



Synthesis and characterization of iron (iii) complexes of some 2-hydroxy-4, 5-dimethylacetophenone substituted hydrazones

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Abstract

The present paper deals with synthesis and characterization of metal complex of some novel 2-hydroxy-4,5-dimethylacetophenone substituted hydrazones. The substituted hydrazones were prepared by reacting 2-hydroxy-4,5-dimethyl acetophenone with corresponding hydrazine, Phenyl hydrazine and (2,4-dinitrophenyl)hydrazine. The Iron (III) metal complexes of general formula ML₃ with newly prepared hydrazone synthesized and characterized by several physicochemical techniques like UV, Infrared, ¹HNMR, decomposition temperature/ melting point, elemental analysis, molar conductance and magnetic susceptibility studies. The analytical data confirmed 1:3 stoichiometry of M:L and based on above analytical technique data suggest that each one Fe (III) complexes have Octahedral geometry. The conductivity data show that each one these complexes are non-electrolytes.

Keywords: transition metal complexes, hydrazone, mutagenicity, non-electrolytes, phenyl hydrazine and (2, 4-dinitrophenyl) hydrazine

Introduction

Transition metal complexes of Schiff base ligands have vital and expanded role in the expansion of coordination chemistry in biological systems since the late 19th century. A large number of Fe(III) complexes, with coordination numbers ranging from 3 to 8 are known. The most common among there is complexes with coordination number 6 have octahedral geometry and this may be measured as their characteristic coordination polyhedron.

Iron is necessary for life and a highly utilized element for all living organisms. It is involved in a extensive variety of physiological processes. Collaboration of dioxygen with iron compounds leading to different iron "oxygen complexes" plays an significant role in the active sites of a large number of iron proteins/enzymes [1-3].

The chemistry of iron is dominated by the +2 and +3 oxidation states i.e. iron (II) and iron (III) complexes e.g. Fe²⁺ and Fe³⁺ complex ions with selected ligands, generally of an octahedral shape, a few tetrahedral iron complexes are mentioned too. The reactions of the aqueous ions iron (II) and iron (III) with ammonia, caustic soda and washing soda are described and explained as are complexes of iron (III) with the chloride ion and cyanide ion.

Iron is that the most abundant element found within the surrounding nature and plays essential role for the survival of terrestrial organisms. Iron also participates in biochemical processes like ribonucleic reduction, photo synthesis, nitrogen reduction, oxygen transport, energy production, and oxygenation. Ligands are designed and functionalized in order to deliver tissue specificity for the declivity of metal toxicity and improvement of pharmacological properties. Several iron (III) complexes have been known as contrast agent for magnetic resonance imaging.

Some Fe complexes have been known for catalytic, antitumor, hypoxic selective cyatotoxins, and antimicrobial activity [4-7]. Iron and its complexes both are known for its DNA harmful property

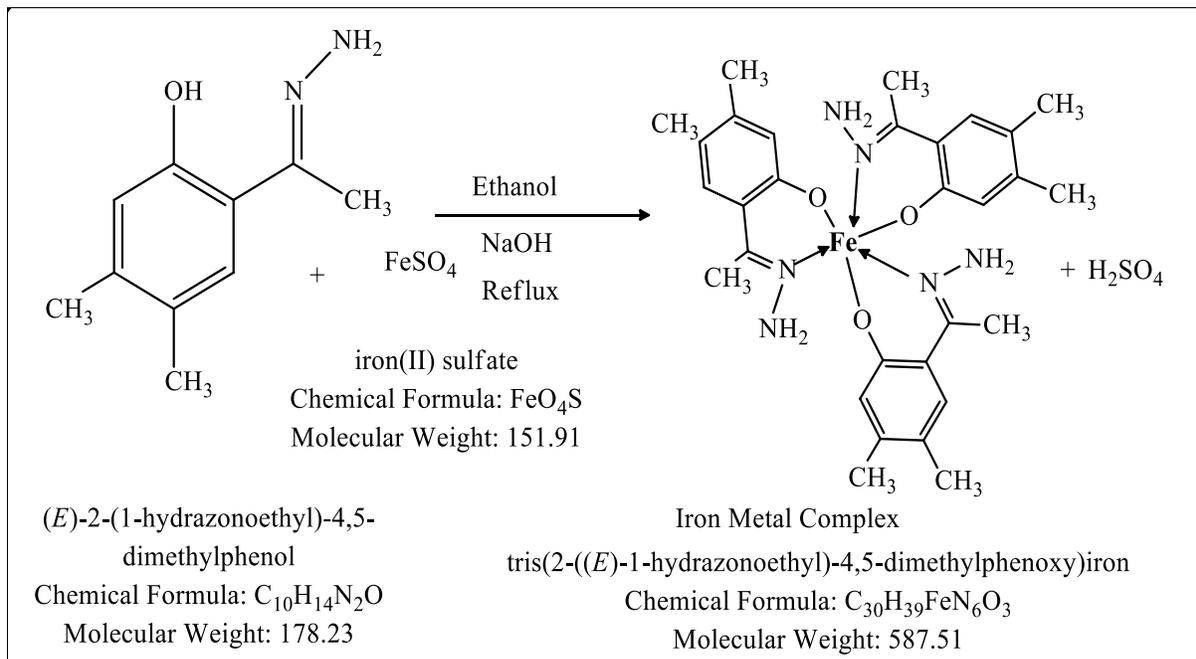
[8-9]. The developments within the field of bioinorganic chemistry have improved the attention in hydrazone complexes, because it's been known that a lot of those complexes may act as lead for biologically significant species [10-15].

Experimental

Materials: The chemicals: The chemicals 2-hydroxy-4,5-dimethylacetophenone, (E)-2-(1-hydrazonoethyl)-4,5-dimethyl phenol, (E)-4,5-dimethyl-2-(1-(2-phenylhydrazono) ethyl) phenol, (E)-2-(1-(2-(2,4-dinitrophenyl) hydrazono)ethyl)-4,5-dimethylphenol, Ferrous Sulfate, sodium hydroxide, ethanol, methanol, chloroform, DMSO, DMF etc., used in this work were of AR Grade, commercially available and used without further purification.

