

## On the Formation of Iron(III) Benzoylacetyl-anilide Complexes: Structural, Elucidation by TGA, IR, Electronic Spectra, Conductance and Potentiometric Studies

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**Summary:** Two new series of iron(III) benzoylacetyl-anilide complexes have been prepared and characterized by elemental analysis, TGA, IR, electronic spectra and conductance measurements. The elemental analyses show that the composition of the solid complexes produced have 1:2 and 1:3 (M:L) molar ratios. TGA and IR spectra indicated that the bonding in 1:3 (M:L) complexes takes place through the enolic-OH group and anilide N-linkage only while in 1:2 (M:L) complexes it takes place through interaction of carboxy OH or SH together with the enolic OH group through H<sup>+</sup> ion displacement. Electronic spectra indicated octahedral geometry around Fe(III) ion. Conductometric and potentiometric titrations indicated the formation of 1:1, 1:2 and 1:3 (M:L) complexes in solutions. The values of the conditional stability constants calculated by potentiometric techniques depend on molecular structure. Deviation of the pK<sub>1</sub> vs log K plots slopes from unity is attributed mainly to steric effect,  $\pi$ -electron back donation from the metal ion or structural changes in the ligand.

### Introduction

A large number of metal complexes of anilide ligands have been reported in literature and function as effective catalysts in many reactions [1-3] which are also present at the active sites of many important biological catalysts [4]. The application of such metal chelates to any one system depends to a large extent on its molecular structure [5]. Accordingly, the aim of the present study was to synthesize and characterize Fe(III) complexes with benzoylacetyl-anilide ligands. The complexes were characterized by elemental analyses, thermogravimetric analysis (TGA) and some spectroscopic techniques viz IR, electronic spectra and conductance measurements. The composition, nature and stability of the complexes formed are also investigated by conductometric and potentiometric techniques.

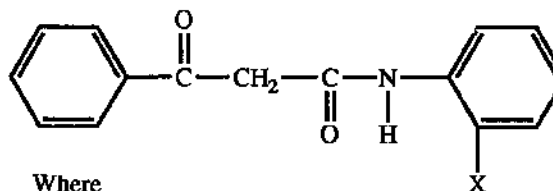
### Experimental

#### i. Preparation of ligands

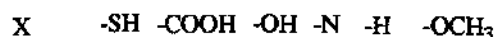
A mixture of ethyl benzoylacetate ester (0.01 mole) and (0.01 mole) of the corresponding aniline or its derivatives were mixed in molten sodium acetate at 120°C for 1/2 hour. The mixture was poured in H<sub>2</sub>O and the precipitate was recrystallized from water/ethanol (50%); the product ob-

tained was filtered off washed with cold water/ethanol several times, finally with ether and then dried in vacuo.

The structure of the ligands was also confirmed by elemental analysis, IR and <sup>1</sup>H-NMR spectra. The ligands used in the present investigation have the following formula:



Where



Ligand abbreviation    L<sub>I</sub>    L<sub>II</sub>    L<sub>III</sub>    L<sub>IV</sub>    L<sub>V</sub>    L<sub>VI</sub>

#### ii. Preparation of complexes

A solution of metal salt (0.001 M) in bidistilled water was added to a solution of the ligand (0.002 M) in the least amount of pure ethanol. The mixture was stirred for one hour during which the solid complexes were separated and then filtered off, washed several times with bidistilled water to

remove any traces of metal ions, finally washed with diethylether and then dried in vacuo.

### iii. Physical measurements

The apparatus and working procedures are the same as described previously [6-8].

## Results and Discussion

### A: Complexes in the solid state

The results of elemental analysis (Table 1) show that the composition of the solid complexes corresponds to 1:2 and 1:3 (M:L) molar ratios and also most of the prepared complexes have one or more water molecules coordinated to the central metal atom which are not removed by static vacuum for three hours at room temperature and also they indicate that the complex formation takes place through proton displacement from the ligand.

