

**ORGANOMETALLICS,
BIOINORGANIC CHEMISTRY,
POLYNUCLEAR HYDROCARBONS
AND UV, IR SPECTROSCOPY****VOL.****1****ORGANOMETALLICS AND
BIOINORGANIC CHEMISTRY**

BLOCK 1**COMPOUNDS OF 3d METALS****3**

BLOCK 2**BIOINORGANIC CHEMISTRY****69**

ORGANOMETALLICS, BIOINORGANIC CHEMISTRY, POLYNUCLEAR HYDROCARBONS AND UV, IR SPECTROSCOPY

This is the elective course of Chemistry in the B.Sc. General programme being offered under CBCS Scheme. The theory course (BCHET-147) has a credit-weightage worth of 4 credits. This course contains two parts, i.e., Part A and Part B. Both of them have a weightage of two credits each. Part A is devoted to the content related to organometallics and bioinorganic chemistry. Part B contains the content related to polynuclear hydrocarbons and UV, IR spectroscopy. These sections have seven units each and you are expected to devote equal time to both these parts.

The first two blocks of Part A deal with organometallics and bioinorganic chemistry.

Block 1 on compounds of 3d metals has four units. In this block you will study about various common inorganic reagents and then you will be introduced to organometallic compounds. The last two units of this block are on metal carbonyl compounds.

Block 2 on 'Bioinorganic Chemistry' has three units. In this block you will study about the metals and biological system, followed by transport of metals and the role of magnesium ion in chlorophyll. The last unit of this block is on the role of iron in oxygen transport.

Block 3 on 'methylene, polynuclear aromatic and heteroaromatic compounds' has three units. It deals with methylene, polynuclear aromatic and heteroaromatic compounds.

Block 4 on 'applications of spectroscopy to simple organic molecules' has four units and deals with ultraviolet-visible spectroscopy and then with the help of it how to identify small organic compounds, specially those with conjugated dienes. The last two units of this block is on IR spectroscopy and how it helps in the determination of the structure of simple organic molecules.

This course is being offered as the elective course.

You are expected to spend a total of about 120 hours for completing this course. This is the average time which is to be spent by a learner on studying the course material, doing self-assessment questions as well as terminal questions given in the blocks and the assignment, attending counseling sessions, watching the audio-video programmes and participating in IRC/ teleconferencing sessions related to this course.

We hope you will find this course quite interesting to study. Our best wishes.

Expected Learning Outcomes

After studying this course, you should be able to

- ❖ understand the preparation, IUPAC nomenclature and important properties of some inorganic reagents;
- ❖ define and classify organometallic compounds along with the concept of hapticity;
- ❖ understand EAN Rule and 18 Electron Rule as applied to carbonyls along with their preparations ;

- ❖ describe the structure of metal carbonyls and explain synergic effects;
- ❖ understand the importance of bioinorganic chemistry;
- ❖ describe the sodium-potassium pump and understand the role of magnesium ions in chlorophyll;
- ❖ describe the salient features of hemoglobin and myoglobin;
- ❖ define active methylene compounds and give their examples,
- ❖ write the IUPAC name of ethyl acetoacetate and explain the keto-enol tautomerism in it,
- ❖ discuss the preparation of ethyl acetoacetate and outline the synthesis of some organic compounds using ethyl acetoacetate;
- ❖ classify the types of polycyclic hydrocarbon and heterocyclic compounds;
- ❖ give IUPAC names of derivatives of polynuclear hydrocarbons and heterocyclic compounds;
- ❖ discuss the different method for preparation and reactions of polynuclear hydrocarbons and heterocyclic compounds;
- ❖ explain electromagnetic radiations and its wave nature;
- ❖ explain using diagrams the $n - \pi^*$, $n - \sigma^*$, $\sigma - \sigma^*$, and $\pi - \pi^*$ transitions;
- ❖ define chromophore, auxochrome, hypsochromic and bathochromic effects, hyperchromic and hypochromic effects in electronic spectra;
- ❖ understand the applications of Electronic Spectroscopy and Woodward rules to predict the absorption maximum for α , β –unsaturated compounds;
- ❖ understand the range of IR Radiation as well as that of the Fingerprint Region;
- ❖ discuss the different types of molecular vibrations; and
- ❖ gain knowledge about the characteristic frequencies of functional groups;

**ORGANOMETALLICS,
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POLYNUCLEAR HYDROCARBONS
AND UV, IR SPECTROSCOPY**

Block

1**COMPOUNDS OF 3d METALS**

UNIT 1**Inorganic reagents 9**

UNIT 2**Organometallic Compounds 23**

UNIT 3**Metal Carbonyl Compounds-I 35**

UNIT 4**Metal Carbonyl Compounds-II 55**

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BLOCK-1: COMPOUNDS OF 3d METALS

This is the elective course of chemistry in the CBCS programme. In this block you will study about methylene, polynuclear aromatic and heteroaromatic compounds. This block has three Units.

Unit 1 deals with the various common inorganic reagents. The preparation, IUPAC nomenclature and important properties of them also discussed.

In unit 2 the definition and classification of organometallic compounds along with the concept of hapticity have been discussed also the structures of some important organometallic compounds have been discussed in detail.

In the unit 3 introduction to the metal carbonyl compounds have been done. The 18 Electron Rule as applied to carbonyls have been discussed alongwith the EAN Rule. The preparation, structure and properties have also been discussed.