Preparation of Fe complex with (E)-2-(1-hydrazonoethyl)-4,5-dimethylphenol metal Complex or tris ((E)-1-hydrazonoethyl)-4,5-dimethylphenoxy)iron

(E)-2-(1-hydrazonoethyl)-4,5-dimethylphenol were synthesized following published procedure [16]. The transition metal complex tris((E)-1-hydrazonoethyl)-4,5-dimethylphenoxy)iron was prepared by dissolution of (E)-2-(1-hydrazonoethyl)-4,5-dimethylphenol ligand (0.019M) in ethanol at hot condition, an ethanolic solution (0.006M) of the Ferrous Sulfate was added drop wise with constant stirring and refluxed for 3 hrs. The resulting reaction mixture was cooled to room temperature and maintains pH 7 to 8 by addition of the 0.10N sodium hydroxide. Thus color green precipitate was formed. The resultant product was filtered, repeatedly washed with ethanol and dried at 40°C to 45°C temperature. The compound was re-crystallized in ethanol for purification and improving description. Reaction scheme preparation of tris ((E)-1-hydrazonoethyl)-4, 5-dimethylphenoxy) iron is given below Scheme 1.

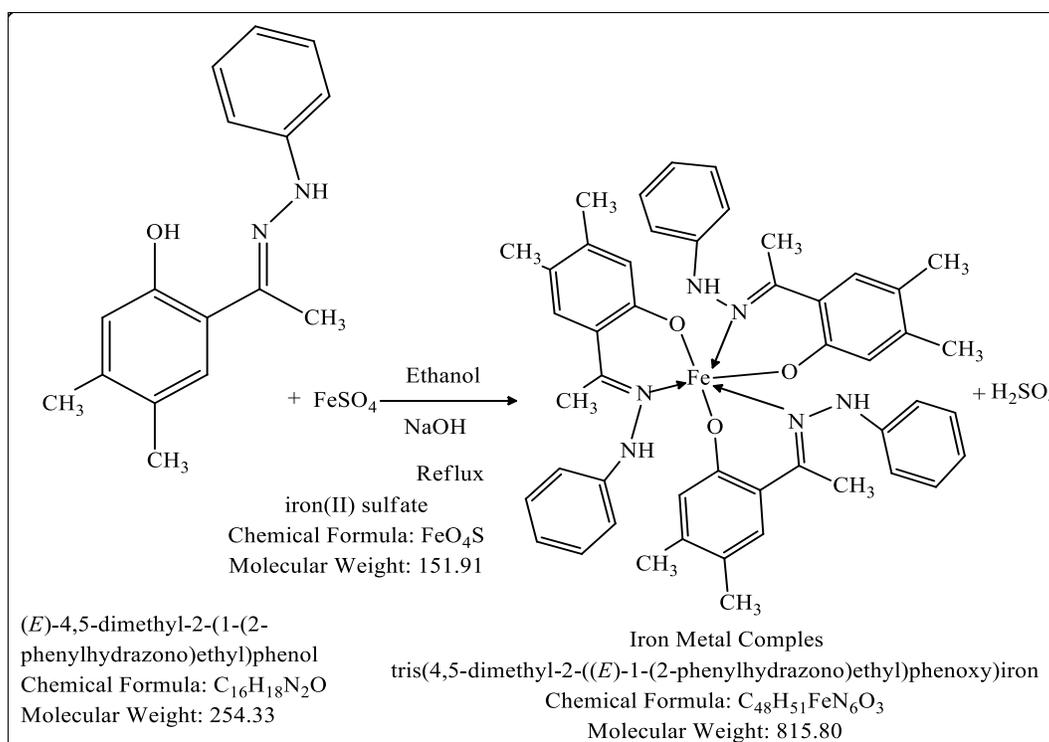


Scheme 1: Reaction scheme preparation of tris (2-((E)-1-hydrazonoethyl)-4,5-dimethyl phenoxy)iron.

Preparation of Fe complex with (E)-4,5-dimethyl-2-(1-(2-phenylhydrazono)ethyl)phenol metal complex Or tris(4,5-dimethyl-2-((E)-1-(2-phenylhydrazono)ethyl)phenoxy)iron:

(E)-4,5-dimethyl-2-(1-(2-phenylhydrazono)ethyl)phenol were synthesized following published procedure¹⁷. The transition metal complex tris(4,5-dimethyl-2-((E)-1-(2-phenylhydrazono)ethyl)phenoxy)iron was prepared by dissolution of (E)-4,5-dimethyl-2-(1-(2-phenylhydrazono)ethyl)phenol ligand (0.0103M) in ethanol at hot condition, an ethanolic solution (0.0034M) of the Ferrous Sulfate was added drop wise with

constant stirring and refluxed for 4 hrs. The resulting reaction mixture was cooled to room temperature and maintains pH 7 to 8 by addition of the 0.10 N sodium hydroxide. Thus blue color precipitate was formed. The resultant product was filtered, repeatedly washed with ethanol and dried at 50°C to 55°C temperature. The compound was re-crystallized in ethanol for purification and improving description. Reaction scheme preparation of tris (4,5-dimethyl-2-((E)-1-(2-phenylhydrazono)ethyl)phenoxy) iron is given below Scheme 2.

