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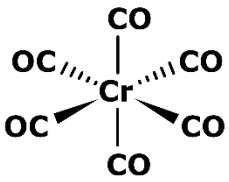
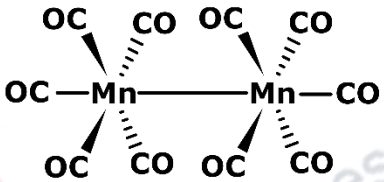
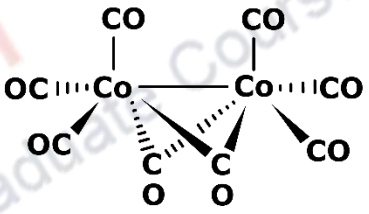
1. Learning Outcomes

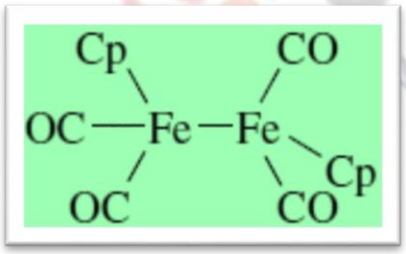
After studying this module, you shall be able to know about

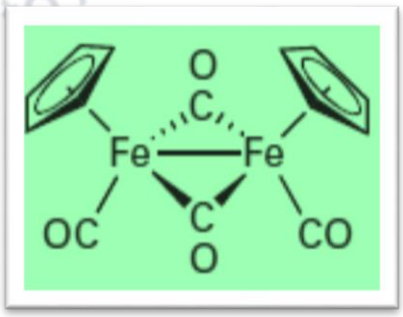
- Metal cluster compounds.
- Metal carbonyl cluster compounds.
- Dinuclear and polynuclear metal carbonyls.
- Structure of polynuclear metal carbonyls.

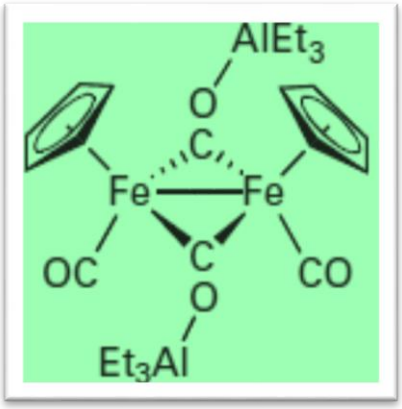
2. Introduction

A large number of mono-, di- and polynuclear metal carbonyls are known in the literature. These are the organometallic metal complexes containing either only carbonyl ligands or a mixture of carbonyl and other ligands. Metal carbonyl complexes are useful precursors for various other organometallic compounds and are applied in organic synthesis as catalysts. The binuclear metal carbonyls are formed by elements having odd number of valence electrons. Due to odd number of valence electrons, these complexes dimerize and form metal-metal bonds where each metal-metal bond increases the electron count on the metals by one. See structures below:

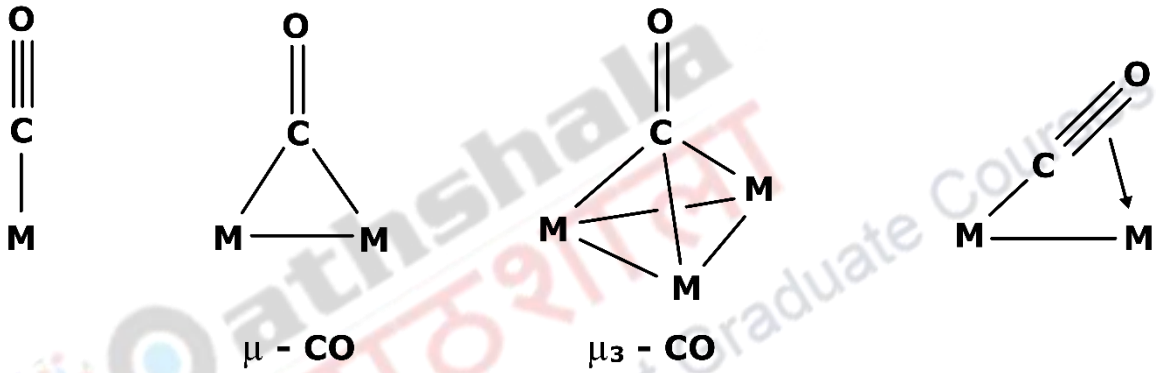
Group	formula		Valence electrons	Structure
6	$Cr(CO)_6$	Cr	6	
		6(CO)	12	
		Total	18	
7	$Mn_2(CO)_{10}$	Mn	7	
		5(CO)	10	
		M—M	1	
		Total	18	
9	$Co_2(CO)_{18}$	Co	9	
		4(Co)	8	
		M—M	1	
		Total	18	