Unit 4 is the last unit of this block where the synergic effects along with the MO diagram of carbon monoxide and use of IR stretching frequency data for its evidence have been included here.

Expected Learning Outcomes

After studying this block, you will be able to

- ❖ identify the oxidation states displayed by chromium, manganese, iron, cobalt, nickel and copper;
- ❖ understand the preparation, IUPAC nomenclature and important properties of some inorganic reagents;
- ❖ define and classify organometallic compounds;
- ❖ understand the concept of hapticity;
- ❖ describe the structures of methyl lithium, Zeise's salt, Ferrocene;
- ❖ understand EAN Rule and 18 Electron Rule as applied to carbonyls;
- ❖ describe the preparation of metal carbonyls through direct combination and reductive carbonylation;
- ❖ understand the structure of metal carbonyls based on Valence Bond approach;
- ❖ describe the properties of mononuclear and polynuclear carbonyl of 3d metals;
- ❖ understand bonding, π -acceptor behaviour of carbon monoxide with reference to MO diagram of CO;
- ❖ explain synergic effects; and
- ❖ understand the use of IR stretching frequency data(as evidence for synergic effect).

UNIT 1

INORGANIC REAGENTS

Structure

1.1	Introduction	Properties of Some Inorganic Reagents
	Expected Learning Outcomes	
1.2	Oxidation States Displayed by Cr, Mn, Fe, Co, Ni and Cu	1.4 Summary
		1.5 Terminal Questions
1.3	Preparation, IUPAC Nomenclature and Important	1.6 Answers

1.1 INTRODUCTION

This is the first unit of this block and you will learn about various common inorganic reagents. Most of these reagents involve transition metals and initially you will be introduced to the oxidation states displayed by chromium, manganese, iron, cobalt, nickel and copper. Thereafter you will be learning about the preparation, IUPAC nomenclature and important properties of some inorganic reagents. In the next unit you are going to learn about the organometallic compounds.

Expected Learning Outcomes

After studying this unit you should be able to:

- ❖ identify the oxidation states displayed by chromium, manganese, iron, cobalt, nickel and copper; and
- ❖ understand the preparation, IUPAC nomenclature and important properties of some inorganic reagents.

1.2 OXIDATION STATES DISPLAYED BY Cr, Mn, Fe, Co, Ni AND Cu

The oxidation states displayed by chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni) and copper (Cu) are going to be discussed in this section. Refer to Table 1.7 and 1.8 of BCHCT 137 where you can see the

oxidation triangles for these elements. The oxidation states of Cr, Mn, Fe, Co, Ni and Cu are listed in Table 1.1. In Unit 1 of BCHCT 137 you have learnt that, the oxidation states shown by the transition elements may be related to their electronic structures which have been already discussed in section 1.2 of that unit. Recalling the electronic configuration of the transition elements we remember that Cr and Cu have additional stability when the *d* orbitals are exactly half filled or completely filled.

If you look at Table 1.1 then you will notice that there is a reduced tendency of display of higher states as we move from left to right. This could be due to steady increase in the effective nuclear charge along the series thus pulling the *d* orbitals into the electron core and not making them readily available for bonding.

Let us first look at chromium (Cr). We have seen that chromium in +6 oxidation state as in K_2CrO_4 is a good oxidizing agent forming Cr^{3+} as the reduction product. This means that in many instances $\text{Cr}(+3)$ is more stable than $\text{Cr}(+6)$.

$\text{M}^{2+}(\text{aq})$ ions are known for most of the metals and $\text{M}^{3+}(\text{aq})$ ions is stable for iron (Fe). However, in the case of iron, $\text{Fe}^{2+}(\text{aq})$ is less stable than $\text{Fe}^{3+}(\text{aq})$ because of the extra stability associated with half-filled (d^5) orbitals in the case of $\text{Fe}^{3+}(\text{aq})$. In the case of Cr, by using the single *s* electron for bonding, we get an oxidation state of (+1): hence by using varying numbers of *d* electrons oxidation states of (+2), (+3), (+4), (+5) and (+6) are possible. Mn has oxidation states (+2), (+3), (+4), (+5) (+6) and (+7). In case of the elements of the first transition series the lowest oxidation state displayed is the number of *s* electrons and the highest oxidation state is the number of *s* and *d* electrons.

The highest oxidation states are often stabilized in the oxides, fluorides and oxoanion compounds, e.g., MnO_4^- , CrO_4^{2-} etc. In these compounds O^{2-} and F^- are difficult to be oxidized by the central metal because oxygen and fluorine are strong oxidizing agents.

TABLE 1.1: Oxidation states of Cr, Mn, Fe, Co, Ni and Cu
(the most common oxidation states are in bold type)

Cr	Mn	Fe	Co	Ni	Cu
+2	+2	+2	+2	+2	+1
+3	+3	+3	+3	+3	+2
	+4	+4	+4	+4	
	+6	+6			
+6	+7				

For any of these metals, once the d^5 configuration is exceeded, the tendency for all the *d* electrons to participate in bonding decreases. Low oxidation states occur particularly with π bonding ligands such as carbon monoxide and dipyridyl. The higher oxidation states are displayed with electronegative elements like oxygen and fluorine. Compounds in higher oxidation states are oxidizing in nature and covalent while those in lower oxidation states are reducing and ionic.

