

# Characterization and biological studies of Mixed Ligand Complexes of Fe(III) With 2-hydroxypropiophenone and $\beta$ -diketones

Neha Jain<sup>1\*</sup>, Jitendra Kumar Gupta<sup>2</sup>

**Abstract:** A series of mixed ligand complexes of Fe (III) of the type  $[\text{Fe}(\text{L})_2\text{L}']$ , (where HL=2-hydroxypropiophenone and HL'= pentane-2,4-dione, 1-phenyl butane-1,3-dione or 1,3-diphenyl propane1,3-dione) have been synthesized by the condensation reaction of iron(III) chloride with a mixture of two different ligands in 1:2:1molar ratios. Physicochemical and spectroscopic methods were used to determine mode of bonding and coordination geometry of newly Synthesized mixed ligand complexes of Fe(III). Room temperature magnetic susceptibility measurements revealed paramagnetic nature of the complexes.

**Keywords:** Mixed ligand complexes, 2-hydroxypropiophenone,  $[\text{Fe} (2\text{-hpp})_2 (\text{dbzm})]$ .

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<sup>1\*</sup>Department of Chemistry, University of Rajasthan, Jaipur - 302004, India

<sup>2</sup>Department of General Surgery, JNUIMSRC Jaipur-302004, India, Email: jainneha0810@gmail.com

**\*Corresponding Author:** Neha Jain

\*Department of Chemistry, University of Rajasthan, Jaipur - 302004, India

**DOI:** - 10.48047/ecb/2023.12.si10.00122

## Introduction

A lot of work has been done to synthesize mixed ligand complexes of transition metals. Revanasiddappa et al<sup>1</sup> have synthesized Fe (III) complexes with lansoprazole drug, that is 2-{3-methyl-4-(2,2,2-fluoroethane)-2-pyridyl)methyl}sulphonylbenz-imidazole. Few mixed lig and complexes of Fe (III)with  $\beta$ -diketones and nitrogen or phosphorus containing lig and s have been reported<sup>2-4</sup>.

In this paper we report some new mixed ligand complexes of Fe(III) . Resulting complexes are characterized by different techniques. On the basis of these studies coordination behaviour and octahedral geometry of new mixed ligand complexes were identified.

## Experimental

### Materials:

1-phenylbutane-1,3-dione(sisco-chem), 1,3-diphenylpropane1,3-dione (Sisco-chem) were purified by recrystallization from butanol prior to use. 2-hydroxypropiophenone (Merck), pentane-2,4-dione (John Baker) and butanol were purified by distillation. Iron (III) chloride A.R. was used as supplied.

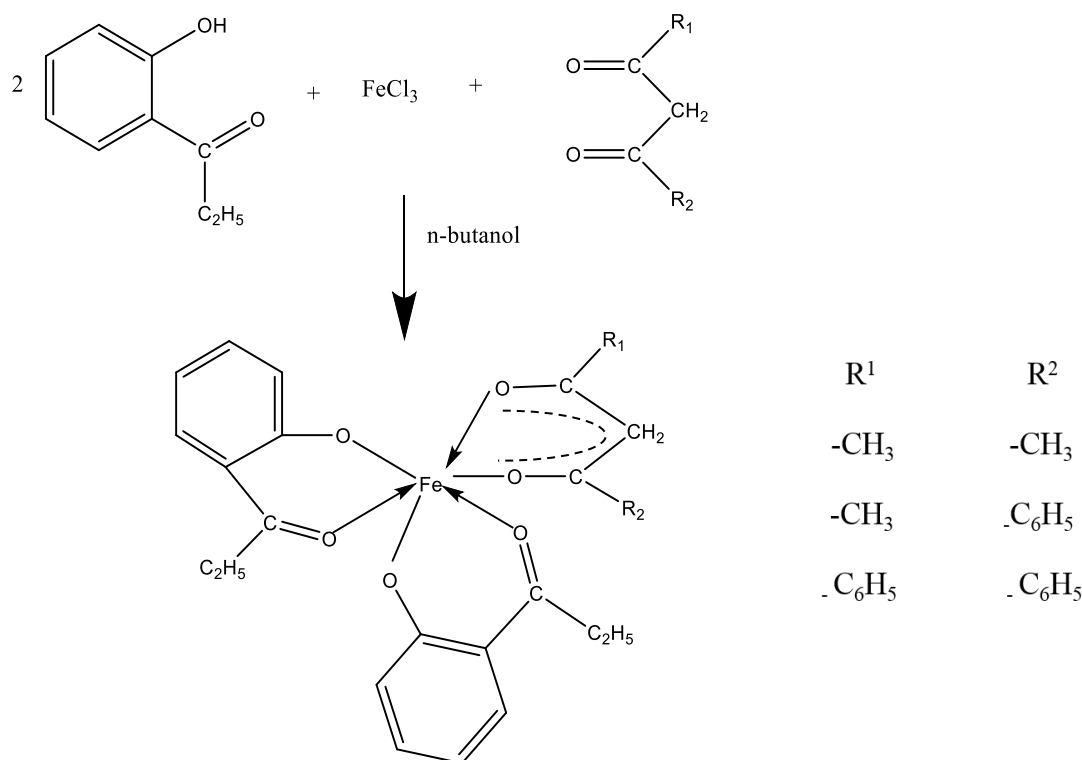
### Analytical methods and physical measurements:

Iron was estimated volumetrically by EDTA using Eriochrome black-T as an indicator<sup>5</sup>. Carbon and hydrogen analyses were carried out on a Heraeus Carlo Erba 1108 instrument.

### Synthesis of mixed ligand complexes of Fe(III) with 2-hydroxypropiophenone and $\beta$ -diketones:

To a butanolic solution of FeCl<sub>3</sub> (5.24 mmol, 0.851g in 10 ml n-butanol), butanolic solution of 2-hydroxypropiophenone (1.48ml) and 1,3-diphenylpropane-1,3-dione (1.10g in 10 ml n-butanol ) were added with constant stirring. The reaction mixture was stirred for about 30-40 minutes. No ppt was obtained. Then, added 5% aqueous sodium hydroxide solution (~4 ml) drop wise to the above reaction mixture to raise the pH up to ~7.0. Stirred the solution for 3-4 hrs and then reflux the reaction mixture on heating mental for 4-5 hours, the ppt began appear. After refluxing, the reaction mixture was kept on room temperature. The ppt was settled down. Filter the solution, washed with butanol and dried properly under reduced pressure.

A similar method was adopted to synthesize mixed ligand complexes of Fe(III) with pentane-2,4-dione, and 1-phenylbutane-1,3-dione.



Scheme 1

## Results and discussion

The reactions of iron (III) chloride with 2-hydroxypropiophenone and  $\beta$ -diketones in 1:2:1 molar ratios result in the formation of mixed ligand complexes of iron (III) (see scheme 1).

### Analytical and Physical measurements of synthesized complexes:

The resulting mixed ligand complexes are obtained in 32-57% yields as reddish or black brown solid. The data of C, H and Fe analyses agree well with the calculated values corresponding to the respective complexes. The complexes decomposed at high temperature on heating. All the physical data are shown in Table 1.

**Table 1:** Analyses and Characterization of Mixed Ligand Complexes [Fe (2-hpp)<sub>2</sub>(dbzm)].

S.No.	Complex Molecular Formula Molecular Weight	Colour Yield%	Decomp. Temp. (°C)	Analysis % Found (calculated)			Molar Cond.(mho cm <sup>2</sup> mol <sup>-1</sup> )	$\mu_{\text{eff}}$ (B.M)
				Fe	C	H		
1.	Fe(2-hpp) <sub>2</sub> (acac) C <sub>23</sub> H <sub>26</sub> O <sub>6</sub> Fe 454.29 g/mol	Blackish Brown 43.70	310	12.29 (12.45)	60.80 (60.98)	5.76 (5.65)	5.47	5.82
2.	Fe(2-hpp) <sub>2</sub> (bzac) C <sub>28</sub> H <sub>28</sub> O <sub>6</sub> Fe 516.37 g/mol	Reddish black 47.17	285	10.81 (10.54)	65.12 (65.34)	5.46 (5.65)	7.21	5.83
3.	Fe(2-hpp) <sub>2</sub> (dbzm) C <sub>33</sub> H <sub>30</sub> O <sub>6</sub> Fe 578.44 g/mol	Red 54.73	298	9.65 (10.01)	68.52 (68.23)	5.22 (5.24)	10.87	5.82

These are insoluble in water or most of the organic solvents like methanol, benzene and carbon tetrachloride but soluble in DMSO and DMF.

