Coordination polymer/ Metal acetylacetonate

M. Sc. Chemistry 4th Sem (402-I / Unit-V)
Ph. D. Course Work -Section-II/U-1

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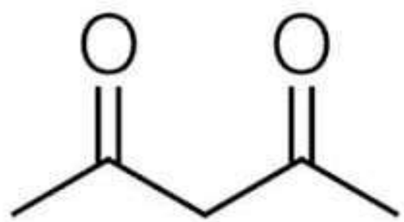
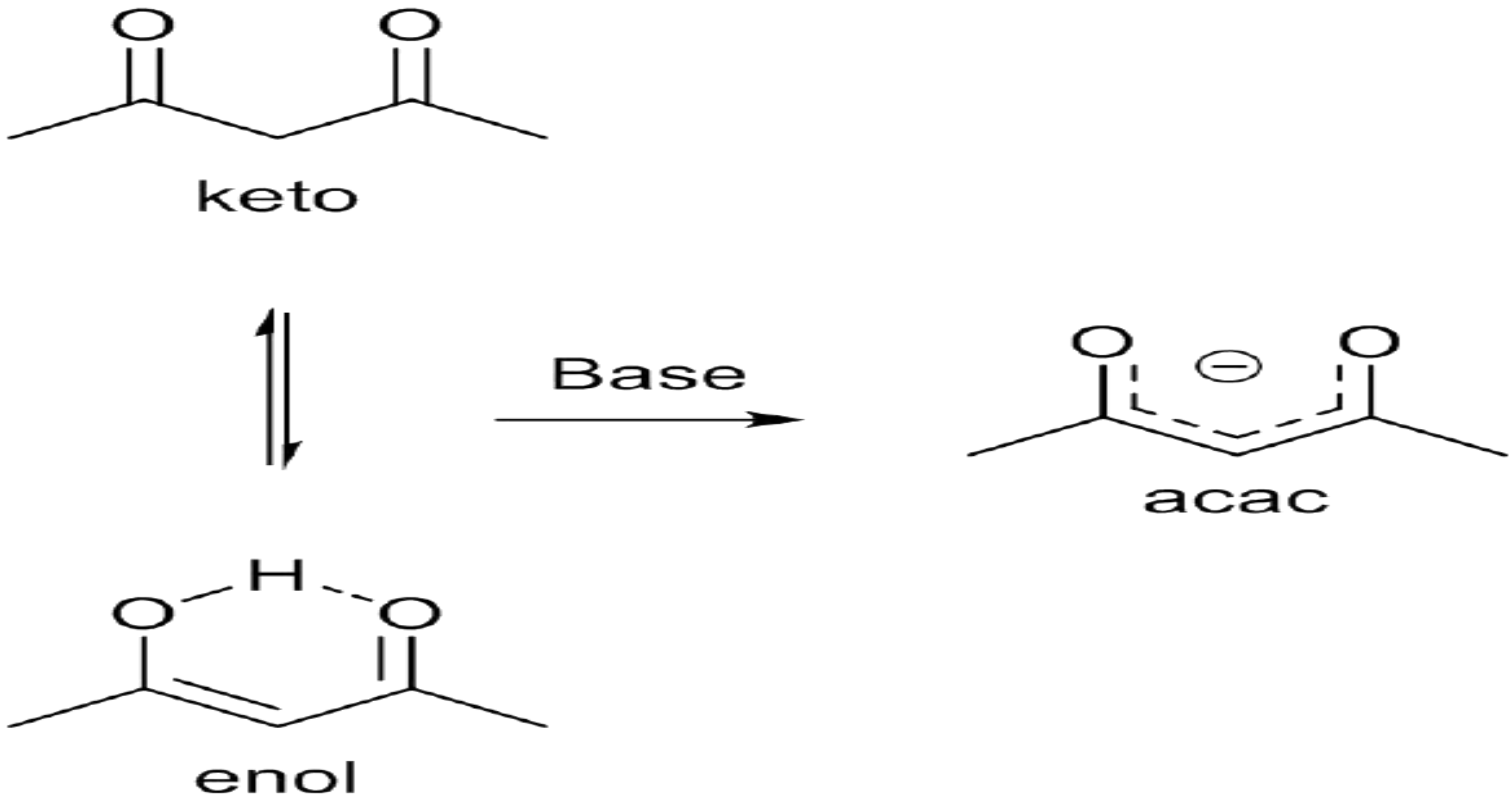
Coordination polymer/Metal acetylacetonate

