, then the second ligand (0.01) mole in ethanol solution has been added one of the amine (anthranilic acid 1.37 or L-alanine, 0.89g or o-phenylenediamine, 1.08g , respectively ) Refluxing has been continued for an extra, half hour, then cooled. The products are isolated by filtration washed with petroleum ether and dried. In basic medium complexes have been prepared applying the same amounts used in neutral medium and after mixing the metal chlorides with the first and second ligand. The pH of the solution has been adjusted 8-9 by adding potassium hydroxide solution (1 M KOH). The mixture has been heated on a water bath for 15 minutes then allowed to stand, cooled filtered off, washed with petroleum ether and dried.

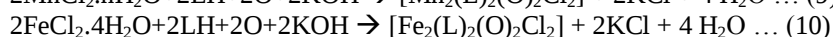
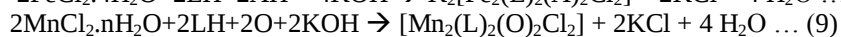
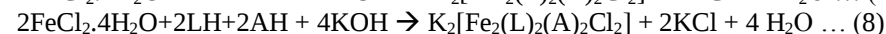
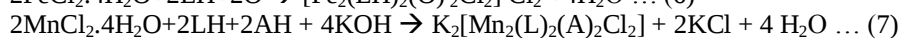
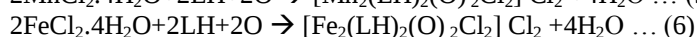
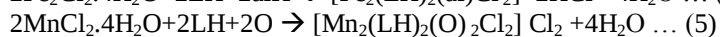
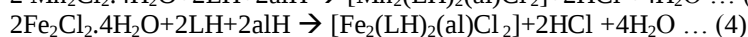
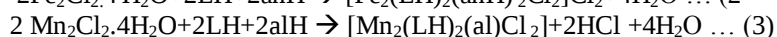
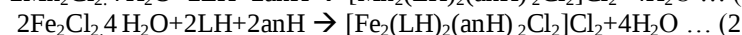
### 3. Analysis and physical measurements

Manganese and Iron contents have been determined by using a Scientific Equipment SensAAGB atomic absorption spectrometer .Conductivity measurement have been carried out with an electrolytic conductivity measuring set LF-42 using  $10^{-3}$  M dim ethyl form amide solution at room temperature. Magnetic susceptibility of the complexes have been

measured by Brucker B.M6. The infrared spectra has been recorded on a Pye-Unicam 1100 infrared spectrophotometer in the 400-4000  $\text{cm}^{-1}$  range using KBr disk. Electronic spectra has been recorded on Shimadzu UV-210A spectrophotometer for  $10^{-3}$  M solutions of the complexes in DMF at 25C using a 1 cm cell. X-ray powder diffraction data for complexes (1 &10) were measured at General Company for Geological Survey and Mining-Bagdad by using Shimadzu X-ray Diffraction 7000 model 2009 and the crystal data for complexes were analyzed by using Match Program Version 1.6c.

## RESULTS AND DISCUSSION

The reaction of manganese (II) and iron (II) chloride with the ligand LH and the amines in both neutral and basic medium can be represented by the following reactions:



Where

A = anH=anthranilic acid or alH=L-alanine, O= o -phenylenediamine; The resulted complexes were colored solid, slightly soluble in water, ethanol and soluble in dimethylformamide metal contents revealed that the complexes have the compositions  $[\text{M}_2(\text{LH})_2(\text{anH})_2\text{Cl}_2]\text{Cl}_2$ ,

$[\text{M}_2(\text{LH})_2(\text{al})_2\text{Cl}_2]$ ,  $[\text{M}_2(\text{LH})_2(\text{O})_2\text{Cl}_2]\text{Cl}_2$ ,  $\text{K}_2[\text{M}_2(\text{L})_2(\text{A})_2\text{Cl}_2]$  and  $[\text{M}_2(\text{L})_2(\text{O})_2\text{Cl}_2]$  in neutral and basic medium, respectively.

The molar values in  $10^{-3}$ M dim ethyl form amide (Table 1) approached these expected for 1:2 electrolytic nature and non electrolytes<sup>(8)</sup>.

The magnetic susceptibilities of the complexes have been determined at room temperature. The spin only magnetic moments of the complexes have been calculated in Bohr Magneton. The manganese (II) complexes show magnetic moments in the range 5.05-5.5B.M corresponding to five unpaired electrons and indicating octahedral geometry and ant ferromagnetic interaction between the adjacent metal cations. The iron (II) complexes show magnetic moments in the range of 7.94 8.39B.M. This value is quite low compared to the calculated magnetic moment value for binuclear ion complexes revealing the presence of four unpaired electrons and indicating high octahedral geometry.