Thermogravimetric analysis (TGA) of iron (III) complexes (Fig. 1) indicated the following:-

- Lattice water molecules associated with complex formation are removed at 25-110°C.
- The anhydrous or unsolvated complexes show thermal stability up to 425, 260 and 230°C for L<sub>I</sub>, L<sub>II</sub> and L<sub>III</sub> respectively.

iii [Fe(L<sub>IV</sub>)]H<sub>2</sub>O and [Fe(L<sub>I</sub>)H<sub>2</sub>O] have higher thermal stabilities than the other complexes since they are stable up to 450°C. This means that the substitution by benzene and Ph-SH rings tends to increase the volatility of the complexes while the substitution by Ph-COOH and Ph-OH tends to decrease the volatility of the Fe(III) complexes.

On examining the IR spectra of iron 1:2 and 1:3 (M:L) complexes, Table-1 in comparison to those of the free ligands, the following can be appointed out:-

a - The spectra of most complexes exhibited a broad band around 3640-3350 cm<sup>-1</sup> which could be assigned to νOH of water molecules associated with complex formation. This fact is also supported from TGA measurements.

b - For 1:3 (M:L) complexes the bands located at 3340-3320 and 1680-1630 cm<sup>-1</sup> are due to ν NH and ν CO respectively. The spectra of the free ligands display obvious shifts to lower frequency on complex formation by -100<sup>-1</sup> and 25 cm<sup>-1</sup> respectively. Thus, the bonding in this case takes place through the carbonyl and amide linkages only.

c- For 1:2 (M:L) complexes are the bands located at 3100-3340 and 1610-1680 cm<sup>-1</sup> are due to ν NH and ν CO respectively. The spectra of the free ligands exhibit obvious shifts to lower frequency on complex formation by 100 and 30 cm<sup>-1</sup> respectively. Thus in case of the 1:2 (M:L) complexes the bond-

Table 1: Microanalysis results, the conditional stability constants and IR spectra of Fe(III) complexes.

Formula	[Fe(L <sub>I</sub> ) <sub>2</sub> ]H <sub>2</sub> O	[Fe(L <sub>II</sub> ) <sub>2</sub> ]H <sub>2</sub> O	[Fe(L <sub>III</sub> ) <sub>2</sub> ]	[Fe(L <sub>IV</sub> ) <sub>3</sub> ]H <sub>2</sub> O	[Fe(L <sub>V</sub> ) <sub>3</sub> ]H <sub>2</sub> O	[Fe(L <sub>VI</sub> ) <sub>3</sub> ] <sub>2</sub> H <sub>2</sub> O
M:L	1:2	1:2	1:2	1:3	1:3	1:3
Colour	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown	Dark brown
%C*	58.50(58.82)	59.80(60.19)	63.80(64.06)	68.30(58.60)	63.40(63.70)	63.70(64.07)
%H*	3.70(3.92)	4.10(4.08)	3.66(3.92)	4.40(4.82)	4.10(4.43)	5.20(5.45)
%N*	4.40(4.58)	4.20(4.39)	4.60(4.98)	5.10(5.32)	10.70(10.62)	4.20(4.67)
%S*	10.00(10.45)	-	-	-	-	-
%M*	8.60(9.15)	8.10(8.78)	9.20(9.96)	6.80(7.11)	6.70(7.08)	6.00(8.23)
Log K <sub>1</sub>	9.9	7.85	6.8	6.36	5.7	5.49
Log K <sub>2</sub>	9.65	7.25	6.4	6.16	5.40	5.066
νOH <sub>water</sub>	3640m	3380	3370	3400-3500	3400-3500	3350
νN-H	3380	3240	3070	3375s	3360-3230	3220
νC=O	1645	1665	-	1675,1640	-	1675,1645
νCONH	1570	1575	1620	1600,1580	1600,1520	1580
νM-N	360s	360m	360m	385s	390m	385s
νM-O	490s	490s	480br	480s	457	470s