### Magnetic moments:

The  $\mu_{\text{eff}}$  values for the complexes are observed in the range 5.10 to 5.89 B.M. as expected for five unpaired electrons. According to the  $\mu_{\text{eff}}$  value of these complexes the metal present in d<sup>5</sup> electronic configuration. Thus, all the complexes are high spin paramagnetic complexes<sup>6</sup>. It lies within the octahedral range which is very close to spin value 5.90 B.M. as the ground term is <sup>6</sup>A<sub>1g</sub> and thus supports the octahedral geometry.

### Electronic spectra

The electronic spectra of Fe(III) mixed ligand complexes have been recorded in the region 300-800 nm and wavelengths for the absorption bands are given in Table 2.

Spectrum of [Fe(hpp)<sub>2</sub>(dbzm)] is reproduced in Fig. 1. The absorption bands are observed at 295 nm (33898 cm<sup>-1</sup>), 320 nm (31250 cm<sup>-1</sup>) and 394 nm (25400 cm<sup>-1</sup>) corresponding to 6A<sub>1g</sub> → 4E<sub>g</sub>(G)

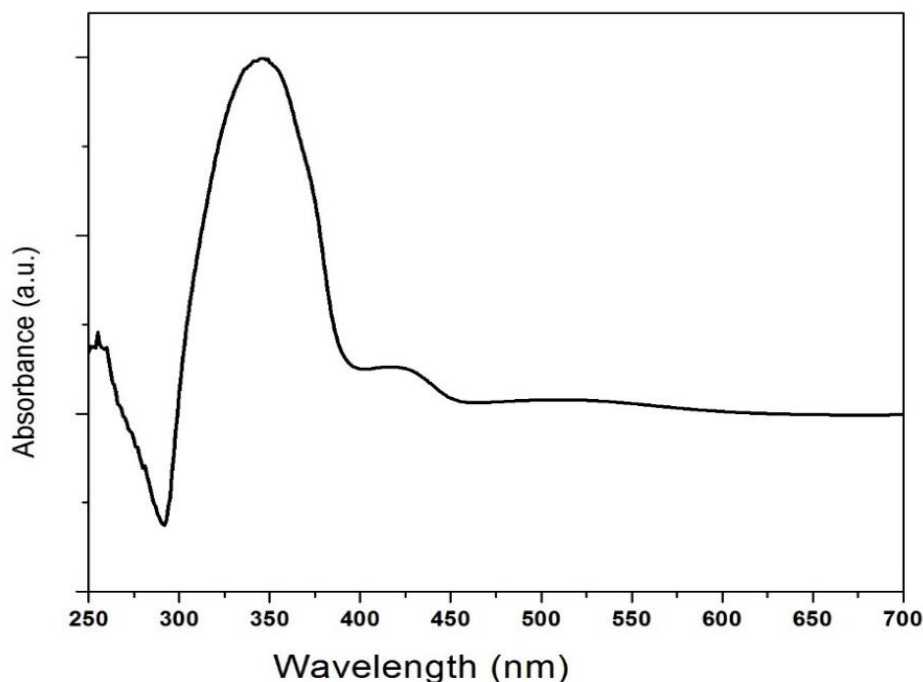
(v<sub>3</sub>), 6A<sub>1g</sub> → 4T<sub>2g</sub>(G) (v<sub>2</sub>) and 6A<sub>1g</sub> → 4T<sub>1g</sub>(G) (v<sub>1</sub>) transitions respectively. Deshmukh *et al.*<sup>7</sup> have observed three bands at 15125, 24032 and 23225 cm<sup>-1</sup> in the case of d<sup>5</sup> Fe(III) complex belong to 6A<sub>1g</sub> → 4T<sub>1g</sub>, 6A<sub>1g</sub> → 4T<sub>2g</sub> and 6A<sub>1g</sub> → 4E<sub>g</sub>, 4A<sub>1g</sub> transitions respectively indicating octahedral geometry.