The ligand geometry (Fig.1) indicates that monometric structure involves much steric hindrance. A dimeric formulation requires appreciable reduction in the value of the magnetic towards the spin only value for unpaired electrons is expected<sup>(9,10)</sup>. In all spectra of metal complexes, the absorption bands due to  $\pi-\pi^*$  and  $n-\pi^*$  transitions that observed in the spectrum of the free ligand is shifted to lower frequencies due to the coordination of the ligand with metal ions.

The spectrum of the binuclear Mn (II) complexes exhibited a series of weak bands in the range of 13812-32362 $\text{cm}^{-1}$ . These bands may be assigned to the transitions;  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{p})$ ,  ${}^6\text{A}_{1g} \rightarrow {}^4\text{E}_g$ ,  ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}$ ,  ${}^6\text{A}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}$ ,  ${}^6\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{p})$  and  ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}$ , respectively. These bands are both Laporte and spin-forbidden. However, due to instantaneous distortion of the octahedral structures around the metal cations.

Fe (II) complexes (Table 1) show a broad absorption band at about 10101 - 34722  $\text{cm}^{-1}$  due to  ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$  transition. Iron (II) complexes of high spin type required quite strong ligand fields to cause the formation of spin paired complexes. It has  $3d^6$  configuration with a free ion ground term  ${}^5\text{D}$ . For the weak field octahedral limit the ground state is  $t_{2g}^4 e_g^2$  and  ${}^5\text{D}$  term split into  ${}^5\text{E}_g$  and  ${}^5\text{T}_{2g}$ , therefore only spin -allowed transition is expected in the electronic spectra of the weak field complexes.

The octahedral iron (II) complexes usually exhibit a broad absorption band which is frequently splits into two components. This splitting is probably due to the Jahn -Teller effect at least in solutions, since it is much larger than that which might arise through spin - orbit coupling.

In the crystals, tetragonal distortion is sometimes present, this would cause a small splitting of  ${}^5\text{T}_{2g}$  level into  ${}^5\text{E}_g$  and  ${}^5\text{A}_{1g}$  and would not account for the splitting of  ${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$  band. In the complexes which have six binding sites of

ligands around the iron atom the  $^5E_g$  level undergoes a more splitting. The greater the dissimilarity of the ligand field strengths of the ligands the greater is the separation between the observed bands <sup>(11,12)</sup>.

**Table 1: Proposed formula, analytical and physical properties of the complexes**

| No. | Complexes                     | Color | M.P°C | $\mu_{eff}$ | %yield | $\Delta_M$ in DMF |
|-----|-------------------------------|-------|-------|-------------|--------|-------------------|
| 1.  | $[Mn_2(LH)_2(anH)_2Cl_2]Cl_2$ | Beige | 258d  | 5.29        | 80     | 167               |
| 2.  | $[Fe_2(LH)_2(anH)_2Cl_2]Cl_2$ | Brown | 267d  | 7.94        | 78     | 159               |
| 3.  | $[Mn_2(LH)_2(al)_2Cl_2]$      | Beige | 249   | 5.05        | 73     | 21                |
| 4.  | $[Fe_2(LH)_2(al)_2Cl_2]$      | Brown | 228   | 8.39        | 76     | 19                |
| 5.  | $[Mn_2(LH)_2(O)_2Cl_2]Cl_2$   | Beige | 266d  | 5.50        | 61     | 160               |
| 6.  | $[Fe_2(LH)_2(O)_2Cl_2]Cl_2$   | Brown | 253d  | 8.23        | 66     | 125               |
| 7.  | $K_2[Mn_2(L)_2(an)_2Cl_2]$    | Beige | 247d  | 5.33        | 60     | 152               |
| 8.  | $K_2[Fe_2(L)_2(an)_2Cl_2]$    | Brown | 272d  | 7.92        | 65     | 169               |
| 9.  | $K_2[Mn_2(L)_2(al)_2Cl_2]$    | Beige | 250d  | 5.27        | 79     | 145               |
| 10. | $K_2[Fe_2(L)_2(al)_2Cl_2]$    | Brown | 267d  | 8.25        | 57     | 150               |
| 11. | $[Mn_2(L)_2(O)_2Cl_2]$        | Beige | 275   | 5.48        | 63     | 15                |
| 12. | $[Fe_2(L)_2(O)_2Cl_2]$        | Brown | 248   | 7.94        | 75     | 12                |