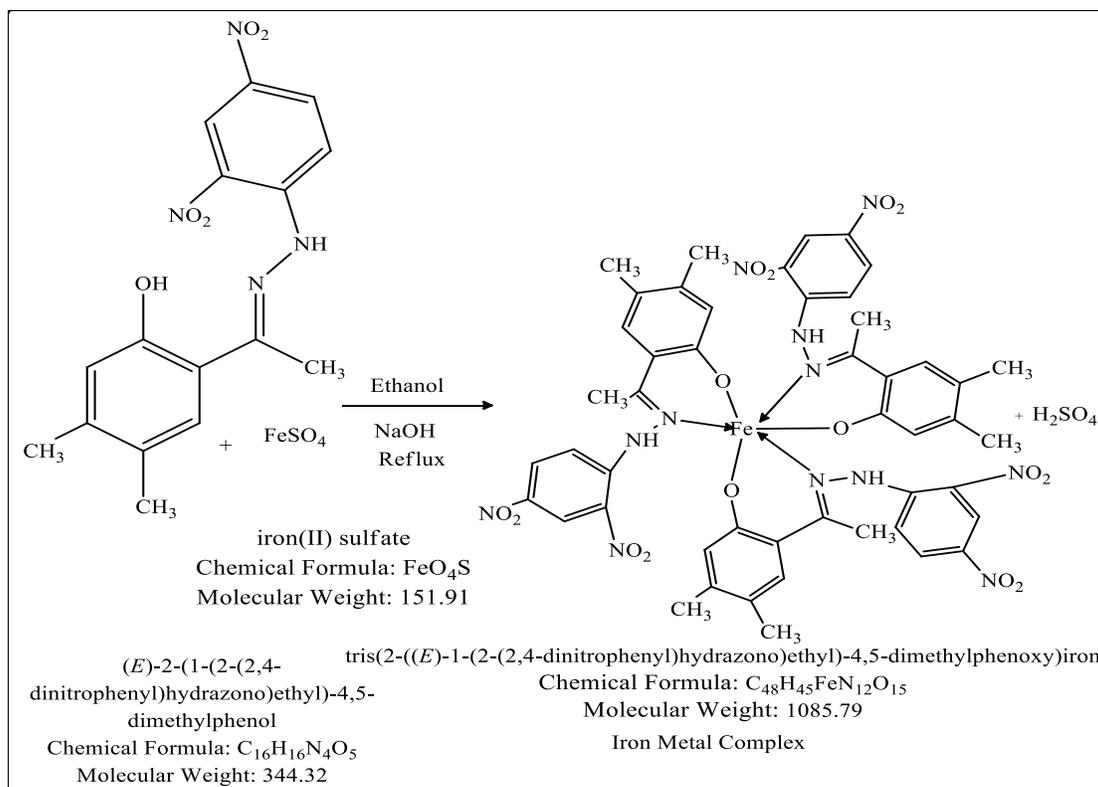


Scheme 2: Reaction scheme preparation of tris(4,5-dimethyl-2-((E)-1-(2-phenyl hydrazono)ethyl)phenoxy)iron

Preparation of Fe complex with (E)-2-(1-(2-(2,4-dinitrophenyl) hydrazono) ethyl)-4,5-dimethylphenol metal complex Or tris(2-((E)-1-(2-(2,4-dinitrophenyl) hydrazono) ethyl)-4, 5-dimethylphenoxy)iron

(E)-2-(1-(2-(2,4-dinitrophenyl)hydrazono)ethyl)-4,5-dimethylphenol were synthesized following published procedure [18]. The transition metal complex tris(2-((E)-1-(2-(2,4-dinitrophenyl) hydrazono)ethyl)-4,5-dimethylphenoxy)iron was prepared by dissolution of (E)-2-(1-(2-(2,4-dinitrophenyl)hydrazono)ethyl)-4,5-dimethylphenol ligand (0.0087M) in ethanol at hot condition, an ethanolic solution

(0.0028M) of the metal salt Ferrous Sulfate was added drop wise with constant stirring and refluxed for 5 hrs. The resulting reaction mixture was cooled to room temperature and maintains pH 7 to 8 by addition of the 0.10 N sodium hydroxide. Thus brown color precipitate was formed. The resultant product was filtered, repeatedly washed with ethanol and dried at 60°C to 65°C temperature. The compound was re-crystallized in ethanol for purification and improving description. Reaction scheme preparation of tris(2-((E)-1-(2-(2,4-dinitrophenyl) hydrazono) ethyl)-4,5-dimethylphenoxy)iron is given below Scheme 3.



Scheme 3: Reaction scheme preparation of tris(2-((E)-1-(2-(2,4-dinitrophenyl) hydrazono)ethyl)-4,5-dimethylphenoxy)iron.

Results and Discussion

The Fe-Metal complexes were analyzed by Infrared spectroscopy, Ultraviolet-visible spectroscopy, ^1H NMR, Carbon-Hydrogen-Nitrogen-Sulphur elemental analyzer, Decomposition temperature/Melting point, Molar Conductance,

Magnetic susceptibility and Iron content by Gravimetric technique. Decomposition temperature / Melting points were recorded using Veego Scientific Device (Model: VMP-AD) in open capillaries and were uncorrected. Some physical properties of Fe-Metal complexes are mentioned in Table 1.

Table 1: Physical properties

Ni-Metal Complex	Chemical Formula and Molecular formula	Color	Solubility	Decomposition Temperature	Yield
tris(2-((E)-1-hydrazonoethyl)-4,5 dimethylphenoxy)iron	$\text{C}_{30}\text{H}_{39}\text{N}_6\text{FeO}_3$ and 587.51	green	- Soluble in methanol, ethanol, Acetonitrile DMSO, DMF - Insoluble in water	> 300 °C	89.67 %
tris(4,5-dimethyl-2-((E)-1-(2-phenyl hydrazono)ethyl)phenoxy)iron	$\text{C}_{48}\text{H}_{51}\text{N}_6\text{FeO}_3$ and 815.80	blue	- Soluble in ethanol, methanol, DMSO, DMF - Insoluble in water	> 300°C	92.00 %
tris(2-((E)-1-(2-(2,4 dinitrophenyl)hydrazono)ethyl)-4,5 dimethylphenoxy)iron	$\text{C}_{48}\text{H}_{45}\text{N}_{12}\text{FeO}_{15}$ and 1085.79	brown	- Soluble in ethanol, methanol, DMSO, DMF - Insoluble in water	> 300°C	76.63%