v<sub>2</sub>/v<sub>1</sub> ratio is 1.230 for the complex. The Racah Parameter (B') for the complexes is 736.8 cm<sup>-1</sup>, is less than free ion value (B = 860 cm<sup>-1</sup>) suggesting a considerable orbital overlap and delocalization of electrons on the metal ion. The nephelauxetic ratio ( $\beta$ ) for the complex is less than one (0.857), suggesting partial covalency in the metal ligand bond.

All these values suggest the high spin octahedral geometry around the metal ion and are in accordance with the reported values in literature.<sup>8</sup> In the high spin octahedral iron(III) complex the charge transfer band dominates the spectrum and largely obscures any of the very weak spin forbidden d-d transitions of a t<sub>2g</sub><sup>3</sup>e<sub>g</sub><sup>2</sup> system, so in high spin octahedral iron(III) complex d-d transition bands are not present.

**Table 2:** Electronic spectral data (cm<sup>-1</sup>) of the mixed ligand complexes [Fe (L)<sub>2</sub>(L')]

S.No.	Complex	<sup>2</sup> T <sub>2g</sub> → $\pi$ *MLCT	$\pi$ → e <sub>g</sub> LMCT	$\pi$ → $\pi$ *Intra-Ligand
1	[Fe(2-hpp) <sub>2</sub> (acac)]	27217-24496	22817	31028
2	[Fe(2-hpp) <sub>2</sub> (bzac)]	25912-22395	22817	28724
3	[Fe(2-hpp) <sub>2</sub> (dbzm)]	26821-23298	24071	29784



**Figure 1.** UV-vis spectrum of the  $[\text{Fe}(2\text{-hpp})_2(\text{dbzm})]$

### Infrared spectra

The absorption bands observed in the IR spectra of the mixed ligand complexes of Fe(III) are recorded at the end of the discussion and the spectrum of representative complex viz.  $[\text{Fe}(\text{hpp})_2(\text{dbzm})]$  is reproduced in **Fig. 2**.

Infrared spectra provide valuable information regarding the nature of carbonyl groups attached to the metal atoms in the  $\beta$ -diketonate complexes. Evidence for the quasi-aromatic behavior of the six membered chelate ring at the structural features of the metal  $\beta$ -diketonate derivatives has also been adduced in some cases from these studies.<sup>9,10</sup>

In the IR spectra of mixed ligand complexes, medium intensity bands observed in the region  $400\text{-}500\text{ cm}^{-1}$ , may be attributed to Fe-O vibrations. Mixed ligand complexes exhibit strong absorption bands in the region  $1620\text{-}1675\text{ cm}^{-1}$ , may be assigned to coordinate C=O groups. Bands due to C=C stretching modes may be assigned in the region  $1520\text{-}1560\text{ cm}^{-1}$ .

In these complexes C=O band is observed at  $1650\text{ cm}^{-1}$ , thus the shift of C=O bands to the lower

wave number side in the mixed-ligand complexes supports the coordination of the C=O group to the metal ion.

Shifting of these bands to lower wave number on complexation with the metal ion has been reported.<sup>11,12</sup> These bands shift to lower wave numbers on chelation with metal ions.<sup>13</sup> In free acetylacetone and benzoylacetone, the  $\nu(\text{C}=\text{O})$  band has been reported at  $1724\text{ cm}^{-1}$  and in 5-chlorosalicylaldehyde, the  $\nu(\text{C}=\text{O})$  band appears at  $1680\text{ cm}^{-1}$ . The mixed ligand complexes exhibit strong absorption bands at  $\sim 1600\text{ cm}^{-1}$  which may be assigned to coordinated  $\nu(\text{C}=\text{O})$  group. Bands at  $1500\text{ cm}^{-1}$  may be due to  $\nu(\text{C}=\text{C})$ . In free 2-hydroxyacetophenone and 2-hydroxypropiophenone bands at  $1650\text{ cm}^{-1}$  and  $1640\text{ cm}^{-1}$  respectively have been assigned to  $\nu(\text{C}=\text{O})$  frequency.