Metal cetylacetonates are coordinationcomplexes derived from the acetylacetonateanion($CH_3COHCHCOCH_2^-$) and metal ions, usually transition metals. The acetylacetonate act as bidentate ligand & is abbreviated by acac$^-$.



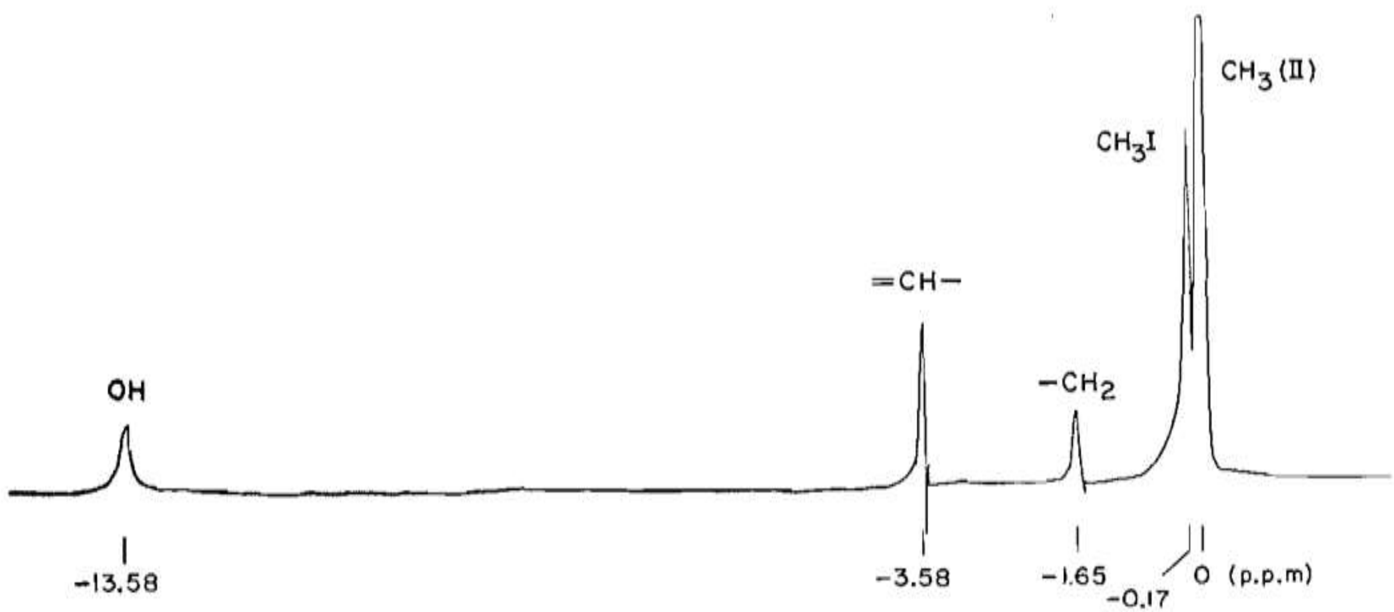
Here acac- ion contains 2-O atoms which have lone pair of electrons & it exists tautomers keto & enol forms.



But enol form is more stable. It is due to lone pair of enol oxygen can delocalize across the 5 atoms to the electro negative carbonyl gr. & hence enol form is good bidentate ligand then keto form.

