

Synthesis and characteristics of Dodeca-carbonyl tri-iron as metallic carbonyl cluster $[\text{Fe}_3(\text{CO})_{12}]$

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Abstract : This Tri iron dodecacarbonyl is organo iron compound with the formula $\text{Fe}_3(\text{CO})_{12}$. It is mono nuclear carbonyl. It is an important starting material in preparative iron Carbonyl chemistry. It is dark green solid that sublimes under vacuum. It is soluble in non-polar organic solvent to give intensely green solutions. Most low nuclearity clusters are pale yellow or orange hot solution of $\text{Fe}_3(\text{CO})_{12}$ decomposes to an iron mirror which can be pyrophoric in air. CO stretching frequencies are important in characterization of carbonyl-containing compound relatively intense and sensitive to bonding and charge vibration.

Keywords - Triron dodecacarbonyl, Non-polar organic solvent pyrophoric carbonyl cluster, Vibrational spectra.

I. INTRODUCTION

Carbon monoxide possesses a unique property of unsaturation by virtue of which it may combine with a large number of metals under suitable conditions. Such compounds of carbon monoxide with metals are termed as Carbonyls. In carbonyls carbon atom can donate its lone pair to transition metal atom (M) forming $\text{OC} \rightarrow \text{M}$ co-ordinate bond. The compound formed by the combination of co-molecule with transition metals also known as metallic carbonyls. In metallic carbonyl co molecules act neutral ligands.

Carbonyl ligand displays a variety of bonding modes in their metal complexes such as terminal and bridging. Due to large number of bonding modes, the structural determination of metal carbonyl complexes is extremely important. The structure of metal carbonyls are determined with the help of various spectroscopic and diffraction studies such as X-ray diffraction, infrared spectroscopy and electron diffraction studies. Mononuclear metal carbonyls have only linear $\text{M}-\text{C} \equiv \text{O}$ linkage.

The terminal and bridging carbonyl groups can be distinguished with the help of IR spectroscopy. The terminal carbonyl group exhibits absorption in the range $1850-2125 \text{ cm}^{-1}$ while bridging carbonyl group does so in the range $1700-1850 \text{ cm}^{-1}$. The shape of metal carbonyl depends upon the nature of hybridisation on central metal. Metal carbonyls are inner orbital complexes and most of them follow 18-electron rule with few exceptions.

II. SYNTHESIS

It can be occasionally obtained from the thermolysis of $\text{Fe}(\text{CO})_5$.

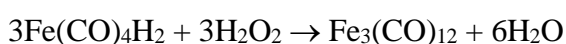


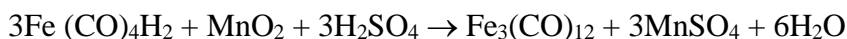
Traces of the compound are easily detected because of its characteristic deep green colour. U.V. photolysis of $\text{Fe}(\text{CO})_5$ produces $\text{Fe}_2(\text{CO})_9$ not $\text{Fe}_3(\text{CO})_{12}$.

(ii) It can be usually prepared by heating toluene solution of $\text{Fe}_2(\text{CO})_9$ to 700°C and then cooling the solution.



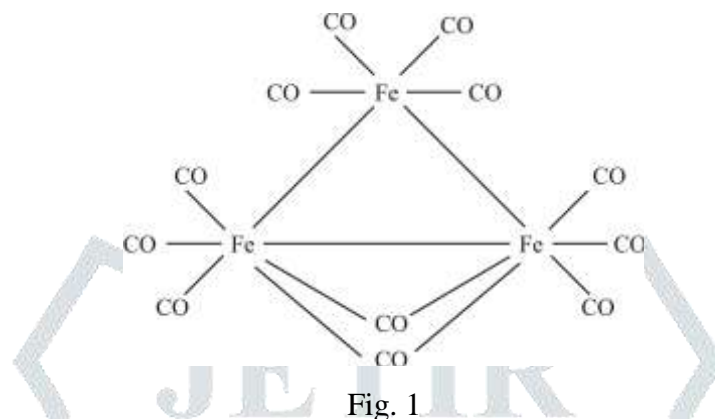
(iii) It can be also obtained by the oxidation of iron carbonyl hydride by hydroperoxide or MnO_2





III. STRUCTURE

The structure of $\text{Fe}_3(\text{CO})_{12}$ has been a matter of its structure by X-ray crystallography retained elusive until 1966 because of a persistent dis-order problem. This dilemma concerning the structure of $\text{Fe}_3(\text{CO})_{12}$ was resolved. When the X-ray diffraction study was completed in 1966. Unambiguously demonstrating that $\text{Fe}_3(\text{CO})_{12}$ has structure in Fig.1 with an isosceles triangular arrangement of iron atoms and only two of the 12-carbonyl group in bridging position.