SAQ 1

Why does Fe have a maximum oxidation state of (+6)?

1.3 PREPARATION, IUPAC NOMENCLATURE AND IMPORTANT PROPERTIES OF SOME INORGANIC REAGENTS

In this section you are going to study about the preparation, IUPAC nomenclature of some inorganic reagents. You are also going to study some of their important properties.

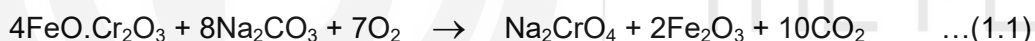
1.3.1 $K_2Cr_2O_7$, $KMnO_4$, $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, $Na_2[Fe(CN)_5NO]$, $Na_3[Co(NO_2)_6]$

Potassium dichromate $K_2Cr_2O_7$

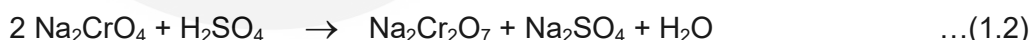
Potassium dichromate is a very important laboratory reagent and you have used it in your practical classes.

Preparation

The industrial preparation of potassium dichromate is generally done from chromite ore ($FeO \cdot Cr_2O_3$). The concentrated ore is treated with excess sodium carbonate and roasted in excess of air whereby, chromium oxide is converted to sodium chromate. The reaction is represented by Eq. 1.1.



The roasted mass is extracted with water when Na_2CrO_4 goes in solution leaving behind insoluble Fe_2O_3 . In Eq. 1.2 you will find the next step, that is conversion of chromate to dichromate with the help of sulphuric acid.



After concentrating the above solution the less soluble sodium sulphate crystallizes out leaving the more soluble sodium dichromate in solution. This saturated solution of $Na_2Cr_2O_7$ is treated with KCl as shown in Eq. 1.3.



NaCl separates out from the hot solution and is removed by filtration and the remaining solution referred to as the mother liquor gives orange crystals of $K_2Cr_2O_7$ when it is cooled.

The chromates and dichromates are interconvertible in aqueous solution depending upon the pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.



Thus there is a pH dependent equilibrium between chromate and dichromate. In acidic medium the predominant species is dichromate and in alkaline medium chromate. This can be represented as:



IUPAC Nomenclature

Potassium dichromate(VI) is the IUPAC nomenclature for potassium dichromate where the oxidation state of chromium is written in brackets in roman letters at the end.

Structure

The dichromate ion is made up of 2 tetrahedra with a common oxygen atom, the Cr atoms are placed at the centre of each tetrahedron. The structures of chromate ion, CrO_4^{2-} and the dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$ are shown below. The chromate ion is tetrahedral whereas the dichromate ion consists of two tetrahedra sharing one corner with Cr–O–Cr bond angle of 126° .

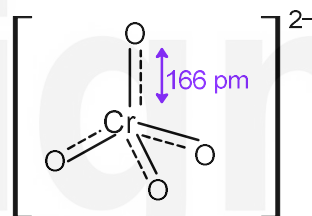


Fig. 1.1: Structure of chromate ion

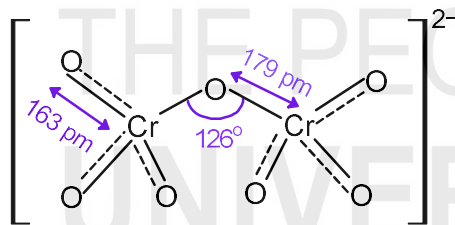


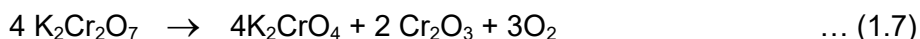
Fig. 1.2: Structure of dichromate ion

Physical Properties

It is an orange solid, moderately soluble in cold water, freely soluble in hot water.

Chemical properties

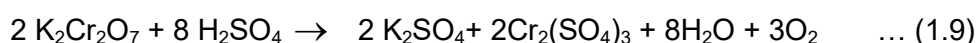
On strong heating of potassium dichromate oxygen is evolved as in Eq. 1.7.



When concentrated H_2SO_4 is added to cooled solution of $\text{K}_2\text{Cr}_2\text{O}_7$, red crystals of CrO_3 are formed as in Eq. 1.8.

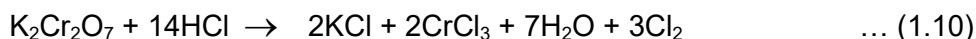


When potassium dichromate is heated with conc. H_2SO_4 , O_2 is evolved.

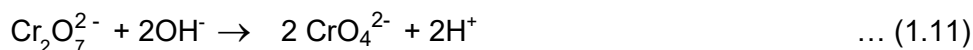


CrO_3 is the anhydride of chromic acid which is used to clean laboratory glassware.

With conc. HCl, Cl₂ is evolved.



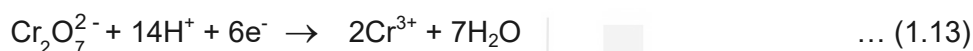
When dilute alkali is added to potassium dichromate, the orange colour of K₂Cr₂O₇ changes to yellow due to formation of K₂CrO₄ as in Eq. 1.11.