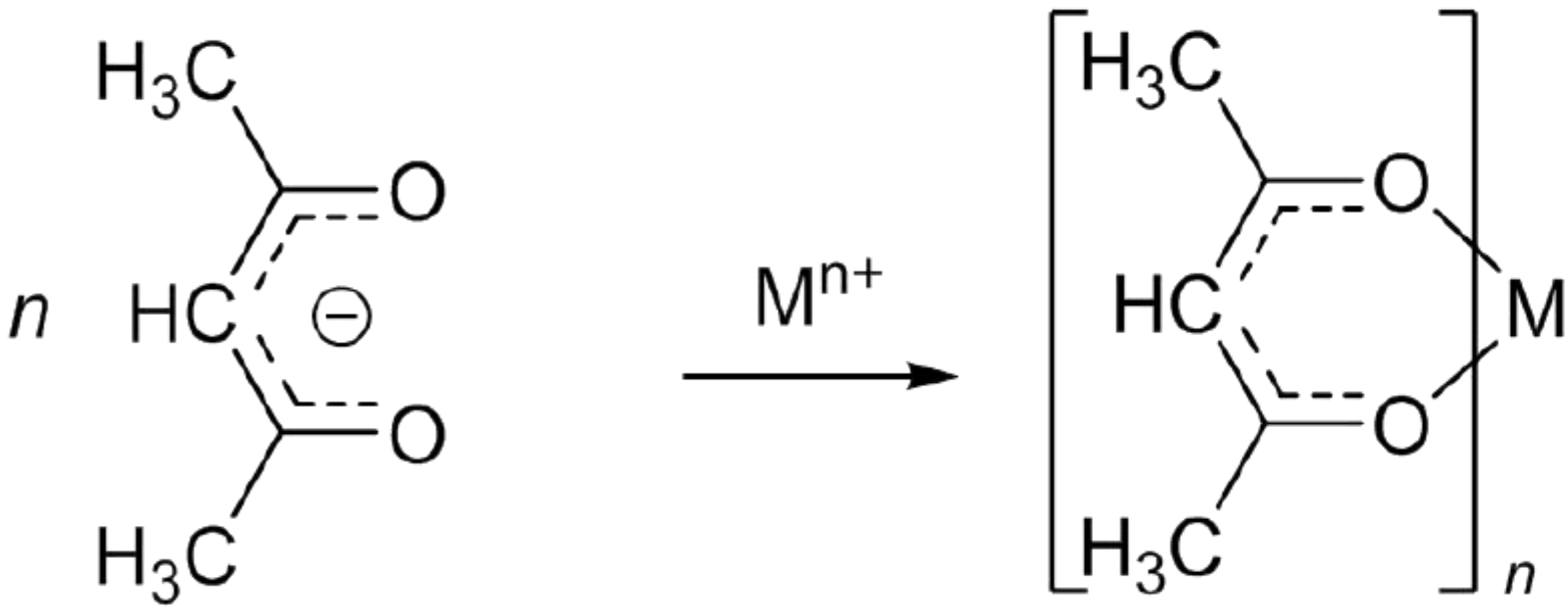
Both keto & enol form of acac can be distinguished by NMR spectra. Keto form gives to peaks due to two types of environment of H (CH_3 & CH_2).

But enol form gives four types of spectral peak due to four different types of environment CH_3, CH_3, CH & OH while an equilibrium state it gives 5 peaks due to 5 different environment present in $acac^-$



Proton resonance spectrum of pure acetylacetone at 40 Mc./s. Chemical shifts are shown in p.p.m. Reading from left to right (low field to high field) the signal assignment is respectively: enol OH group, enol =CH— group, keto —CH_2— group, keto CH_3 groups, and enol CH_3 groups.

The $acac^-$ anion can act as a ligand towards metal ions, typically forming a bidentate complex where the metal is bound to the two oxygen atoms, thus forming a 6-membered ring. Metal $acac^-$ compounds are typically isolated as crystalline solids that are neutral, hence an M^{n+} metal forms a complex with *n* $acac^-$ ligands.



Preparation & properties of important metal acetylacetonate complexes.