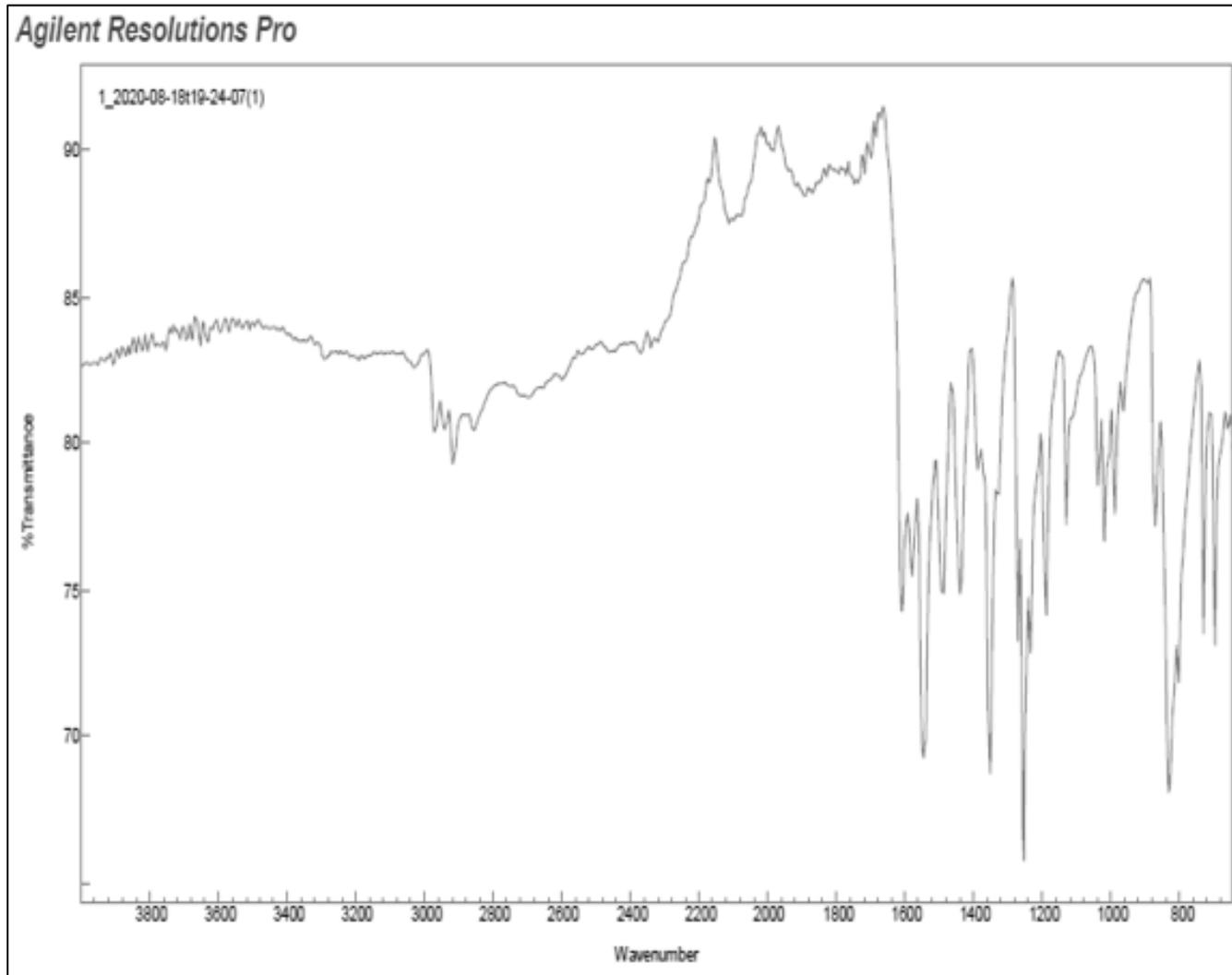
Infrared analysis

The IR spectra of Fe-Metal complexes were recorded in the region of 4000–400 cm^{-1} using FTIR spectrometer of model Agilent Resolutions Pro by direct sampling method.

The IR spectral data along with the possible assignments of Fe-Metal complexes are provided in Table 2, followed by IR spectra performed by IR direct solid method, use of Agilent Resolutions Pro and IR spectrum are showed in Figure 1, 2, 3.

Table 2: Hydrazone Iron metal complex IR frequency, cm^{-1}

Bond/functional group	frequency, cm^{-1}		
	Tris (2-((E)-1-hydrazonoethyl)-4,5-dimethyl phenoxy) iron	Tris (4,5-dimethyl-2-((E)-1-(2-phenyl hydrazono)ethyl) phenoxy) iron	Tris (2-((E)-1-(2-(2,4-dinitrophenyl) hydrazono)ethyl)-4,5-dimethyl phenoxy)iron
N-H	3218	3285	3296
C-H	3032	3098	3045
C-H stretch aromatics	2971	2918	2965
C=N	1612	1618	1614
C-C	1548	1506	1507
C=C (aromatic ring)	1494	1493	1418
N-O	---	---	1331
C-O	1257	1248	1261
N-N	1194	1142	1115
O-Fe	Below 600	Below 600	Below 600