$\mu_{eff}$  = Magnetic moment for in Bohr Magneton

$\Delta_M$  = Molar Conductance in  $ohm^{-1} cm^2 mol^{-1}$

**Table 2: Electronic spectral data of the complexes (values in  $cm^{-1}$ )**

| No. | $V_1$ | C.T   |
|-----|-------|-------|
| 1.  | 13812 | 32362 |
| 2.  | 11389 | 34722 |
| 3.  | 14705 | 31500 |
| 4.  | 10460 | 33557 |
| 5.  | 14880 | 28855 |
| 6.  | 11389 | 34722 |
| 7.  | 14925 | 28500 |
| 8.  | 10183 | 29850 |
| 9.  | 14598 | 31980 |
| 10. | 12004 | 29250 |
| 11. | 14880 | 28890 |
| 12. | 10101 | 28328 |

**Table 3: Elemental analysis of the complexes**

| Comp. No. | Complexes                     | % Found (Calc.) CHN, M |                  |                  |                  |
|-----------|-------------------------------|------------------------|------------------|------------------|------------------|
|           |                               | C                      | H                | N                | M                |
| 1         | $[Mn_2(LH)_2(anH)_2Cl_2]Cl_2$ | 55.05<br>(54.88)       | 3.83<br>(3.78)   | 9.06<br>(8.83)   | 8.81<br>(8.67)   |
| 2         | $[Fe_2(LH)_2(anH)_2Cl_2]Cl_2$ | 54.94<br>(54.80)       | (3.61)<br>(3.77) | (9.01)<br>(8.81) | 9.00<br>(8.81)   |
| 3         | $[Mn_2(LH)_2(al)_2Cl_2]$      | 54.93<br>(54.69)       | 3.86<br>(4.01)   | 10.33<br>(10.20) | 10.04<br>(10.20) |
| 4         | $[Fe_2(LH)_2(al)_2Cl_2]$      | 54.43<br>(54.59)       | 4.16<br>(4.00)   | 10.22<br>(10.19) | 10.10<br>(10.19) |

|    |                                                                |         |        |         |        |
|----|----------------------------------------------------------------|---------|--------|---------|--------|
| 5  | $[\text{Mn}_2(\text{LH})_2(\text{O})_2\text{Cl}_2]\text{Cl}_2$ | 55.73   | 4.00   | 11.77   | 9.22   |
|    |                                                                | (55.62) | (3.97) | (11.58) | (9.10) |
| 6  | $[\text{Fe}_2(\text{LH})_2(\text{O})_2\text{Cl}_2]$            | 36.36   | 3.43   | 11.77   | 9.33   |
|    |                                                                | (55.53) | (3.96) | (11.57) | (9.25) |
| 7  | $\text{K}_2[\text{Mn}_2(\text{L})_2(\text{an})_2\text{Cl}_2]$  | 54.71   | 3.36   | 9.13    | 8.90   |
|    |                                                                | (54.67) | (3.45) | (8.79)  | (8.79) |
| 8  | $\text{K}_2[\text{Fe}_2(\text{L})_2(\text{an})_2\text{Cl}_2]$  | 54.60   | 3.42   | 9.00    | 8.80   |
|    |                                                                | (54.58) | (3.45) | (8.78)  | (8.78) |
| 9  | $\text{K}_2[\text{Mn}_2(\text{L})_2(\text{al})_2\text{Cl}_2]$  | 42.71   | 3.52   | 9.69    | 9.50   |
|    |                                                                | (42.62) | (3.75) | (9.54)  | (9.37) |
| 10 | $\text{K}_2[\text{Fe}_2(\text{L})_2(\text{al})_2\text{Cl}_2]$  | 42.67   | 3.50   | 9.35    | 9.60   |
|    |                                                                | (42.55) | (3.74) | (9.53)  | (9.53) |
| 11 | $[\text{Mn}_2(\text{L})_2(\text{O})_2\text{Cl}_2]$             | 61.13   | 4.29   | 12.50   | 9.80   |
|    |                                                                | (59.10) | (4.22) | (12.31) | (9.67) |
| 12 | $[\text{Fe}_2(\text{L})_2(\text{O})_2\text{Cl}_2]$             | 59.15   | 4.29   | 12.33   | 9.90   |
|    |                                                                | (58.99) | (4.31) | (12.29) | (9.83) |