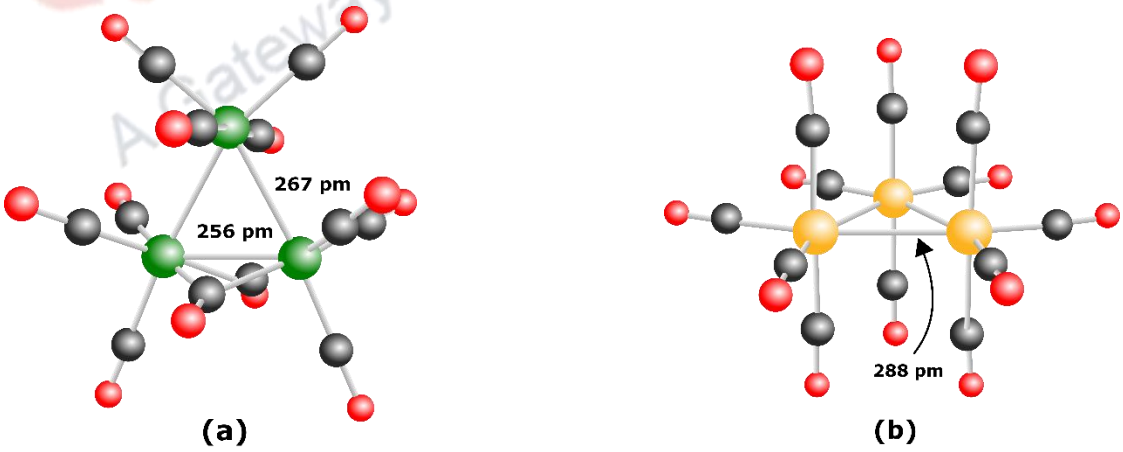


Simple metal carbonyls have well defined and symmetrical shapes. Thus hexa-carbonyls are octahedral, penta-carbonyls are trigonal bipyramidal, tetra-carbonyls are tetrahedral and decacarbonyl complexes have two square pyramidal groups joined by a metal-metal bond. On the other hand, bridging carbonyls possess one or more carbonyl ligands shared between two or more metal atoms in a polynuclear metal complex. Various types of bonding modes of carbonyl ligands in its metal complexes are

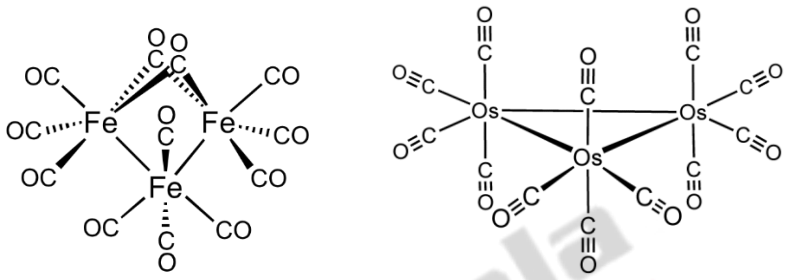


μ - CO μ3 - CO

Polynuclear metal carbonyls complexes are the carbonyl complexes consisting of more than two metal ions in them.