3 mL acetylacetone and 40 mL distilled water followed by 8 mL of dilute (5 mol L^{-1}) ammonia solution are taken in a conical flask. Dissolve aluminium sulphate $[Al(SO_4)_3 \cdot 16\ H_2O]$ in 30 mL distilled water. To this solution, add the ammoniacal acetylacetone solution gradually with stirring. After complete addition of acetylacetone, check that the solution is neutral. If the solution is still acidic, add further small portions of ammonia solution. Place the flask in an ice bath until a cream coloured precipitate forms. Filter the product using Buchner filtration, wash with small amounts of cold distilled water and dry the product in a vacuum desiccator.

Co^{3+} Complex

2.5 g of cobalt carbonate and 20 mL of acetylacetone are heated to 90°C with stirring. While heating, add dropwise 30 mL of a 10% hydrogen peroxide solution, covering the flask with a watch glass between additions. The complete addition of hydrogen peroxide should take around 30 minutes. Continue to heat for a further 15 minutes, followed by cooling in an ice bath. The dark green precipitate is filtered.

$$CoCO_3 + 2\,CH_3COCH_2COCH_3 \longrightarrow CO_2 + H_2O + Co(CH_3COCHCOCH_3)_2$$

$$2\,Co^{2+} + H_2O_2 \longrightarrow 2\,Co^{3+} + 2\,OH^-$$

$$2\,CoCO_3 + H_2O_2 + 15\,CH_3COCH_2COCH_3 \longrightarrow 2\,CO_2 + 4\,H_2O + 2\,Co(CH_3COCHCOCH_3)_3$$

The H-NMR spectrum of $Co(acac)_3$ has sharp resonances much like the aluminium complex. From this it can be determined that the complex is diamagnetic. Octahedral Co(III) -$3d^6$ have two possible electron configurations, high spin or low spin. The high spin complex has 4 unpaired electrons in t_{2g}^4 & e_g^2 and would therefore be paramagnetic.

The low spin complex has no unpaired electron in t_{2g}^6 which is diamagnetic, thus the cobalt complex adopts a low spin configuration.

Mn^{3+} Complex

Dissolve 2.6 g of manganese chloride ($MnCl_2 \cdot 4\,H_2O$) and 6.8 g of sodium acetate in 100 mL of distilled water and add 10 mL acetylacetone. Dissolve 0.52 g of potassium permanganate ($KMnO_4$) in 25 mL of distilled water and add to the acetylacetonate solution, with stirring, over a period of about 10 minutes. After stirring for 10 minutes, add a solution of sodium acetate (6.3 g) in 25 mL distilled water, with stirring, over a period of about 10 minutes. Continue stirring and heat the flask on a hot plate to 60-70°C.