The IR spectra of the first ligand LH showed characteristic absorption bands at 2800-3400, 1630 and 1590  $\text{cm}^{-1}$  which are due to the stretching vibration of  $\nu\text{OH}$ ,  $\nu\text{C}=\text{N}$  and  $\nu\text{N}=\text{N}+\text{C}=\text{C}$ , respectively. In the spectra of complexes formed in neutral medium the OH band appears as a wide band due to the intra molecular H- bonding with basic azomethine nitrogen (Fig. 1); it was more difficult to observe the coordination due to the presence of different groups and hydrogen bonding. Whatever, in these complexes this wide band was retained, whereas for complexes prepared in basic medium, it was very difficult to observe the disappearance of this band, but it was well known that this band was disappeared due to the deprotonation of the ligand and the formation of ionic form<sup>(13,14)</sup>. Further proof of the coordination of OH is provided by appearance of new bands in the region 455-475  $\text{cm}^{-1}$  assigned to M-O mode. The next strong band in the ligand spectra at 1630  $\text{cm}^{-1}$  which was attributed to  $\text{C}=\text{N}$  stretching vibration. The appearance of this new band due to the Schiff base azomethine linkage confirm the formation of the ligand LH, whatever this band shifted towards lower frequency in the spectra of all complexes, indicating that the ligand is coordinated to the metal atoms through azomethine nitrogen. Additional bands are observed at about 417-440  $\text{cm}^{-1}$  establishing strongly the formation of M-N bands<sup>(15)</sup>. In the ligand spectra a band due to  $\nu\text{N}=\text{N}$  at 1590  $\text{cm}^{-1}$  was shifted towards lower frequency in the spectra of all the complexes indicating that the ligand is coordinated to the metal atoms through one of the nitrogen atom, but it was well known that this band was a specific band due to extensive coupling amongst  $\nu\text{C}=\text{C}$ ,  $\nu\text{C}=\text{N}$  and  $\nu\text{N}=\text{N}$  modes respectively<sup>(16)</sup>. The presence at other bands at 1710, 1685 and 1555  $\text{cm}^{-1}$ , which were attributed to coumarin ring, -OCH<sub>3</sub> and azo group, respectively. These bands remained unaltered on complexation indicated that there is no coordination through these groups and metal ion.

The infrared spectra of anthranilic acid or o-phenylenediamine showed a wide band in the region 3200-3600  $\text{cm}^{-1}$  due to the stretching vibration of carboxylic OH and NH<sub>2</sub> group. This wide range was due to hydrogen bonding. In the spectra of the complexes, it was more difficult to observe the coordination due to the presence of different groups and hydrogen bonding. Whatever, in the complexes prepared in neutral medium this wide band was shifted to lower frequency. Whereas for complexes prepared in basic medium it was very difficult to observe the disappearance of this band, but it was well known that this band was disappeared due to the deprotonation of anthranilic acid and formation of ionic form<sup>(14,15)</sup>. The strong evidence of the coordination of this group came from the observed band at 1600-1620  $\text{cm}^{-1}$ . In the spectra of ligand 1630  $\text{cm}^{-1}$ , which can be assigned to the C=O band of the carboxyl group is shifted to lower frequency for complexes. This means that the oxygen atom of the carboxyl group is involved in the complexation. Moreover, the band of NH<sub>2</sub> group (3380)  $\text{cm}^{-1}$  is shifted to lower frequency. This indicates the participation of this group in chelation. The bands at 455-475  $\text{cm}^{-1}$  and 420-440  $\text{cm}^{-1}$  correspond to  $\nu\text{M}-\text{O}$  and  $\nu\text{M}-\text{N}$  vibrations respectively. The appearance of these band is very strong evidence for the involvement of carboxyl and amino groups in coordination<sup>(16)</sup>.