Or

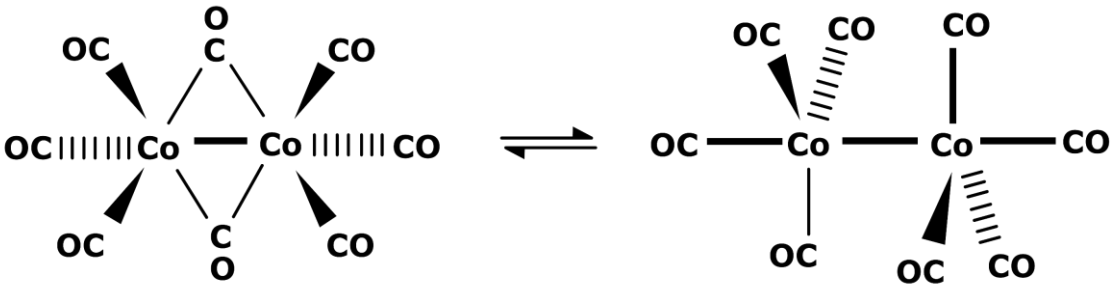


(a) (b)

Polynulear metal carbonyls (a) $Fe_3(CO)_{12}$ and (b) $Os_3(CO)_{12}$

3. Transition metal based dinuclear metal carbonyls

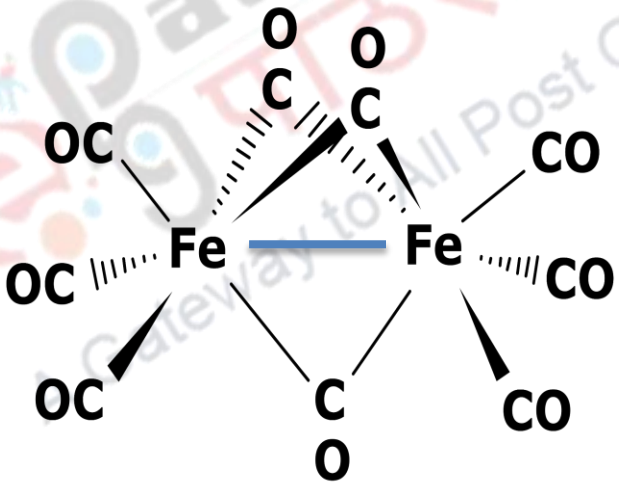
Most of the mononuclear metal carbonyl complexes obey 18-electron rule and are stable, except $V(CO)_6$ which has 17-electrons and on theoretical grounds, has the ability to undergo dimerization by forming a V-V bond. However, the dimerization is not favourable due to steric reasons. Few of the dimeric carbonyl complexes are $Co_2(CO)_8$, $Fe_2(CO)_9$, $M_2(CO)_{10}$ (where M = Mn, Tc and Re and M-M bond distances are 290, 303 and 304 pm respectively). In the IR spectrum of $Co_2(CO)_8$ in hexane, bands belonging to only terminal carbonyls are observed whereas in the solid state IR spectrum, the bands belonging to terminal and bridging CO ligands are seen. This indicates that there is equilibrium in the two types of structures of the complex as shown below:



C_{2v} symmetry (solid state) ***D_{3d} symmetry (in solution)***

Co-Co bond distance: **254 pm** **270 pm**

The $Fe_2(CO)_9$ molecule consists of two octahedron sharing a triangular face containing three bridging carbonyl groups. The coordination number of Fe atom in $Fe_2(CO)_9$ is 7 rather than 6 where each Fe atom is attached to three terminal carbonyl groups, three bridging carbonyls and one other Fe atom.