$$Mn^{2+} + 2\,CH_3COCH_2COCH_3 \longrightarrow 2\,H^+ + Mn(CH_3COCHCOCH_3)_2$$

$$Mn(VII) + 4\,Mn(II) \longrightarrow 5\,Mn(III)$$

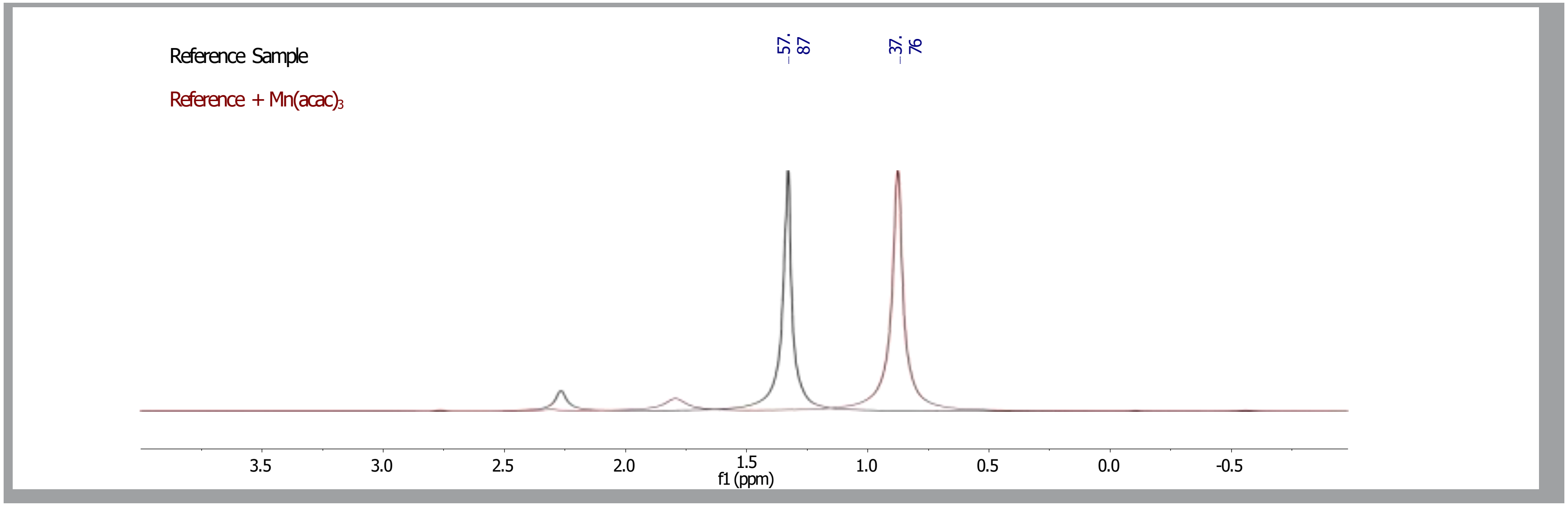
Overall: $$5\,Mn^{2+} + MnO_4^- + 15\,CH_3COCH_2COCH_3 \longrightarrow 7\,H^+ + 4\,H_2O + 5\,Mn(CH_3COCHCOCH_3)_3$$

Manganese chloride

Potassium permanganate

Tris(acetylacetonato)manganese

Evans method is used to determine the magnetic moment and therefore electronic structure of $Mn(acac)_3$.

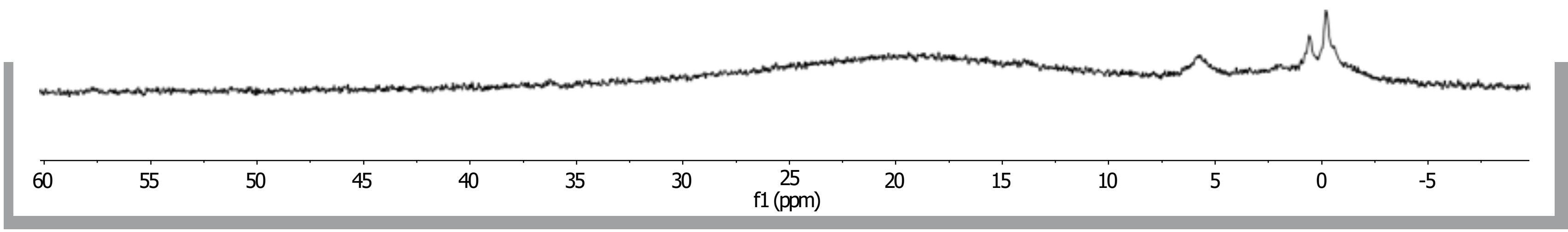


H-NMR spectrum of the reference sample (black) and the reference with $Mn(acac)_3$ (red) overlaid. The peaks are labelled in Hz.