The spectra of all alanine complexes exhibit a band at 3320  $\text{cm}^{-1}$  attributed to the presence of NH<sub>2</sub> group, which appeared at 3380  $\text{cm}^{-1}$  in the free ligand shifted to lower frequency suggests that the amino group is involved in

complexation with the metal ions<sup>(17)</sup>. Further proof of the coordination to the N atom is provided by the appearance of new bands (M-N) in the (M-N) in the 420-431  $\text{cm}^{-1}$  on the other hand, the band due to  $\nu \text{COO}^-$  at 1690  $\text{cm}^{-1}$  shifted towards lower frequency and the band due to  $\nu \text{(OH)}$  at 3445-3451  $\text{cm}^{-1}$  disappeared in both neutral and basic medium which may be an evidence for coordination of this group with metal ion. It is worth while mentioning here that the amino acid exist as zwitter ions,  $\text{NH}_3^+ \text{AA} \cdot \text{COO}^-$  (AA means Amino Acid) and in the complexes,  $\text{NH}_3^+$  gets deprotonated and binds the metal through the neutral  $\text{NH}_2$  group. Moreover, the non ligand bands appeared at 455-475  $\text{cm}^{-1}$  assigned to M-O mode. Conclusively, indicated that the amino acid (L. alanine) is coordinated to the metal ion through this group<sup>(18)</sup>.

This confirms the previous conclusion, that chelation take place via  $\text{COOH}$  and  $\text{NH}_2$  groups. The occurrence of  $\nu \text{M-Cl}$  band not be inferred from the infrared spectra of the complexes because the band due to this group occurred beyond the range of our infrared spectrophotometer. On the other hand, new bands were observed around 555-574  $\text{cm}^{-1}$  due to ionic chloride that remained outside the coordination sphere. Moreover, the presence of Cl-band is checked by  $\text{AgNO}_3$  test. These observations were in good agreement with the conductance values which have been supported the given formulation of the complexes.

**X-ray powder diffraction analysis**. The XRD patterns of the compounds are completely different from those of the starting materials, demonstrating the formation of coordination compounds. the unit cell parameters Miller indices (hkl) along with observed and calculated  $2\theta$  angle, d values, and relative intensities were also calculated by using Match<sup>(19)</sup> program, and It is found that Mn(II) and Fe(II) complexes have orthorhombic and monoclinic structures. As shown in Tables (4 & 5).

**Table 4 : Crystal data and structure refinement for complex 1**

| No | Complex                                     | 1                                                                |
|----|---------------------------------------------|------------------------------------------------------------------|
| 1  | Molecular Formula                           | $[\text{Mn}_2(\text{LH})_2(\text{anH})_2\text{Cl}_2]\text{Cl}_2$ |
| 2  | Molecular weight                            | 1197                                                             |
| 3  | Crystal system                              | Orthorhombic                                                     |
| 4  | Space group                                 | P-4(61)                                                          |
| 5  | Unit cell parameters ( $\text{\AA}^\circ$ ) | a= 14.166, b= 14.549, c= 15.187                                  |
| 6  | Cell Volume ( $\text{\AA}^3$ )              | 3130.06 $\text{\AA}^3$                                           |
| 7  | Z                                           | 8                                                                |
| 8  | $\theta$ range, deg                         | 1.93 – 46.58                                                     |
| 9  | Index ranges                                | $0 \leq h \leq 6$<br>$0 \leq k \leq 8$<br>$0 \leq L \leq 8$      |