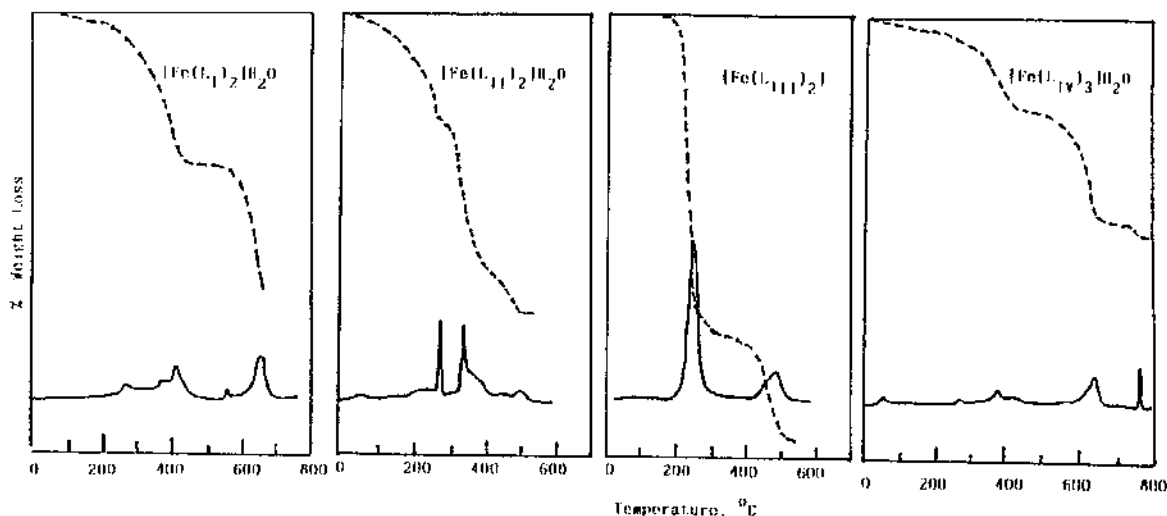


Fig. 1: Thermograms of Fe(III) complexes.

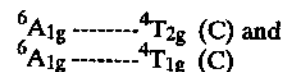
ing between the metal ion and ligands takes place through the interaction of carboxy OH or SH and NH groups with the metal ion. The band due to the enolic OH group which exists in the spectra of free ligands is still observed at the same position in the spectra of the metal chelates but with little intensity one of which indicates that enolic OH group does not participate in the formation of the 1:2 (M:L) complexes.

d- The participation of enolic OH group in chelate formation through proton displacement arises from the disappearance of  $\nu$  OH and  $\nu$  C-OH for all 1:2 (M:L) complexes in comparison to those present in the free ligands at  $1510-1520\text{ cm}^{-1}$  and  $1130-1140\text{ cm}^{-1}$  respectively.

e - The two new bands observed at  $445-490\text{ cm}^{-1}$  and  $360-390\text{ cm}^{-1}$  for all 1:2 and 1:3 (M:L) complexes, which are not observed in the spectra of the free ligands, can be assigned to  $\nu$  M-O and  $\nu$  M-N respectively.

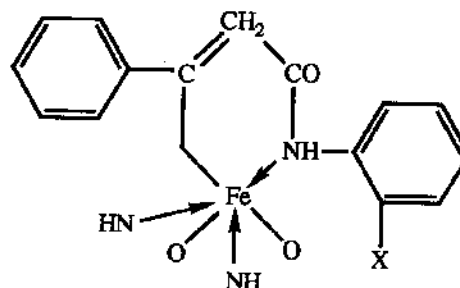
The electronic absorption spectra of the Fe(III) complexes in DMF solution with all ligands under investigation exhibit four absorption bands with  $\lambda$  max situated at 255-265, 280-290, 385-425 and  $560-650\text{ nm}$ . The first two bands are assigned to  $\pi-\pi^*$  transition within the aromatic ring and anilide nucleus respectively. The last two bands can be as-

singed to the electronic transitions of the  $\text{Fe}^{+3}$  ion due to electronic states:



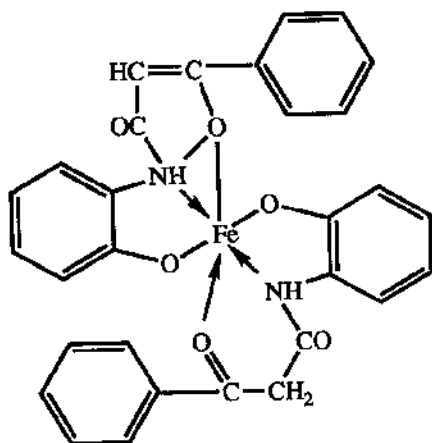
These spectral patterns indicate on octahedral arrangement of the co-ordinated atoms or groups around the central Fe(III) ion.

Based on the above results gained from TGA, IR and electronic spectra, the 1:3 Fe(III) complexes with octahedral geometry exhibit the following geometry:-



For ligands  $L = L_{IV}$ ,  $L_V$  and  $L_{VI}$ ;  $X = N$ ,  $H$  and  $\text{OCH}_3$  respectively.

The 1:2 (Fe(III) complexes having octahedral geometry can be formulated as:-



For ligands  $L = L_I, L_{II}$  and  $L_{III}$ ; we have SH, COOH or OH groups respectively.

#### B: The stoichiometry of the iron (III) complexes in solution

The stoichiometry of the complexes formed between Fe(III) ion with the anilide ligands is investigated by conductance measurements and potentiometric titration.

#### i. Conductometric titrations

Conductometric titration can be applied for testing complex formation in solution by titrating a known volume of the metal ion in solution having a definite concentration with the chelating agent. The conductance measured after correction for dilution is then plotted vs the volume of the reagent added. The conductance molar ratio curves are characterized by some breaks, the position of which gives information about the presence of the different complexed species that can exist in solution under prevailing experimental conditions. The results obtained are shown in Fig. 2. It is found that the titration curves exhibit 1:2 and 1:3 (M:L). The data obtained indicate that the  $H^+$  ions are displaced from the ligand on complex formation so that complex formation should take place through a covalent link formation between the metal ion and the ligand groups.

#### ii Potentiometric method

Since the formation of Fe(III) chelates with anilide compounds is associated with the liberation of  $H^+$  ions from the ligands. It is possible to apply

