# Iron (III) complexes of α, β-unsaturated β-ketoamines

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**Abstract.** Iron (III) complexes of the type $Fe(R-L)_3$, where $R-L$ is a Schiff base derived from a β-diketone L, (acetoacetanilide, AN; acetoaceta-p-toluidide, AP and benzoylacetone, BA) and primary amines $RNH_2$ (ammonia, methyl amine or ethyl amine) have been synthesised and characterised by analysis, magnetic moment, electronic, infrared and Mössbauer spectra.

## 1. Introduction

There is an extensive interest in the chemistry of Schiff bases and their complexes (Holm *et al* 1968; Combes and Combes 1892; Holtzclaw *et al* 1958; Vijay and Tandon 1975). A very large number of imine derivatives of β-diketones are known (Combes and Combes 1892; Holtzclaw *et al* 1958; Vijay and Tandon 1975). However, metal chelates of the β-diketo-imines have not been exhaustively studied. The complexes of Schiff bases, derived from acetylacetone and primary amines, with copper (Combes and Combes 1892; Holtzclaw *et al* 1958), nickel (Archer 1963), titanium, chromium, iron and cobalt (Srivatsava *et al* 1974) have been reported. Here we report the synthesis and characterisation of iron (III) chelates derived from primary amines and acetoacetanilide (R-AN), acetoaceta-p-toluidide (R-AP) and benzoylacetone (R-BA).

## 2. Experimental

All the solvents and reagents used were guaranteed reagents. Acetoacetanilide and benzoylacetone were from Fluka. Acetoaceta-p-toluidide was prepared by refluxing 1:1 mixture of p-toluidine and ethylacetoacetate in xylene. 3-(amino) crotonanilide (H-AN) (Knorr 1892), 3-(methylamino) crotonanilide (CH₃-AN) (Knorr and Taufkirch 1892), 3-(amino) crotonophenone (H-BA) (Knoevenagel 1903), 3-(methylamino) crotonophenone (CH₃-BA) (Beyer 1891) were prepared by reported procedures. Other Schiff bases were prepared by adding aqueous amine solutions to the ethanolic solution of appropriate β-diketone at 0°C. The ligands were isolated by concentration and purified by recrystallisation from ethanol. The purity and composition of the ligands were confirmed by analysis and pmr spectra.

The iron(III) complexes were prepared by the following general procedure. Ethanolic solution of ferric chloride and appropriate ligand in 1:3 ratio were heated on a water bath for approximately 30 min and then cooled. The red complex separated was filtered, washed with ether and dried over $P_2O_5$. Yield $\sim 80\%$. Magnetic susceptibilities were measured on a standard Guoy balance using $Hg[Co(NCS)_4]$ as the calibrant. Ultraviolet and visible spectra of the complexes in dimethyl formamide solutions of the complexes were measured on a Unicam SP700A spectrophotometer. The infrared measurements of the solid ligands and complexes were recorded on Carl Zeiss UR10 spectrometer. The paramagnetic resonance spectra of the ligands in $CDCl_3$ were recorded on Varian T-60 spectrometer. The Mössbauer spectra were recorded by EC, MBS 35 spectrometer with constant acceleration mode, the $\gamma$-ray source being $^{57}Co$ in palladium. Carbon, hydrogen and nitrogen in the complexes were determined by microanalytical methods. Iron was estimated by titrating against standard EDTA after decomposing the complexes with perchloric acid.

## 3. Results and discussion

### 3.1. *Nature of the ligands*

In principle, the Schiff bases employed can exist in keto or enol form. These ligands behave in a similar fashion like other Schiff base ligands derived from acetylacetone and primary amines which have been proved to exist in enol form (Holtzclaw *et al* 1958). This is established by the fact that all the ligands exhibit $\nu_{CO}$ in the region $<1600$ cm$^{-1}$. In keto form they would be expected at higher frequencies $\sim 1700$ cm$^{-1}$. Only in the case of the ligand H-AP a band at 1705 cm$^{-1}$ is observed suggesting the presence of keto form. The enol forms of the ligands were further confirmed from their pmr spectra in $CDCl_3$. The signal expected at $\sim 3.5\delta$ for $CH_2$ protons in keto form are absent in all except in H-AP ligand, while they exhibit signals characteristic of $-CH$ proton of enol form (R-AN$\sim 4.45\delta$, R-AP$\sim 4.4\delta$, R-BA$\sim 5.6\delta$). Each ligand exhibits a broad signal around $\sim 9.2\delta$ (R-AN, R-AP) and $\sim 11\delta$ (R-BA) assignable to hydrogen bonded NH proton. The ligand H-AP exhibits a weak signal at $3.53\delta$ due to the keto form and the intensity ratio indicated that the ligand contains $22\%$ keto form. The ligands have been assigned the structure A (figure 1). The other prominent infrared bands observed in the ligands are, a number of bands between 1400-
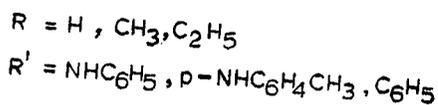