**Table 5 : Crystal data and structure refinement for complex 10**

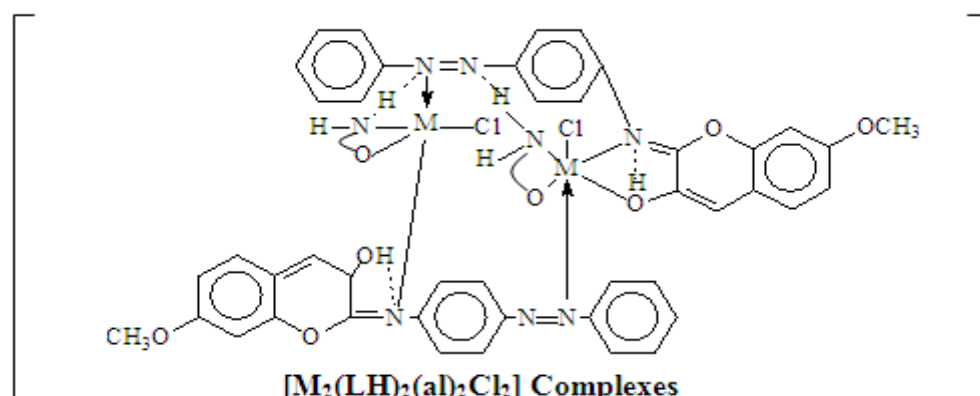
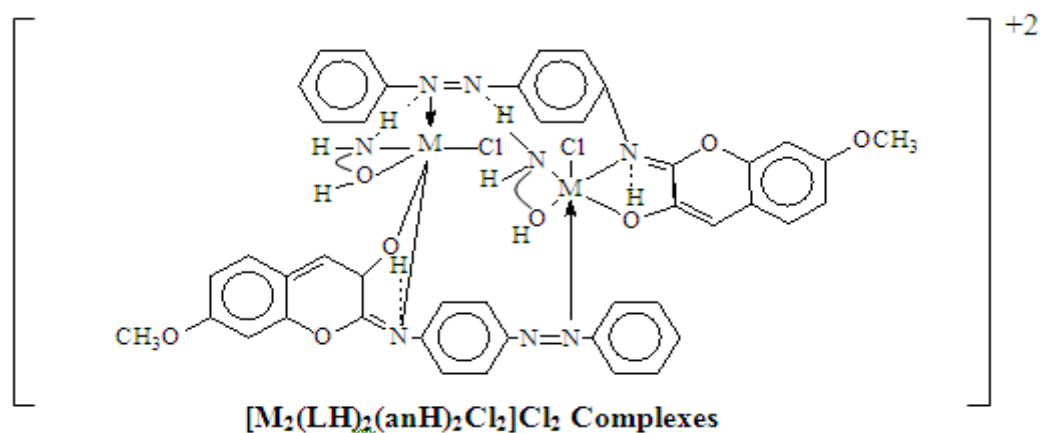
| No | Complex                                     | 10                                                                |
|----|---------------------------------------------|-------------------------------------------------------------------|
| 1  | Molecular Formula                           | $\text{K}_2[\text{Fe}_2(\text{L})_2(\text{al})_2\text{Cl}_2]$     |
| 2  | Molecular weight                            | 1175                                                              |
| 3  | Crystal system                              | Monoclinic                                                        |
| 4  | Space group                                 | Pca (61)                                                          |
| 5  | Unit cell parameters ( $\text{\AA}^\circ$ ) | a= 14.166, b= 14.549, c= 15.0187                                  |
| 6  | Cell Volume ( $\text{\AA}^3$ )              | 2202.86 $\text{\AA}^3$                                            |
| 7  | Z                                           | 6                                                                 |
| 8  | $\theta$ range, deg                         | 9.69 – 52.11                                                      |
| 9  | Index ranges                                | $17 \leq h \leq 14$<br>$13 \leq k \leq 10$<br>$25 \leq L \leq 25$ |

## CONCLUSION

According to various physicochemical, spectral and the measurements of XRD analysis the crystal geometries of some complexes has been established, and we concluded that the metal ions are hexacoordinate with most probable octahedral geometries has been suggested for most complexes. Whereas the analytical and spectroscopic ir data showed that ligand (LH) acts as tridentate coordinated to the metal ions through oxygen hydroxyl group, one nitrogen atom of N=N group and azomethine nitrogen atoms.

Table 6: IR data of the complexes (values in  $\text{cm}^{-1}$ )

| No. | $\nu_{\text{C=N}}$ | $\nu_{\text{(N=N)}} + \nu_{\text{(C=C)}}$ | $\nu_{\text{N-H}}, \nu_{\text{H-bonding}}, \nu_{\text{O-H}}, \nu_{\text{C=O}}, \nu_{\text{COOH}}$ | $\nu_{\text{NH}_2}$ | $\nu_{\text{Cl ionic}}$ | $\nu_{\text{M-O}}$ | $\nu_{\text{M-N}}$ |
|-----|--------------------|-------------------------------------------|---------------------------------------------------------------------------------------------------|---------------------|-------------------------|--------------------|--------------------|
| LH  | 1630               | 1590                                      | 2800-3400                                                                                         | -                   | -                       | -                  | -                  |
| 1.  | 1615               | 1525                                      | 2800-3400                                                                                         | 3300                | 575                     | 455                | 420                |
| 2.  | 1615               | 1525                                      | 3450-3600<br>2800-3600                                                                            | 3300                | 575                     | 455                | 420                |
| 3.  | 1615               | 1525                                      | 3450-3600<br>2800-3600                                                                            | 3300                | -                       | 455                | 420                |
| 4.  | 1610               | 1530                                      | 3450-3600<br>2800-3600                                                                            | 3320                | -                       | 465                | 440                |
| 5.  | 1610               | 1530                                      | 3450-3600<br>2800-3600                                                                            | 3320                | 575                     | 465                | 440                |
| 6.  | 1610               | 1530                                      | 3450-3600<br>2800-3600                                                                            | 3320                | 575                     | 465                | 440                |
| 7.  | 1615               | 1530                                      | 2800-3200                                                                                         | 3250                | -                       | 455                | 440                |
| 8.  | 1615               | 1530                                      | 2800-3200                                                                                         | 3250                | -                       | 455                | 440                |
| 9.  | 1610               | 1530                                      | 2800-3200                                                                                         | 3320                | -                       | 465                | 430                |
| 10. | 1610               | 1530                                      | 2800-3200                                                                                         | 3320                | -                       | 465                | 430                |
| 11. | 1610               | 1530                                      | 2800-3200                                                                                         | 3320                | -                       | 465                | 430                |
| 12. | 1605               | 1525                                      | 2800-3200                                                                                         | 3250                | -                       | 475                | 425                |