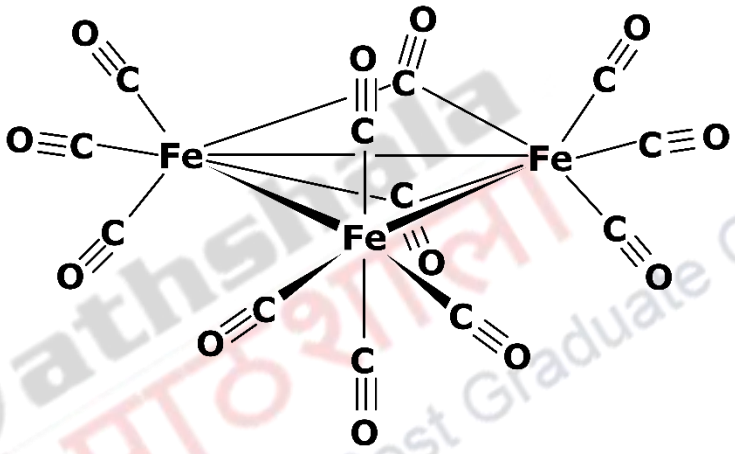
Fe-Fe bond distance: 246 pm

4. Poynuclear metal carbonyls

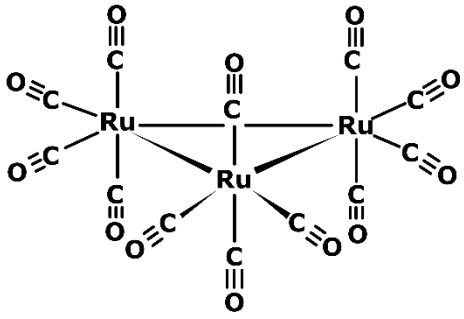
Iron, ruthenium and osmium of group 8 of the periodic table form trinuclear metal carbonyls of the type $M_3(CO)_{12}$. For example, $Fe_3(CO)_{12}$ has been described by using X-

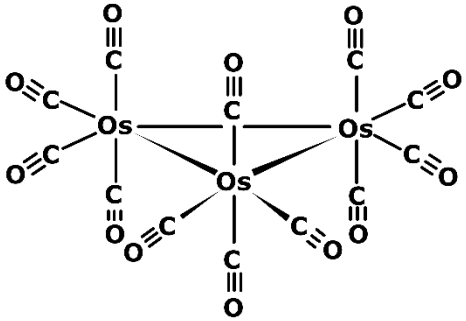
ray diffraction and IR absorption studies. The Fe–Fe atoms are linked together by a Fe–Fe covalent bond with bond length equals to 280 pm. Each of the two Fe atoms is attached to three terminal carbonyl groups and two bridging carbonyl groups. These two Fe atoms are attached to a third Fe atom by covalent bond. The third Fe atom is attached

to four terminal carbonyl groups and no bridging carbonyl group.



$Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ have triangular planar arrangement of three metal atoms which are held together by three M–M bonds. Each metal atom is attached to four terminal carbonyl groups and no bridging carbonyl group.





The Ru-Ru and Os-Os bond lengths are pm and 2.87-2.88 pm respectively

The $Os_3(CO)_{12}$ molecule has approximately D_{3h} symmetry. In $Ru_3(CO)_{12}$ molecule, the average Ru-CO(axial) bond distance is 189 pm whereas the average Ru-CO(equitorial) bond distance is 193 pm.

5. Summary

- Cluster compounds contain metal-metal single or multiple bonds and form rings or linear chains. Apart from containing σ and π bonds, cluster complexes also display δ bonds.
- Metal cluster compounds are formed by almost all the metal atoms, metal clusters consisting of transition metals are known in large numbers. These metal-metal bonds containing complexes can be homo-nuclear, i.e. consisting of one type of metal atoms, and hetero-nuclear which consist of two or more types of metal atoms.
- Dinuclear metal carbonyls are generally formed by Co, Re, Mn, Tc and Fe.
- Polynuclear metal carbonyls are formed by Fe, Ru, Os and Rh.