$$R = H, CH_3, C_2H_5$$
$$R' = NHC_6H_5, p-NHC_6H_4CH_3, C_6H_5$$

**Figure 1.**

**Table 1.** Analytical data of $Fe(R-L)_3$ complexes.

| Complexes | % C found | (calc.) | % H found | (calc.) | % N found | found | % Fe found | (calc.) |
|---|---|---|---|---|---|---|---|---|
| Fe(H-AN)₃ | 62·13 | (61·97) | 5·51 | (5·68) | 14·03 | (14·46) | 9·92 | (9·61) |
| Fe(CH₃-AN)₃ | 63·34 | (63·57) | 6·45 | (6·26) | 12·82 | (13·48) | 9·14 | (8·97) |
| Fe(C₂H₅-AN)₃ | 65·11 | (64·97) | 6·58 | (6·77) | 11·97 | (12·63) | 8·77 | (8·40) |
| Fe(H-AP)₃ | 64·22 | (63·57) | 6·33 | (6·26) | 13·54 | (13·48) | 9·23 | (8·97) |
| Fe(CH₃-AP)₃ | 65·07 | (64·97) | 6·86 | (6·77) | 12·74 | (12·63) | 8·74 | (8·40) |
| Fe(C₂H₅-AP)₃ | 66·43 | (66·20) | 7·32 | (7·21) | 12·11 | (11·88) | 7·79 | (7·90) |
| Fe(H-BA)₃ | 66·93 | (67·18) | 5·74 | (5·59) | 8·06 | (7·84) | 10·55 | (10·42) |
| Fe(CH₃-BA)₃ | 69·32 | (68·53) | 6·53 | (6·23) | 7·08 | (7·23) | 10·10 | (9·66) |
| Fe(C₂H₅-BA)₃ | 71·17 | (69·69) | 6·98 | (6·77) | 6·59 | (6·77) | 9·31 | (9·01) |

1600 cm$^{-1}$, assignable to $\nu_{C=C}$, $\nu_{C=N}$ and benzene ring vibrations (Avram and Mateescu 1966) and broad bands in the region 3200–3500 cm$^{-1}$ assignable to hydrogen bonded $\nu_{OH}$ and $\nu_{NH}$ vibrations. The vibrations observed around 750–800 cm$^{-1}$ and 1200 cm$^{-1}$ are assignable to $\pi CH$ and $\delta CH$ respectively (Nakamoto 1963).

### 3.2. Nature, bonding and structure of the complexes

Elemental analysis (table 1) indicate the metal-to-ligand ratio to be 1:3. The conductance data show that the complexes are non-electrolytes in dimethyl formamide. The magnetic moments of the complexes at room temperature (300°K) are in the range 5·9–6·00BM, suggesting that the complexes are high spin type.

The infrared spectra of the complexes are almost identical with those of the respective ligands except that the bands around 3200–3400 cm$^{-1}$ vanish indicating that the enolic hydrogen has been replaced by the metal. The observation that the bands assignable to $\nu_{OH}$ and $\nu_{NH}$ are absent in the complexes indicate the co-ordination of both nitrogen and oxygen to the metal. Similar bonding mode has been assigned for other ketoamine complexes (Holtzclaw *et al* 1958; Srivatsava *et al* 1974). The complexes can be assigned the structure B (figure 1).