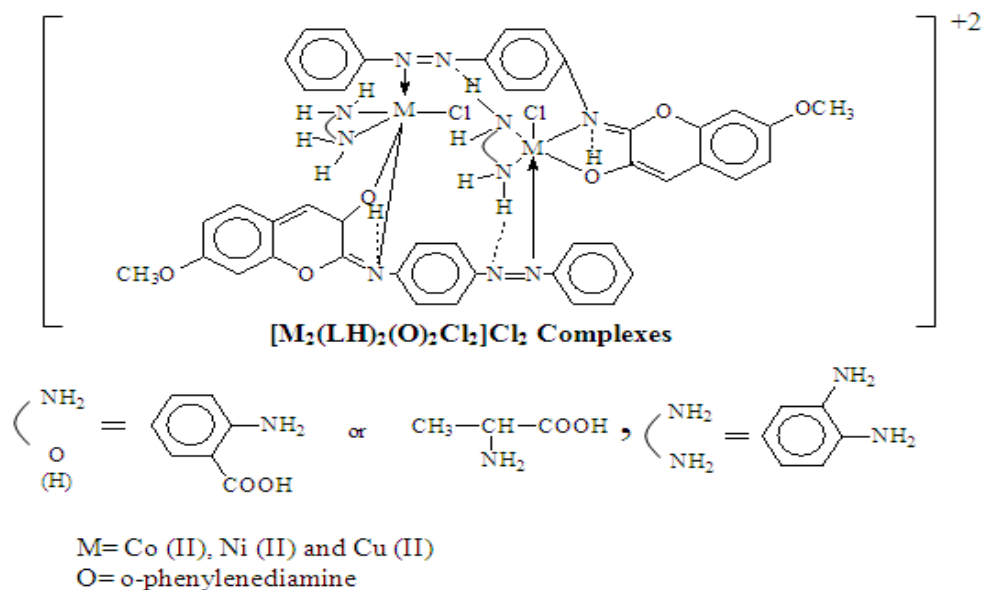


Figure (2): structures of the mixed ligand complexes in neutral medium

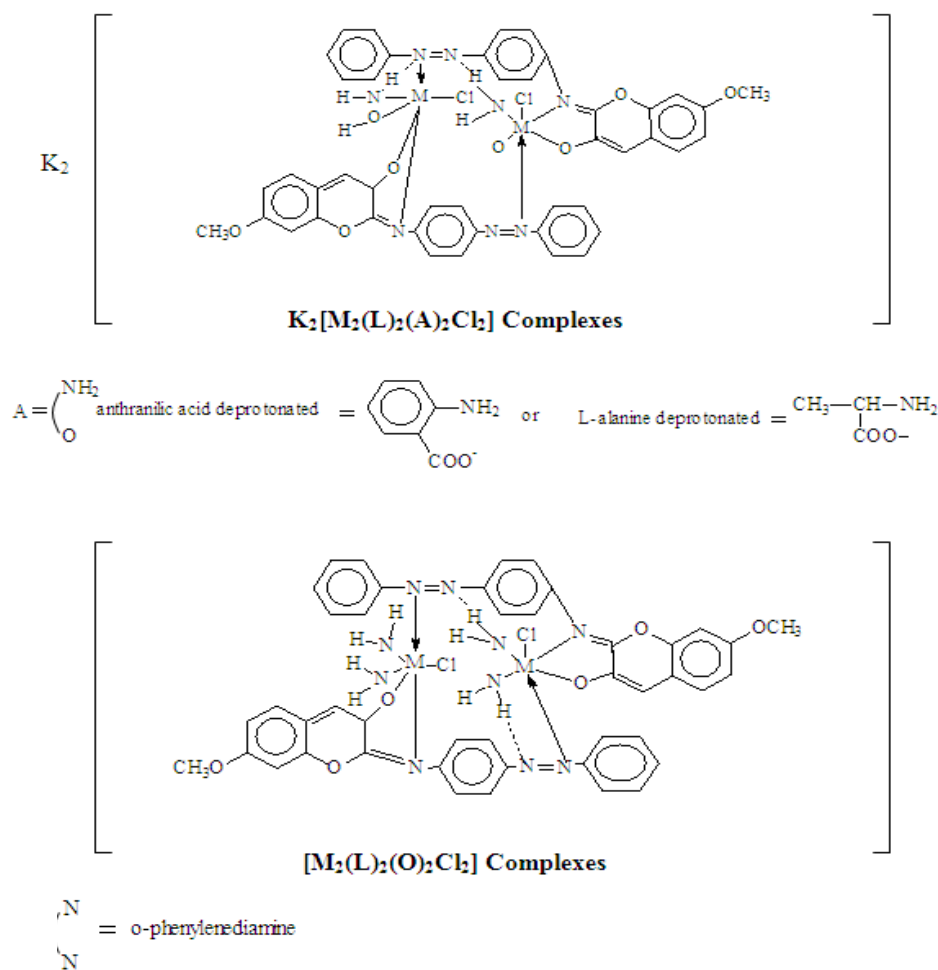


Figure (3): Structures of the