Iron(II) chloride

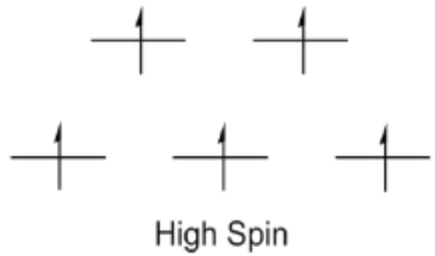
Tris(acetylacetonato)iron

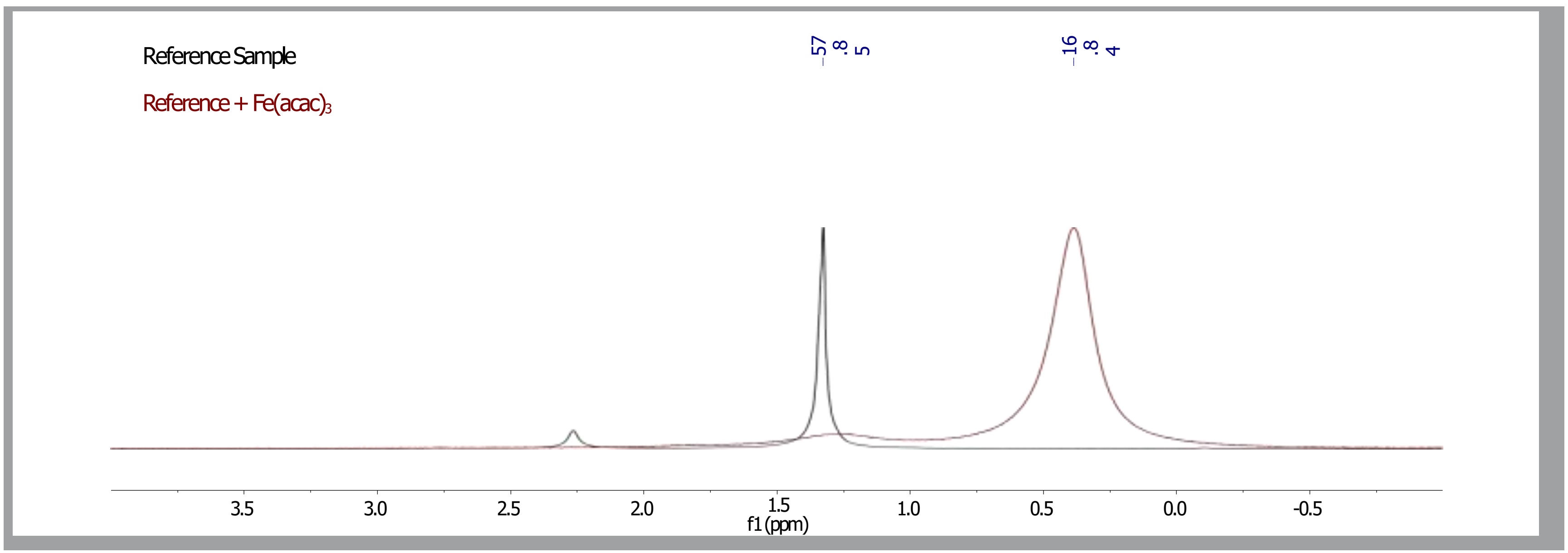
Recrystallise a small sample from warm methanol. The resulting red crystals should be filtered using Buchner filtration, rinsed with small portions of cold methanol and dried in a vacuum desiccator. H-NMR spectrum of the product which is paramagnetic in nature.



^{1}H-NMR spectrum of $Fe(acac)_3$.

Like the manganese complex, the ^{1}H-NMR spectrum of $Fe(acac)_3$ contains broad, downfield resonances, suggesting that the complex is paramagnetic. Octahedral Fe(III) centres have two possible electron configurations, high spin or low spin . Fe(III) is d^5, thus both configurations have unpaired electrons and would therefore be paramagnetic.





^{1}H-NMR spectrum of the reference sample (black) and the reference with $Fe(acac)_3$ (red) overlaid. The peaks are labelled in Hz.

References & further reading

S & Atkins, Oxford Inorganic Chemistry, Fourth Edition
Alagappa university, M. Sc. Chemistry
Pearson, Inorganic chemistry
Fmiza Hammer Synthesis & reaction of organometallic compound

Thanks For Watching!