Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (Third Year)
Subject : Chemistry
Paper Code : CHC 109
Paper Title : Inorganic Chemistry(Section A)
Module Name : Polynuclear metal carbonyl : Preparation and Structures of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$
Module No : 09
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Notes:

Polynuclear metal carbonyl:

Iron Ennea carbonyl $Fe_2(CO)_9$

Preparation and Structure

It is prepared by dissolving iron pentacarbonyl in glacial acetic acid and the solution is exposed to UV radiation for six hours. On cooling with water, golden yellow crystals of ennea carbonyl precipitates. These are then separated by filtration.

$$Fe(CO)_5 \xrightleftharpoons{\text{UV, 6 h}} Fe_2(CO)_9 + CO$$

On heating to 50° C it decomposed to give $Fe_3(CO)_{12}$

$$3Fe_2(CO)_9 \longrightarrow 3Fe(CO)_5 + Fe_3(CO)_{12}$$

X-ray diffraction and IR spectra have shown the presence of two types of carbonyl groups in $Fe_2(CO)_{12}$

Terminal CO groups as observed in mononuclear carbonyls.

Briedge Co groups which bridge the two Fe atoms.

Out of the total nine CO groups, six are terminal CO groups and three are bridge CO groups. The terminal Co groups are attached to the Fe atoms by normal σ - dative bonds. But the bridge CO groups form two single covalent bonds with the two metal atoms. There is also one Fe - Fe bond with a bond distance of 2.46 A°. This distance is same as in the metallic Iron. Due to this Fe-Fe bond there is absence of unpaired electron and the molecule is diamagnetic. Even though some π - bonding is believed to be there the following structure of $Fe_2(CO)_9$ is without π – bonding.

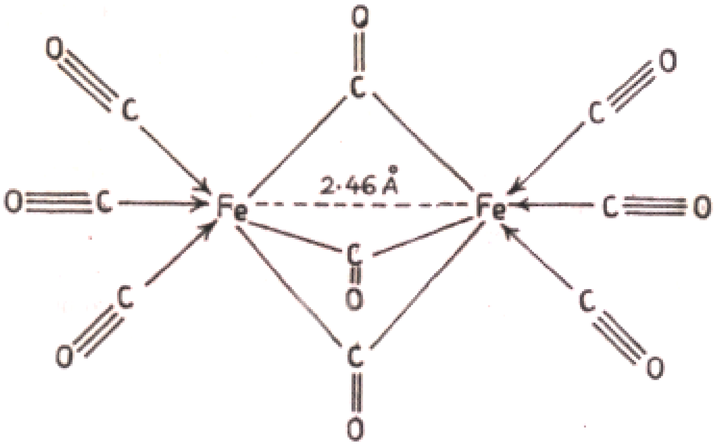

Fig. 8.6. Structure of $Fe_2(CO)_9$

The geometry of the molecule is, two distorted octahedra having one face in common. The terminal CO groups are found at the free corners of the octahedra, while the bridging carbonyl groups are at the corners of the common face.

Iron Didecacarbonyl $Fe_3(CO)_{12}$

Preparation and Structures of $Fe_3(CO)_{12}$

i. It is obtained by the disproportionation of $Fe_2(CO)_9$

dissolved in toluene at 70° C. On cooling green crystals of $Fe_3(CO)_{12}$ gets separated.

$$3Fe_2(CO)_9 \longrightarrow 3Fe(CO)_5 + Fe_3(CO)_{12}$$

ii. It is also prepared by the oxidation of iron carbonyl hydride with manganese dioxide or hydrogen peroxide

$$3Fe(CO)_4H_2 + 3MnO_2 + 3H_2SO_4 \longrightarrow Fe_3(CO)_{12} + 3MnSO_4 + 6H_2O$$

$3Fe(CO)_4H_2 + 3H_2O_2 \longrightarrow Fe_3(CO)_{12} + 6H_2O$

The structure of $Fe_3(CO)_{12}$ has been established on the basis of X-ray analysis, Mossbauer spectra and IR spectra. The three Fe atoms nearly form equilateral triangle but one of the Fe atoms is bonded only by Fe-Fe bond and it has no attachment with bridging carbonyl groups. $Fe_3(CO)_{12}$ is believed to be formed by substitution of one of the bridging CO groups in $Fe_2(CO)_9$ by cis-$Fe(CO)_4$ group.

In all three polynuclear carbonyls, in addition to x-ray crystal structure determination, the presence of bridging CO group is established on the basis of IR spectra. The CO stretching frequencies for terminal CO groups are found in the 1900 – 2050 cm^{-1} region, while those for the bridging CO groups are found at lower frequencies(1800 to 1900 cm^{-1})

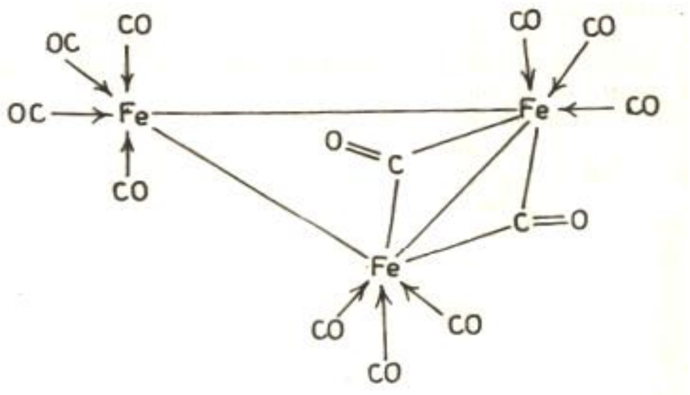

Fig. 8.7. Structure of $Fe_3(CO)_{12}$

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