mixed ligand complexes in basic medium

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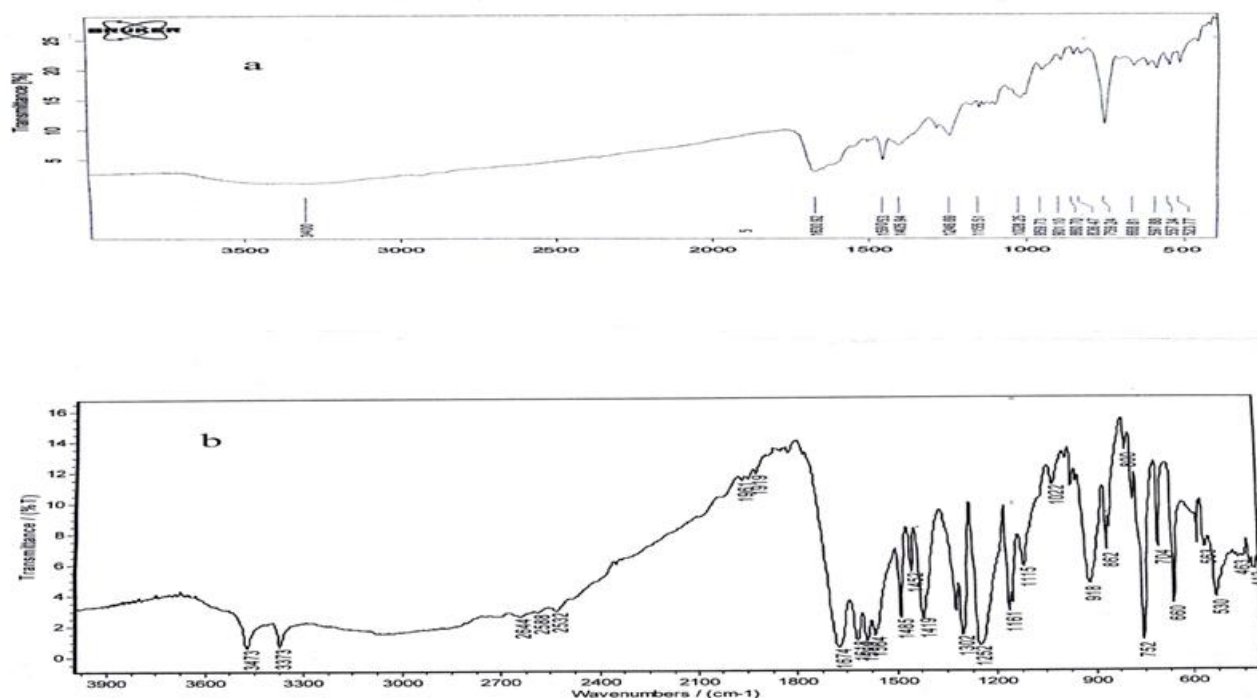


Fig. 4: IR spectra of the ligand LH(a) and complex 7