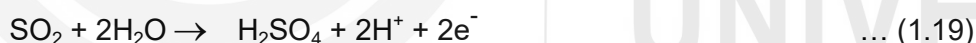
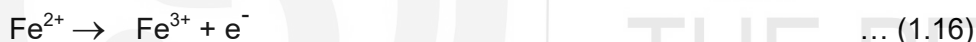
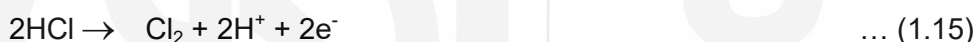
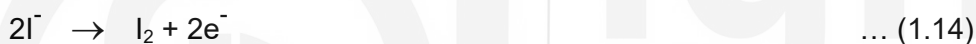
This yellow K₂CrO₄ again changes to orange K₂Cr₂O₇ when acid is added to it as per the Eq. 1.12.



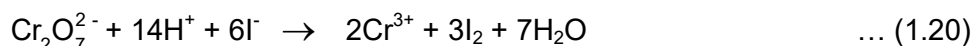
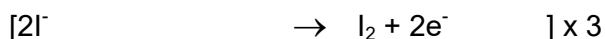
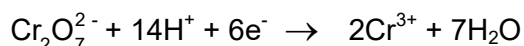
The most important property of K₂Cr₂O₇ is its role as an oxidizing agent. In acidic medium K₂Cr₂O₇ is a powerful oxidizing agent and gets reduced to the green Cr³⁺. The relevant reaction (half equation) where the change in the oxidation state of chromium is from +6 to +3 is shown (Eq. 1.13).



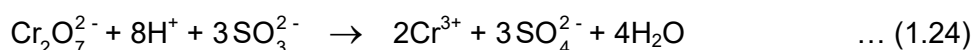
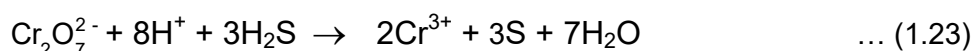
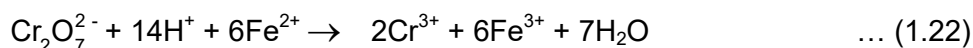
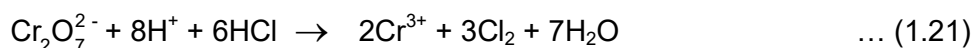
In presence of dilute sulphuric acid K₂Cr₂O₇ oxidizes KI to I₂, HCl to Cl₂, Fe(II) to Fe(III), H₂S to S, sulphites to sulphates and SO₂ to H₂SO₄. The half reactions are shown from Eq. 1.14 to Eq. 1.19.

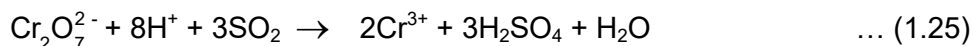


The consolidated reaction may be obtained by adding Eq. 1.13 with the appropriate half reaction (Eq. 1.14 to 1.19) after multiplying by an integer to cancel the number of electrons. An example is shown below:



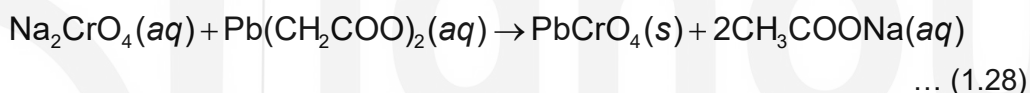
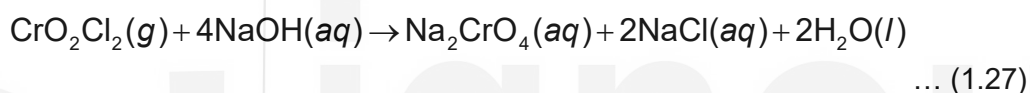
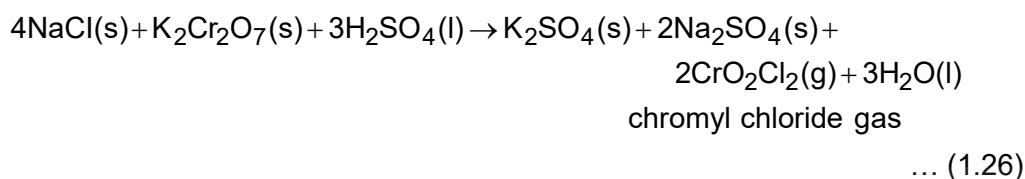
Similarly, you can get,





Chromyl Chloride Test

This is a confirmatory test for chloride ions which is done using potassium dichromate. In a dry test tube, about 0.5 g of dry mixture containing chloride ions are taken, thereupon 0.5 g of $\text{K}_2\text{Cr}_2\text{O}_7$ and 2 cm^3 of conc. H_2SO_4 are added, on heating red vapours of chromyl chloride are evolved. If these vapours are passed in dil. NaOH solution, a yellow solution will be obtained. If the solution is acidified with acetic acid and then lead acetate solution is added, a yellow precipitate of lead chromate forms, which is soluble in NaOH, and this confirms the presence of chloride ions.



Due to the formation of chromyl chloride gas, this test is called **chromyl chloride test**. The test fails if the mixture contains chlorides of Hg^{2+} , Sn^{2+} , Pb^{2+} or Ag^+ .

Uses

Potassium dichromate is a very important chemical used in leather industry and as an oxidant for preparation of many azo compounds.