The electronic spectra of the complexes were recorded in dimethylformamide. In iron (III) high spin complexes, all the *d-d* transitions are expected to be weak as they are spin-forbidden. Four such transitions are expected for octahedral high spin iron(III) complexes (Lever 1968). The electronic spectral data are given in table 2. The bands around 560 nm, 530 nm and 500 nm can be assigned to the following transitions respectively

$$6A_{1g} \rightarrow 4T_{1g}, \quad 6A_{1g} \rightarrow 4T_{2g} \quad \text{and} \quad 6A_{1g} \rightarrow 4A_{1g}.$$
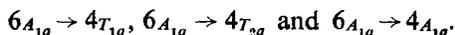
The other transition $6A_{1g} \rightarrow 4T_{2g}$ (D) perhaps overlaps with intense charge transfer or ligand transitions. In many complexes transitions

$$6A_{1g} \longrightarrow 4T_{1g} \quad \text{and} \quad 6A_{1g} \longrightarrow 4T_{2g}$$
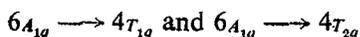
are not observed perhaps because of their very low intensity. These assignments agree well with those reported for similar complexes (Srivatsava *et al* 1974). The high

**Table 2.** Electronic spectra and Mössbauer data of $Fe(R\text{-}L)_3$ complexes.

| Complex | Charge transfer/ Ligand transitions in nm | $^6A_{1g} \to {}^4A_{1g}$ in nm | $^6A_{1g} \to {}^4T_{2g}$ in nm | $^6A_{1g} \to {}^4T_{1g}$ in nm | Möss bauer data | |
|---|---|---|---|---|---|---|
| | | | | | Isomer shift $\delta^*$ in mm/sec | Quadrupole splitting in mm/sec |
| $Fe(H\text{-}AN)_3$ | 268, 283 sh, 330 sh | 502 | 535 sh | 615 sh | 0·74 | 0·57 |
| $Fe(CH_3\text{-}AN)_3$ | 276 b, 318 sh | 490 | 520 sh | 560 sh | 0·61 | 0·57 |
| $Fe(C_2H_5\text{-}AN)_3$ | 274 b, 326 | 480 | — | — | 0·51 | 0·57 |
| $Fe(H\text{-}AP)_3$ | 268, 290 sh, 328 sh | 490 | — | — | 0·75 | 0·42 |
| $Fe(CH_3\text{-}AP)_3$ | 267, 282 sh, 321 sh | 480 | — | — | 0·64 | 0·70 |
| $Fe(C_2H_5\text{-}AP)_3$ | 267, 280 sh, 315 sh | 480 | — | — | 0·64 | 0·32 |
| $Fe(H\text{-}BA)_3$ | 270, 300, 395 | 485 | — | — | — | — |
| $Fe(CH_3\text{-}BA)_3$ | 275, 290, 400 | 465 | — | — | — | — |
| $Fe(C_2H_5\text{-}BA)_3$ | 268, 295, 390 | 455 | — | — | — | — |

sh = shoulder,  b- broad.

*with respect to sodium nitroprusside.

intensities are perhaps due to intensity stealing from neighbouring ligand or charge transfer transitions.

Mössbauer data are given in table 2.   The chemical shifts are with respect to sodium nitroprusside.   All the Mössbauer spectra consist of a doublet at room temperature. The isomer shifts of the complexes are in the range observed for analogous iron (III) complexes (Bankcroft *et al* 1967, Garg *et al* 1970).   The values of isomer shifts for $Fe(R\text{-}AN)_3$ are higher than that for $Fe(AN)_3$ (Garg *et al* 1974) probably due to the presence of electron donating R-N group. This probably results in the decrease of back donation from iron to the ring system with consequent increase in the isomer shifts.   In $Fe(R\text{-}AN)_3$ and $Fe(R\text{-}AP)_3$ complexes isomer shifts decrease in the order ammonia > methylamine > ethylamine, indicating the strength of $\pi$-bonding in the order ethylamine > methylamine > ammonia.   Quadrupole splitting is the same for all $Fe(R\text{-}AN)_3$ complexes, while $Fe(Me\text{-}AP)_3$ shows abnormal large quadrupole splitting.   The reason for this is not clear.   Quadrupole splitting depends upon bonding characteristics of the ligands as well as contribution from the lattice, the latter might be responsible for the abnormal splitting in $Fe(Me\text{-}AP)_3$ complex. $Fe(R\text{-}BA)_3$ complexes gave very broad Mössbauer spectra and consequently could not be analysed.

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