**Fig 1:** IR of tris(2-((E)-1-hydrazonoethyl)-4,5-dimethylphenoxy)iron

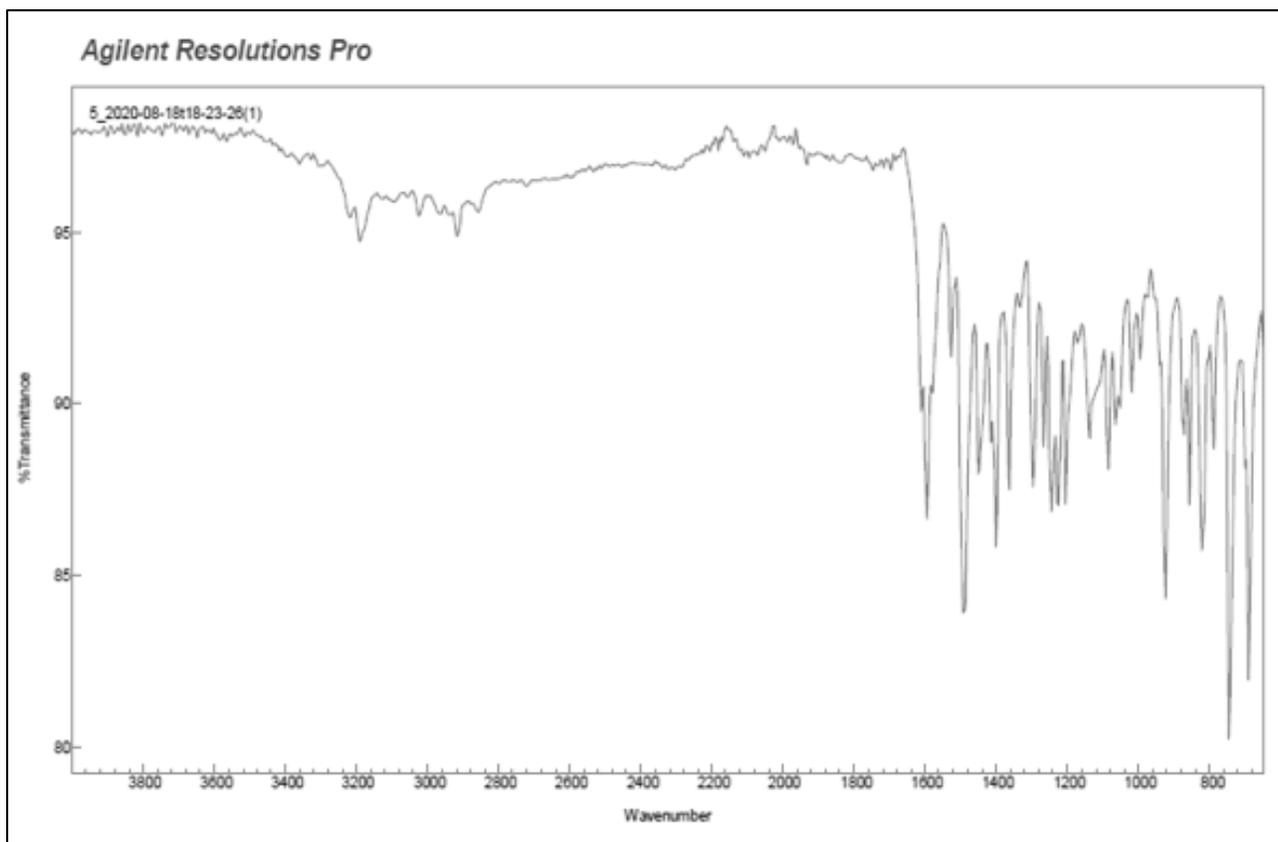


Fig 2: IR of tris (4,5-dimethyl-2-((E)-1-(2-phenylhydrazono)ethyl) phenoxy)iron

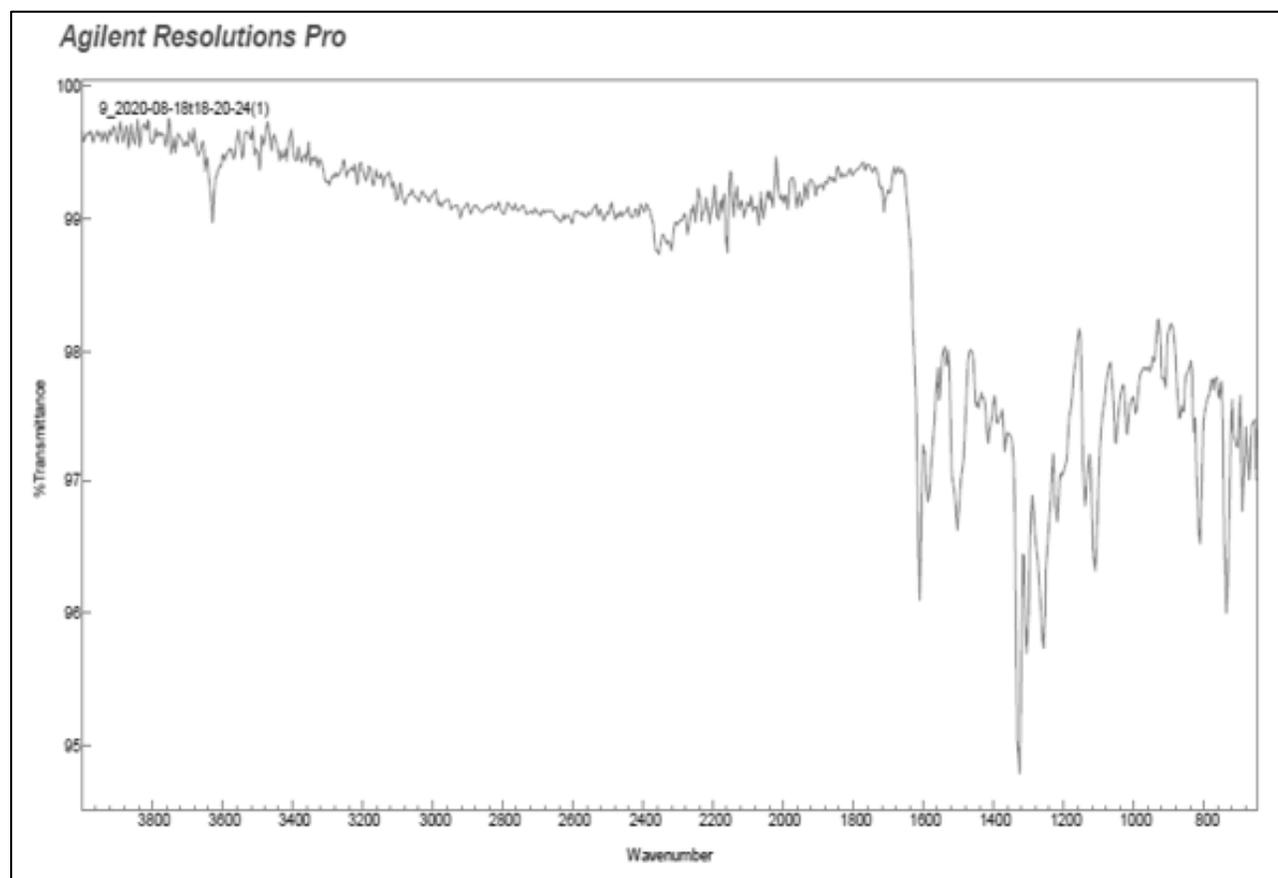


Fig 3: IR of tris (2-((E)-1-(2-(2,4-dinitrophenyl)hydrazono)ethyl)-4,5-dimethylphenoxy)iron

UV analysis

The UV spectra of the Fe-Metal complexes in methanol were recorded on SPECORD 50 PLUS-233 H 1409C Spectro photo meter, using a quartz cell of 1 cm optical path where methanol

was used as a blank. The UV spectrum is shown in Figure 4, 5, 6. The spectra shows λ (bands maximum in nm) are provided in Table 3.

Table 3: Ni-Metal Complex

	Wavelength nm
tris(2-((E)-1-hydrazonoethyl)-4,5 dimethylphenoxy)iron	254, 312,790,850
tris(4,5-dimethyl-2-((E)-1-(2 phenylhydrazono) ethyl) phenoxy) iron	281,354,718,854
tris(2-((E)-1-(2-(2,4-dinitrophenyl)hydrazono)ethyl)-4,5-dimethyl phenoxy)iron	245, 315,728,856

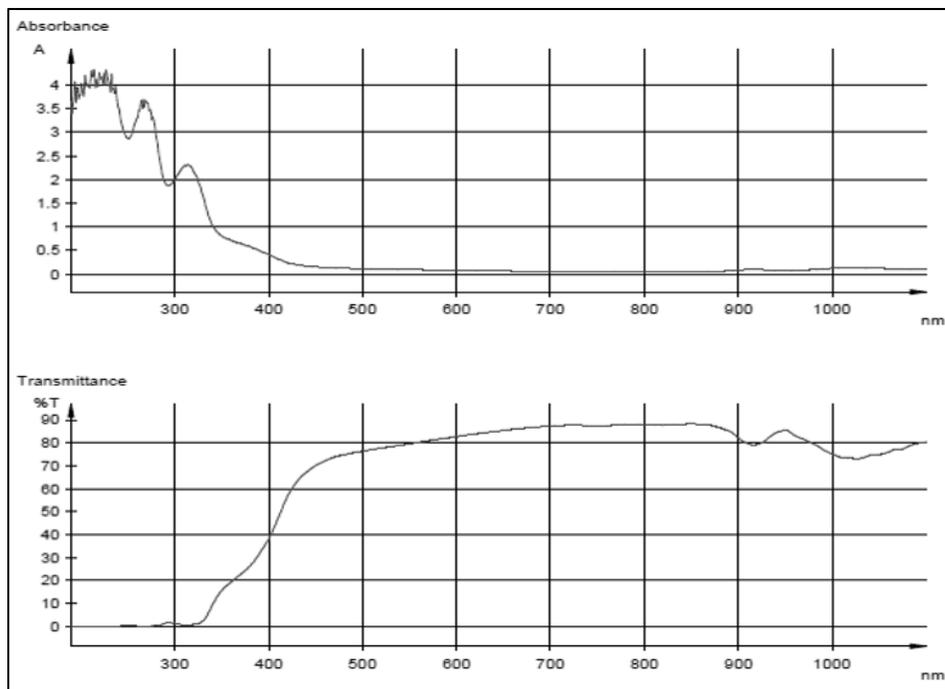


Fig 4: UV-Visible Spectra of tris(2-((E)-1-hydrazonoethyl)-4,5-dimethylphenoxy)iron