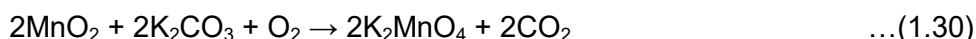
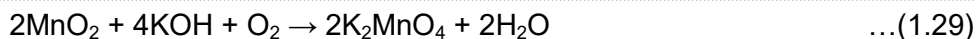
$\text{K}_2\text{Cr}_2\text{O}_7$ is widely used as a volumetric reagent for estimation of Fe(II), iodide etc. It is used as a primary standard in volumetric analysis. In acidic solution, its oxidising action have already been discussed in this unit before.

It is also used as an oxidizing reagent in organic synthesis. Apart from this preparation of chromium compounds like chrome red, chrome yellow etc. which are used as pigments are done from potassium dichromate. Also, it finds uses in tanning of leather, and as cleansing agent for glassware along with conc. H_2SO_4 .

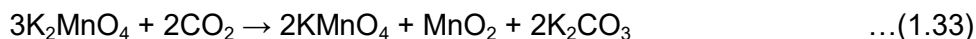
Next let us study about **potassium permanganate (KMnO_4)**. The most important and well known salt of permanganic acid is KMnO_4 .

Preparation

It is prepared from pyrolusite ore. The ore is fused either with KOH or K_2CO_3 in presence of atmospheric oxygen or any other oxidising agent such as KNO_3 . The mass turns green with the formation of potassium manganate, K_2MnO_4 (Eq. 1.29 and 1.30).



Next, the fused mass is extracted with water and a chlorine or ozone or carbon dioxide bubbled through the solution to convert manganate into permanganate as shown in Eq. 1.31 to Eq. 1.33.

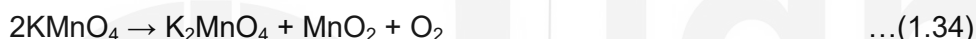


Physical Properties

It is a dark purple coloured crystalline compound with a lustre. It is fairly soluble in water.

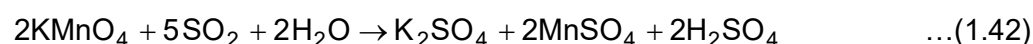
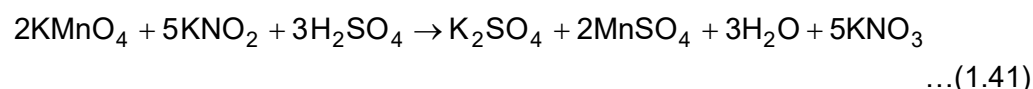
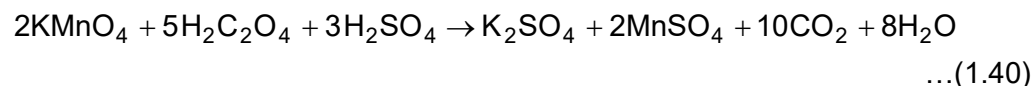
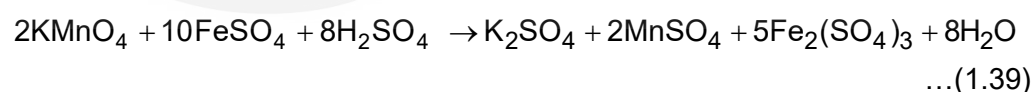
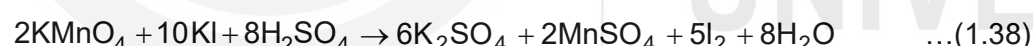
Chemical Properties

When heated alone or with an alkali, it decomposes evolving oxygen as in Eq. 1.34 and 1.35.

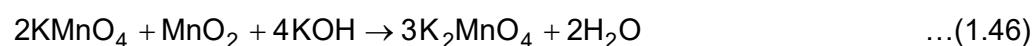
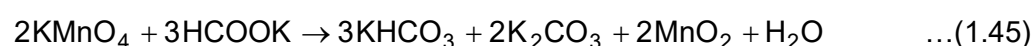
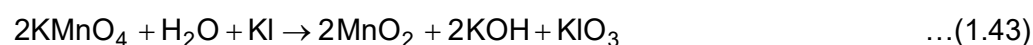


Potassium permanganate is a powerful oxidising agent and acts as an oxidising agent in alkaline, neutral or acidic solutions and itself gets reduced, the relevant reactions are given in Eq. 1.36 to 1.46 given below.

In acidic medium,



In neutral or alkaline medium,



In acidic medium KMnO_4 is reduced to Mn^{2+} , in alkaline medium it reduces to MnO_2 which is a black solid and in neutral solution it reduces to K_2MnO_4 , which is green.

Uses

KMnO₄ is used as an oxidising agent in laboratory and industry. In volumetric estimations, the solution is first standardised before use. The estimations are carried out in acidic medium. For maintaining acidic medium only dilute H₂SO₄ is used. HCl or HNO₃ are not used because HCl reacts with KMnO₄ and produce Cl₂ gas while HNO₃, itself reacts as an oxidising agent. Alkaline potassium permanganate is called Baeyer's reagent. This reagent is used in organic chemistry for the test of unsaturation. KMnO₄ is used in the manufacture of saccharin, benzoic acid, acetaldehyde, etc. It is also used in qualitative analysis for detecting halides, sulphites, oxalates. It is widely used as a disinfectant and germicide. A very dilute solution of KMnO₄ is employed for washing wounds and gargling of mouth sores. It is also used for purifying well water.