Thus the lowering of  $\nu(\text{C}=\text{O})$  bands in the mixed ligand complexes as compared to free ligands, supports the coordination of C=O group to the metal atom. Such shifts of  $\nu(\text{C}=\text{O})$  to lower wave number side ( $\sim 1605\text{ cm}^{-1}$ ) have been reported by Panda and Mohapatra.<sup>14</sup>

**Table 3.** IR absorption bands of mixed ligand complexes  $[\text{Fe}(\text{L})_2(\text{L}')]$  in  $\text{cm}^{-1}$

S.No.	Complex	$\nu_{\text{C}=\text{O}}$	$\nu_{\text{C}=\text{C}}$	$\nu_{(\text{C}-\text{O})}$	$\nu_{\text{M}-\text{O}}$
1	$[\text{Fe}(2\text{-hpp})_2(\text{acac})]$	1620	1500	1350	520, 410
2	$[\text{Fe}(2\text{-hpp})_2(\text{bzac})]$	1640	1490	1380	520, 450
3	$[\text{Fe}(2\text{-hpp})_2(\text{dbzm})]$	1620	1540	1320	500, 410



Figure 2. IR Spectrum of  $[\text{Fe}(2\text{-hpp})_2(\text{dbzm})]$

### Antibacterial screening:

Antibacterial activities of 2-hydroxypropiophenone and the metal complexes have been determined against bacteria *E. coli*, *Enterococci*, *Staphylococcus aureus* and *Streptococcus pneumonia*. These were evaluated by the disc diffusion technique.<sup>15</sup> The data for the antibacterial activities of the compounds have been recorded in (Table 4). It is observed that metal chelates have higher activity than the free ligand, which can be explained on the basis of Overtone's concept<sup>16</sup> and Tweedy's chelation theory.<sup>17</sup> According to overtone's concept of cell permeability the lipid membrane that surrounds

the cell favors the passage of only lipid soluble material. Thus the liposolubility is an important factor that controls the antimicrobial activity. On chelation, the polarity of the metal ion is reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of the electrons over the whole chelate ring and enhances the lipophilicity of the complex. This increased lipophilicity enhances the penetration of the complexes into the lipid membrane and blocking of metal binding sites on the enzymes of the microorganisms.

Table 4: Zone of inhibition of mixed ligand complexes  $[\text{Fe}(\text{L})_2(\text{L}')]_{\text{in mm}}$ .

S. No	Complex	<i>E.coli</i>	<i>Entrococci</i>	<i>Staphylococcus aureus</i>	<i>Streptococcus pneumonia</i>
1	2-hydroxypropiophenone (HL)	8	12	10	6
2	$[\text{Fe}(2\text{-hpp})_2(\text{acac})]$	9	8	9	12
3	$[\text{Fe}(2\text{-hpp})_2(\text{bzac})]$	10	9	14	12
4	$[\text{Fe}(2\text{-hpp})_2(\text{dbzm})]$	16	18	16	16
5	<b>Ciprofloxacin</b>	20	22	20	20
6	<b>DMSO</b>	0	0	0	0

### Conclusions

We have successfully synthesized mixed ligand complexes of Fe(III) having an octahedral geometry. All complexes are high spin paramagnetic in nature, is assessed from magnetic moment data. In the IR spectra of the complexes, shifting of  $\nu(\text{C}=\text{O})$  to lower wave number side supports the chelation of the ligand to the metal atom and also support the absence of coordinated water molecules in the complexes. The complexes are biologically active and exhibit enhanced antibacterial activities as compared to their parent ligands, hence further study of these complexes could lead to interesting results.

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