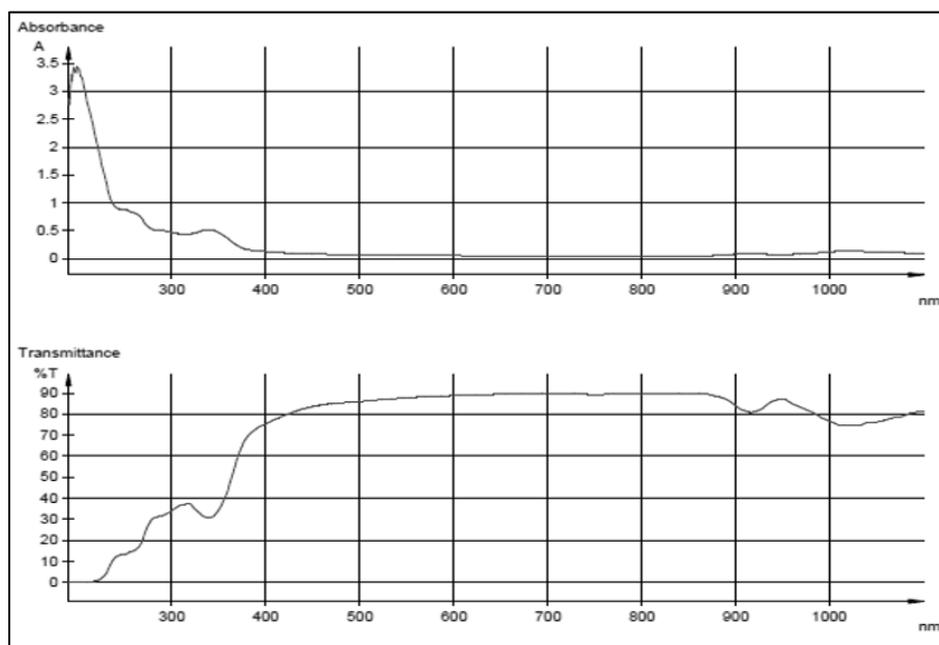


Fig 5: UV-Visible Spectra of tris(4,5-dimethyl-2-((E)-1-(2-phenylhydrazono)ethyl)phenoxy)iron

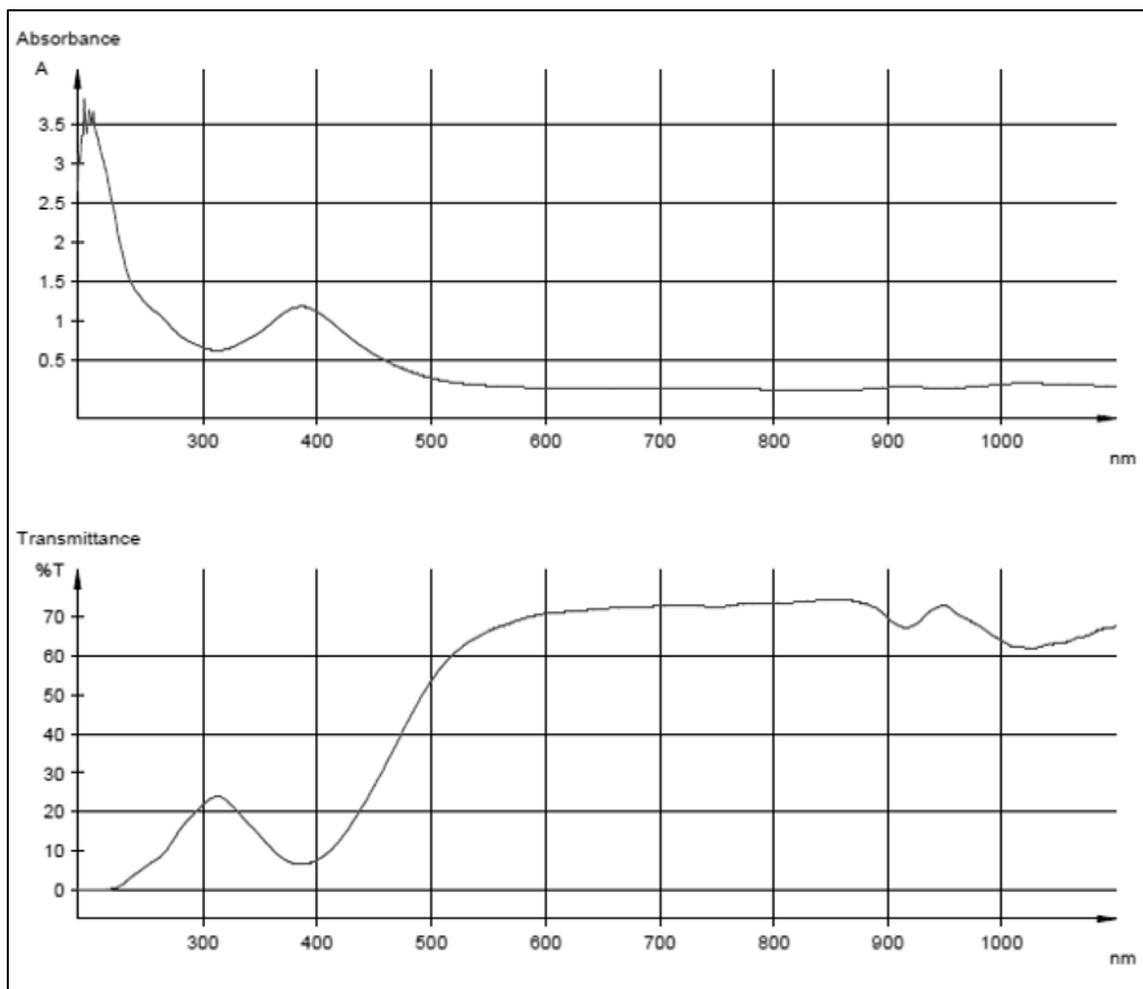


Fig 6: UV-Visible Spectra of tris(2-((E)-1-(2-(2,4-dinitrophenyl)hydrazono)ethyl)-4,5-dimethylphenoxy)iron

Elemental analysis (CHNS)

Formation of Fe-Metal complexes were further confirmed by elemental analysis which was recorded by Vario MICRO CHNS analyzer. The elemental analysis data of Cu-Metal complexes and Cu is confirmed by Gravimetric technique is summarized in Table 4.