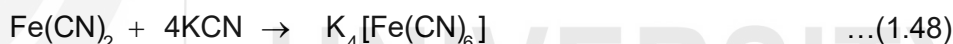
IUPAC Nomenclature

The IUPAC nomenclature for KMnO₄ is potassium manganate(VII) where the oxidation state of manganese is written in brackets in roman letters at the end.

Next we are going to study about **potassium ferrocyanide K₄[Fe(CN)₆]**

Preparation

The laboratory preparation of this reagent is done by addition of a solution of potassium cyanide to a solution of ferrous sulphate till the precipitate of ferrous cyanide dissolves. Then the solution is evaporated to crystallisation point to get the desired product as in Eq. 1.47 and 1.48.



Commercially it is prepared from coal gas which contains ~ 0.2 % HCN as impurity. It is passed through a washer containing ferrous sulphate and potassium hydroxide when the reaction occurs as in Eq.1.49 and 1.50:



IUPAC Nomenclature

The IUPAC nomenclature for K₄[Fe(CN)₆] is potassium hexacyanoferrate(II) where the oxidation state of iron is written in brackets in roman letters at the end.

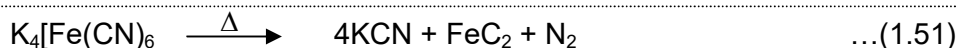
Physical Properties

It exists as lemon yellow crystals, is a trihydrate and loses water of crystallization at 140 °C.

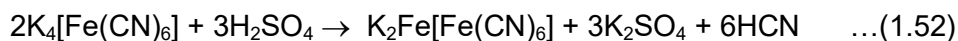
Chemical Properties

On heating, nitrogen gas evolves.

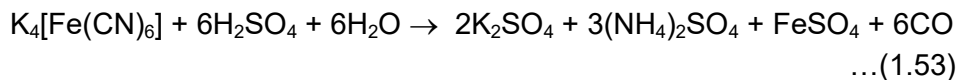
In BCHCL 138, you have done the qualitative detection of cations where the reagents potassium ferro/ferricyanide were used extensively.



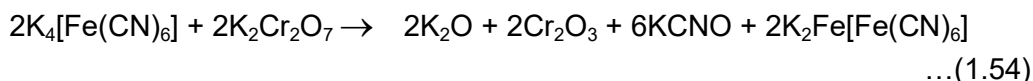
With dilute H_2SO_4 , HCN is evolved.



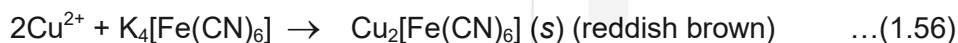
With hot conc. H_2SO_4 , CO is evolved.



When fused with $\text{K}_2\text{Cr}_2\text{O}_7$, potassium cyanate is formed.



It reacts with Zn^{2+} , Cu^{2+} , Fe^{3+} to give characteristic precipitate/ coloration which is used to detect these ions.



Structure

Metal cyanides are generally found to have a complicated polymeric structure both in the hydrate and anhydrous salts. Similarly, solid potassium ferrocyanide has a complicated polymeric structure where the octahedral ferrocyanate centres are crosslinked with potassium ions that are bound to the cyanide ligands. On dissolution the $\text{K}^+ \cdots \text{NC}$ linkages break. The hybridization is d^2sp^3 (this has been discussed in detail in section 5.3.1 of Unit 5 in the previous course BCHCT 137), CN^- is a strong field ligand, complex is diamagnetic. In simple terms the $[\text{Fe}(\text{CN})_6]^{4-}$ is octahedral according to Valence Bond theory (which you have learnt in details in Unit 8 of BCHCT 131) and the structure is as shown below:

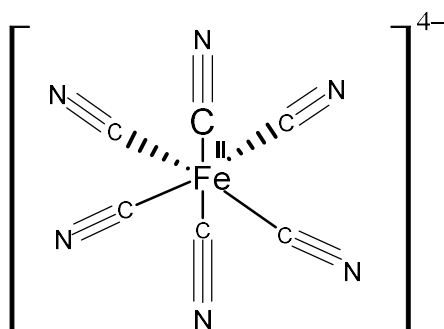


Fig. 1.3: Structure of Ferrocyanide Ion.

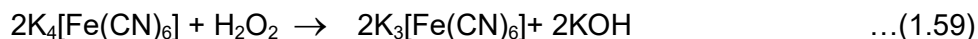
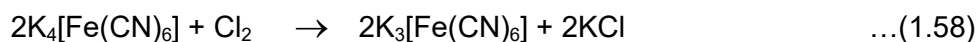
Uses

In the laboratory, on reacting with tripositive iron, potassium ferrocyanide gives a Prussian blue colour. It is widely used as a reagent for detection of metal ions in the laboratory.

Potassium ferricyanide $K_3[Fe(CN)_6]$

Preparation

It is prepared by the oxidation of potassium ferrocyanide by chlorine or hydrogen peroxide.



It can also be prepared by the electrolytic oxidation of alkaline ferrocyanide solution.

IUPAC Nomenclature

The IUPAC nomenclature for potassium ferricyanide is potassium hexacyanoferrate(III) where the oxidation state of iron is written in brackets in roman letters at the end.