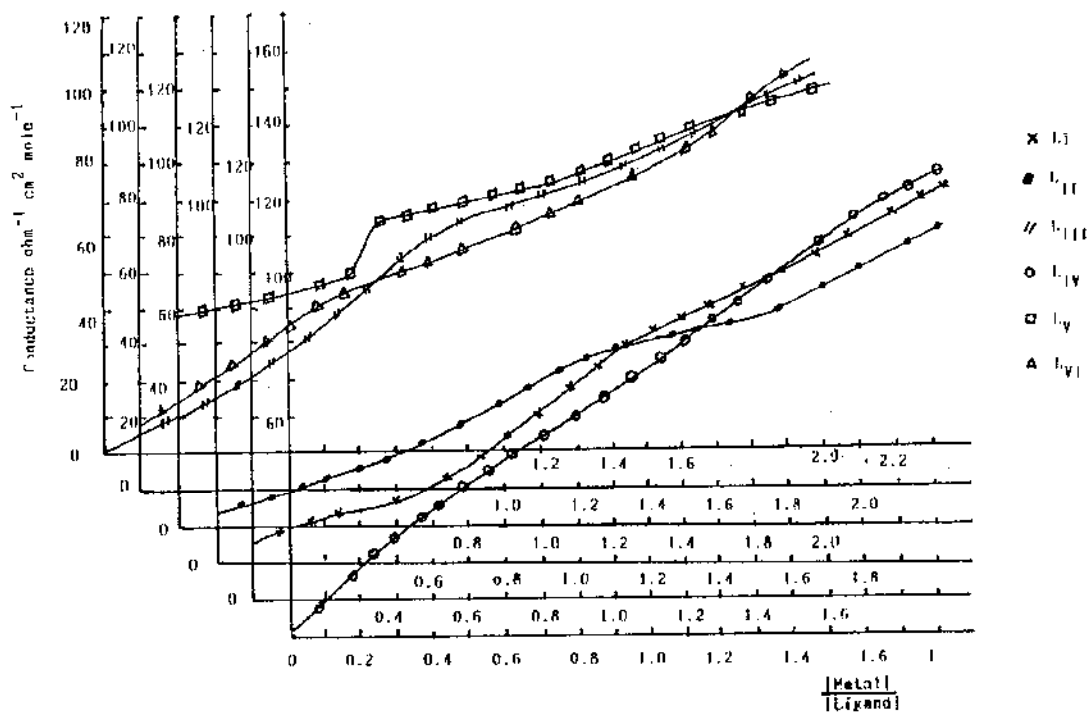


Fig. 2: Conductometric titration of Fe(III) complexes with anilide ligands L

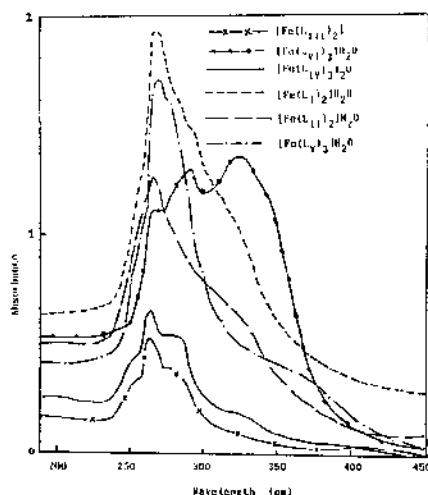


Fig. 3: Electronic absorption spectra of Fe(III) complexes with the anilide ligands in DMF solvent.

the pH-metric method for the determination of the composition and conditional stability constants of the chelates formed [9].

The pH titration curves of the Fe(III) chelates under investigation are S-shaped, the volume of alkali consumed in the titration corresponds to the liberation of one  $H^+$  ion or two per metal ion on complex formation. The titration curves of Fe(III) chelates exhibit some inflections within the 8.5 - 10.5 pH range which can be ascribed to the formation of some different types of complexes, probably of the hydroxo type [10].

The formation curves obtained for the different complexes investigated are expanded over the range 0.5 and 0.2 - 0.3 n showing a distinct break indicating that the stoichiometric ratio are 1:1, 1:2 and 1:3 (M:L) and which are in good agreement with the results gained from conductometric titrations.

The conditional stability constant of the two types of chelates,  $\log K_1$  and  $\log K_2$ , were then determined by the method of Bjerrum [11] and Albert [12] applying the least square method and the graphical representation method ( $n$  vs  $pl$ ). The data obtained, (Table 1), indicate that the values of the conditional stability constant depends on both the

nature of the ligand as well as the metal ion. Generally, the  $\log K$  values for the same metal ion increase as the donor property of the substituent (X) increases. The plot of  $\log K_1$  or  $\log K_2$  as a function of the "Taft constant" for the same metal ion is a linear relation. The negative values of the slope indicate that metal complexation is favoured by high electron densities at the coordination sites, a factor which favours increased covalent nature of the metal - ligand bond. Straight lines of non-unit slope were obtained on plotting  $\log \beta_1$  vs  $pK_1$  for the metal chelates under investigation, deviation from a slope of unity is attributed mainly to steric effect,  $\pi$ -electron back donation from the metal ion, or structural changes in the ligand which alter the strength of the donor atom within the ligands [13].

The stability of the chelates decreases on going from  $L_I$  to  $L_{VI}$ :  $L_I > L_{II} > L_{III} > L_{IV} > L_{VI}$ .

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