Magnetic susceptibility

The magnetic moment (μ_{eff}) values at room temperature for Fe (III) complexes complexes was in the range of 4.5 to 5.3 B.M. These values are expected for Octahedral geometry of Fe (III) complexes at room temperature and further supported by electronic spectral data is summarized in Table 5.

Table 5: Magnetic susceptibility

Fe-Metal complex	μ_{eff} value
tris(2-((E)-1-hydrazoneethyl)-4,5-dimethylphenoxy)iron	4.77
tris(4,5-dimethyl-2-((E)-1-(2-phenylhydrazono)ethyl)phenoxy)iron	4.98
tris(2-((E)-1-(2-(2,4-dinitrophenyl)hydrazono)ethyl)-4,5-dimethyl phenoxy)iron	5.06

Molar Conductance ($\text{mho.cm}^2.\text{mol}^{-1}$)

The molar conductance values at room temperature were measured in Methanol (10^{-3} M) on an Elico digital direct reading conductivity meter model CM-180 is summarized in Table 6.

Table 6: Molar Conductance

Fe-Metal complex	Molar Conductance $\text{mhos cm}^2 \text{mol}^{-1}$
tris(2-((E)-1-hydrazoneethyl)-4,5 dimethyl phenoxy) iron	0.090
tris(4,5-dimethyl-2-((E)-1-(2-phenylhydrazono)ethyl)phenoxy)iron	0.099
tris(2-((E)-1-(2-(2,4-dinitrophenyl) hydrazono)ethyl)-4,5-dimethyl phenoxy)iron	0.097

3.6 ^1H NMR

We tried all Fe-complex ^1H NMR and observe the spectrum of the complex differs from that of the free ligand in the following aspects:

1. Resolution is very poor due to the low solubility of Fe-Metal complexes in DMSO.
2. The disappearance of the signal due to the imine group, is attributed to its involvement in coordinating the Iron ion ^[19].

3. The spectrum displays a multiple signal at δ (6.58–7.63 ppm) assigned to aromatic ring protons.

The ^1H NMR Spectra of metal complexes are shown in Figure 7, 8, 9.