Physical Properties

It is a dark red crystalline solid, less stable than potassium ferrocyanide.

Chemical Properties

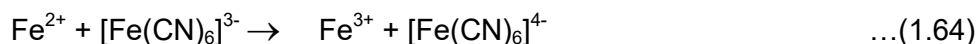
It may be reduced to ferrocyanide in alkaline medium and thus is an oxidizing agent.



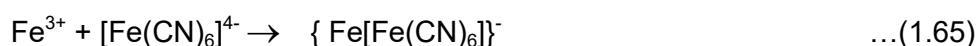
It oxidizes H_2S , PbO , SO_2 to S , PbO_2 , H_2SO_4 as shown below (Eq. 1.61, 1.62 and 1.63),



When treated with a $Fe(II)$ salt a blue colouration (Turnbull's Blue) is obtained. Actually $Fe(II)$ is oxidized to $Fe(III)$ by ferricyanide, which in turn is reduced to ferrocyanide. These reactions are shown in Eq. 1.64 and Eq. 1.65.



These then react giving Turnbull's blue.



Structure

Potassium ferricyanide also has a similar complicated polymeric structure as potassium ferrocyanide. The hybridization is d^2sp^3 , inner orbital complex with one unpaired electron (this has been discussed in detail in section 5.3.1 of Unit 5 in the previous course BCHCT 137). In simple terms the $[Fe(CN)_6]^{3-}$ is octahedral according to Valence Bond theory (which you have learnt in details in Unit 8 of BCHCT 131) and the structure is as shown in Fig. 1.4:

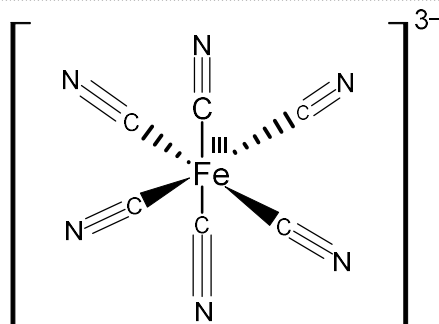


Fig. 1.4: Structure of Ferricyanide Ion.

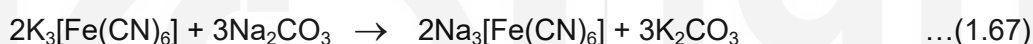
Uses

Similar to potassium ferrocyanide, potassium ferricyanide also forms Prussian blue in the presence of Fe^{2+} ions, and therefore may be used to detect metal ions.

Sodium nitroprusside, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$

Preparation

It is obtained by boiling $\text{K}_4[\text{Fe}(\text{CN})_6]$ with dilute HNO_3 and neutralizing with Na_2CO_3 . The solution is filtered and evaporated to give red crystals.



IUPAC Nomenclature

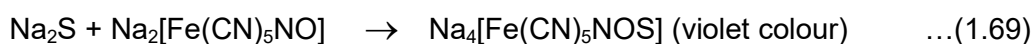
The IUPAC nomenclature for sodium nitroprusside is sodium pentacyanonitrosoferrate(II) where the oxidation state of iron is written in brackets in roman letters at the end.

Physical Properties

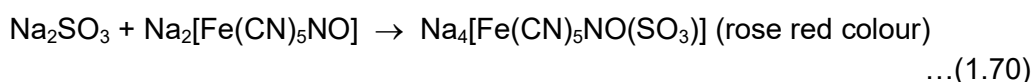
It is a red crystalline solid, soluble in water; however the aqueous solution is unstable.

Chemical Properties

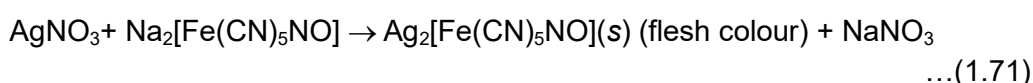
It is used in qualitative analysis for the detection of S^{2-} and S in organic compounds.



With alkali sulphites a rose red colour is obtained. This test distinguishes SO_3^{2-} from $\text{S}_2\text{O}_3^{2-}$.



With AgNO_3 , a flesh colour precipitate is obtained.



When added to aldehydes and ketones having $\text{H}_3\text{C}-\text{C}=\text{O}$ group followed by NaOH a deep red colour is obtained.

Structure

NO is a 3 electron donor as it is an odd electron molecule. Fe(III) accepts an electron from NO forming Fe(II) and the NO^+ thus obtained acts as a 2 electron donor. Fe(II) is a d^6 system and NO^+ a strong field ligand, thus the resultant complex is octahedral (as shown in Fig. 1.5) and diamagnetic.

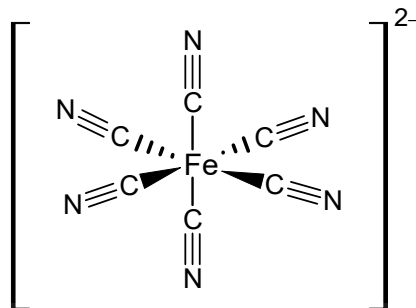
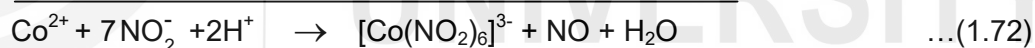
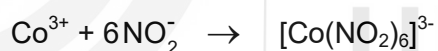
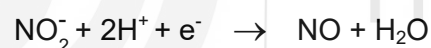


Fig. 1.5: Structure of Nitroprusside Ion.