In Fig. (1) each of the two Fe- atom is linked with three terminal carbonyl groups, two bridging carbonyl groups. The remaining the third Fe-atom is linked with four terminal carbonyl groups and to each of the two Fe atoms. Three Fe-Fe bonds are also present Fe-Fe bond distance has been found to be equal to 2.8\AA .



The anion $[\text{HFe}_3(\text{CO})_{11}]^-$ is structurally related to $\text{Fe}_3(\text{CO})_{12}$.

It is red violet anion ($\lambda_{\text{max}} = 540 \text{ nm}$). It may be prepared by the following methods.

- Oxidation of an alkaline solution of $\text{HFe}_3(\text{CO})_4$.
- Reaction of $\text{Fe}(\text{CO})_5$ with an appropriate base such as aqueous triethylamine at 80°C .
- Ultraviolet irradiation of $\text{HFe}(\text{CO})_4$ with $\text{Fe}(\text{CO})_5$ X-ray diffraction of triethyl ammonium salt $[(\text{C}_2\text{H}_5)_3\text{NH}] [\text{HFe}_3(\text{CO})_{11}]^-$ indicates structure in Fig. II $[\text{H}_3\text{Fe}_3(\text{CO})_{11}]^-$ anion.

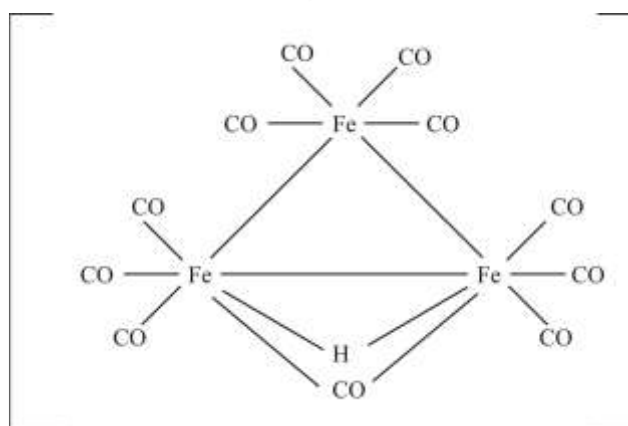
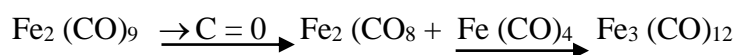


Fig. II

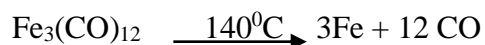
Hydride replacing one bridging co ligand.

When we compare the structure of $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$ we find that structure of $\text{Fe}_3(\text{CO})_{12}$ can be obtained by replacing bridging carbonyl group ($>\text{C}=\text{O}$) present in $\text{Fe}_2(\text{CO})_9$ by $\text{Fe}(\text{CO})_4$.

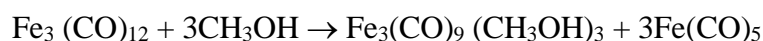
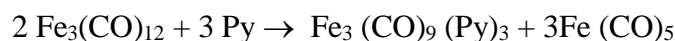


IV. PROPERTIES

- (i) Soluble in organic solvents like toluene, alcohol ether and pyridine.
- (ii) When heated to 140°C $\text{Fe}_3(\text{CO})_{12}$ decomposes to give metallic iron and co.



(iii) Like most metal carbonyls, $\text{Fe}_3(\text{CO})_{12}$ undergoes substitution reactions. These reactions occurs with pyridine and methyl alcohol.



- (iv) Action of No -

At 85°C it reaction with No + O from iron dicarbonyl dinitrosyl $\text{Fe}(\text{CO})_2(\text{NO})_2$.



V. CONCLUSION

Similar to iron analogous, Ruthenium and Osmium complexes are useful starting material for the preparation of many other metal carbonyl derivatives. However the metal-metal bonds appeared to be much stronger than those in iron triangles $\text{Fe}_3(\text{CO})_{12}$.

$\text{Fe}_3(\text{CO})_{12}$ is hazardous as a source of volatile iron and as a source of carbon monoxide solid samples especially when finally divided and residues from reactions can be pyrophoric which can ignite the organic solvents used for such reactions.

Metal carbonyls are toxic by skin contact inhalation, or ingestion in part because of their ability to carbonylate haemoglobin to give carboxy hemoglobin which prevent the binding of oxygen.

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