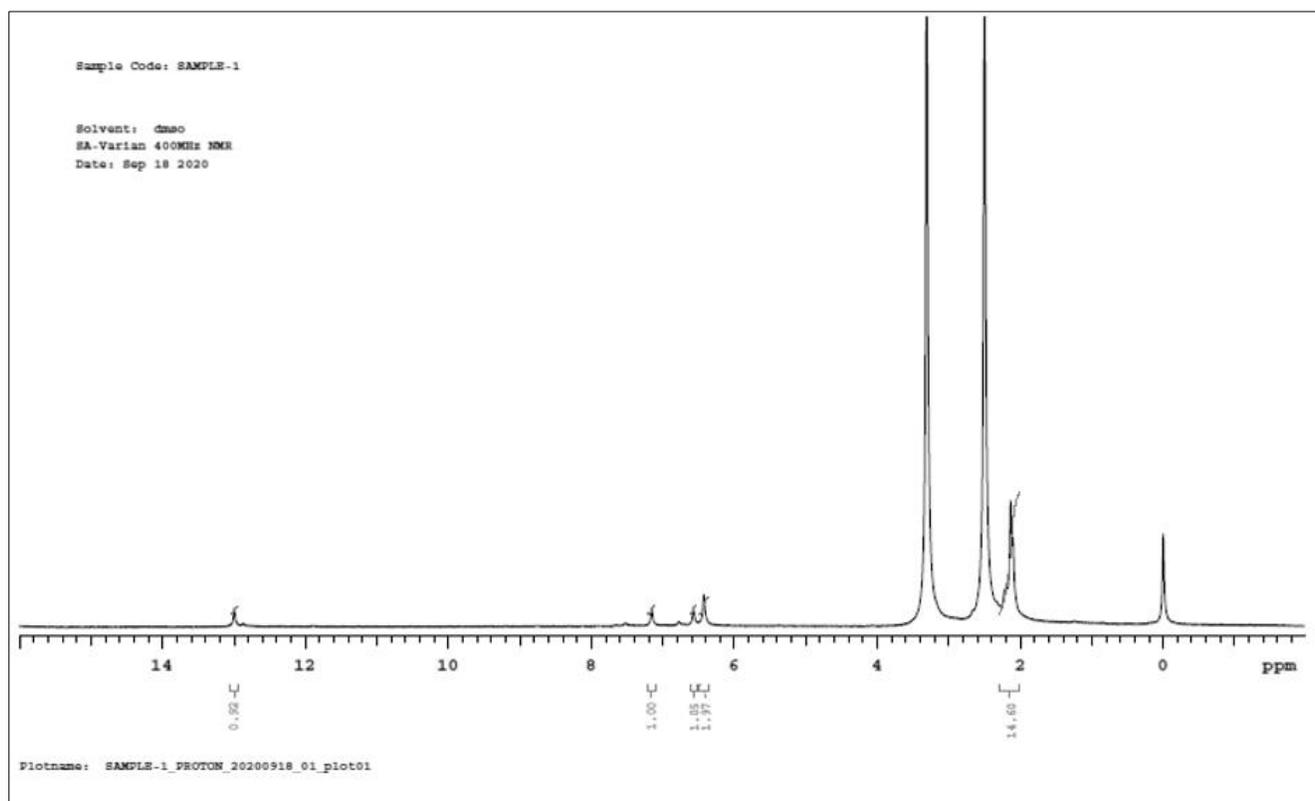


Fig 7: ^1H NMR of tris(2-((E)-1-hydrazoneethyl)-4,5-dimethylphenoxy)iron

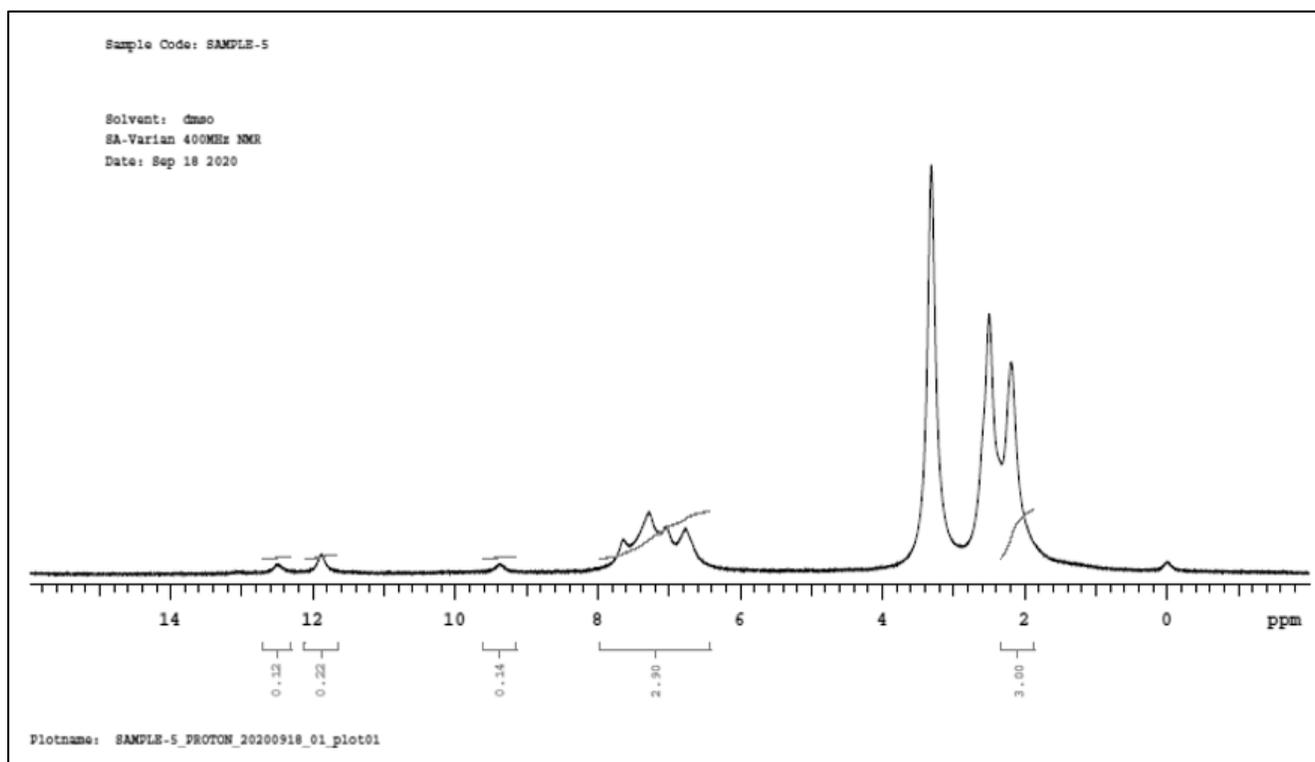


Fig 8: ^1H NMR of tris(4,5-dimethyl-2-((E)-1-(2-phenylhydrazone)ethyl)phenoxy)iron.

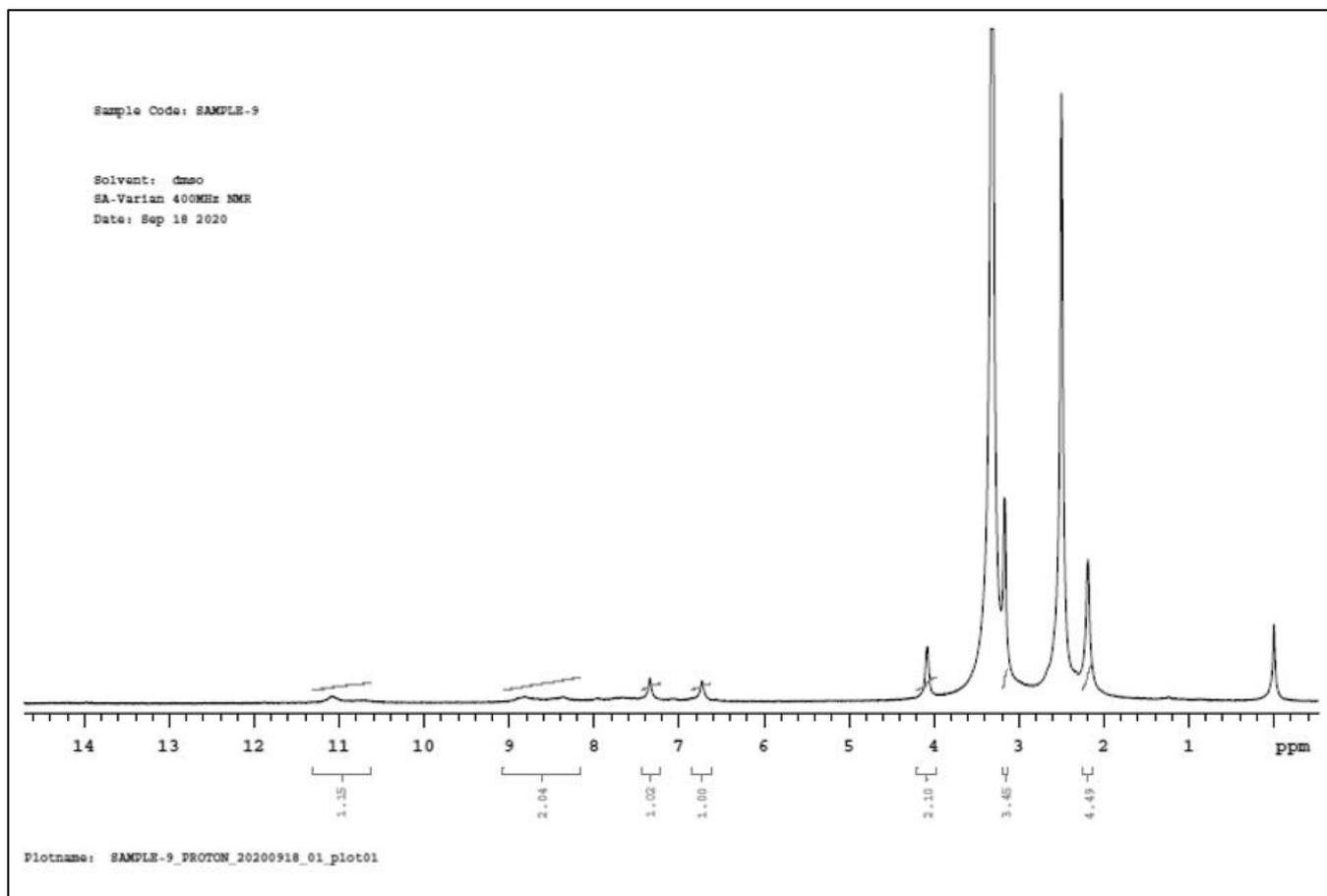


Fig 9: ^1H NMR of tris (2-((E)-1-(2-(2,4-dinitrophenyl)hydrazono)ethyl)-4,5-dimethyl phenoxy) iron

Conclusion

All Fe complexes are characterized by elemental analysis, IR, UV Visible spectrophotometer, ^1H NMR, Molar Conductance and Magnetic susceptibility measurement, gravimetric analysis. Based on above results it suggests the Octahedral geometry for the Fe (III) complexes and the conductivity data show that each one these complexes are non-electrolytes.

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