Lastly, we are going to study about the reagent **sodium cobaltinitrite**, $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$.

Preparation

It is obtained by adding a solution of sodium nitrite in acetic acid to a Co(II) salt. The NO_2^- oxidizes Co(II) to Co(III) which then reacts with excess NO_2^- .



IUPAC Nomenclature

Sodium hexanitrocobaltate(III) is the IUPAC nomenclature for sodium cobaltinitrite where the oxidation state of cobalt is written in brackets in roman letters at the end.

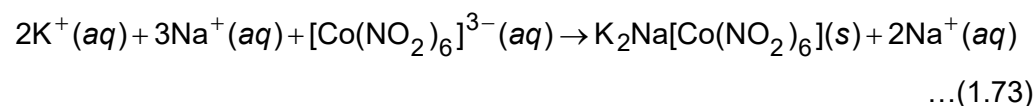
Physical Properties

It is soluble in water but the solution is unstable. It is a yellow-coloured salt.

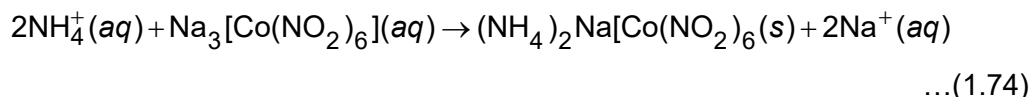
Chemical Properties

It reacts with K^+ and NH_4^+ to give a yellow precipitate which serves as confirmatory tests for these ions.

Potassium is detected in aqueous solution by addition of sodium hexanitritocobaltate (III), $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$, precipitates as in Eq. 1.57:



Ammonium ions are detected in aqueous solution, where formation of a yellow precipitate with sodium hexanitritocobaltate (III), $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ takes place as in Eq. 1.74:



The presence of strong acid destroys the nitrite ion. Therefore, sodium nitrite(s) should invariably be added to the reagent solution before performing this test. Preferably use a freshly prepared solution. Presence of oxidising agents and OH^- ions change the composition of the reagent and renders it ineffective.



Structure

Its structure is octahedral (as shown in Fig. 1.6). It forms inner orbital, diamagnetic complex.

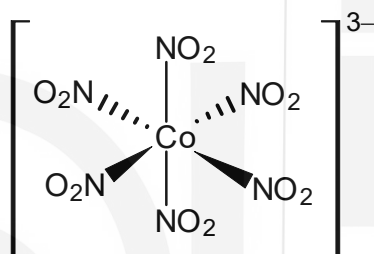


Fig. 1.6: Structure of Cobaltinitrite Ion.

SAQ 2

Give the general method of writing the IUPAC names of the compounds potassium ferrocyanide and sodium nitroprusside.

1.4 SUMMARY

So in this unit you have learnt about the various inorganic reagents. First of all you learnt about the oxidation states displayed by Cr, Mn, Fe, Co, Ni and Cu. Thereafter discussions were done on the preparation, IUPAC Nomenclature and important properties of some inorganic reagents. In the next unit you are going to learn about the organometallic compounds.

1.5 TERMINAL QUESTION

1. Why does manganese show oxidation states varying from +2 to +7, whereas copper shows only +1 and +2 oxidation states?
2. Give the industrial preparation of potassium dichromate along with the involved chemical equations.
3. Give the usefulness of sodium nitroprusside as a lab reagent for detecting cations in a mixture.

1.6 ANSWERS

Self Assessment Questions

1. For the transition metals of the first series, once the d^5 configuration is exceeded, the tendency for all the d electrons to participate in bonding decreases.
2. Potassium hexacyanoferrate(II) is the IUPAC nomenclature for potassium ferrocyanide where the oxidation state of iron is written in brackets in roman letters at the end. Similarly, Sodium pentacyanonitrosoniumferrate(II) is the IUPAC nomenclature for sodium nitroprusside.

Terminal Questions

1. Looking at Table 1.1, it is evident that there is a reduced tendency of higher states as we move from left to right. This could be due to steady increase in the effective nuclear charge (discussed in the course BCHCT 137) along the series thus pulling the d orbitals into the electron core and not making them readily available for bonding.
2. The industrial preparation of potassium dichromate is generally done from chromite ore ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$). Eq. 1.1 must be given here where the concentrated ore is treated with excess sodium carbonate and roasted in excess of air. As a result, chromium oxide is converted to sodium chromate.
3. Sodium nitroprusside is used in qualitative analysis for the detection of S^{2-} and S in organic compounds as shown in Eq. 1.69, 1.70 and 1.71. (Balanced equations must be written).

UNIT 2

ORGANOMETALLIC COMPOUNDS

Structure

2.1	Introduction	2.3	Concept of Hapticity
	Expected Learning Outcomes	2.4	Structures of methyllithium, Zeise's salt and Ferrocene
2.2	Definition and Classification	2.5	Summary
	Ionic	2.6	Further Reading
	Covalent -Sigma bonded		
	Non Classical, Multicentre Bonding and π Complexes		

2.1 INTRODUCTION

In this unit you will be introduced to organometallic compounds. Organometallic compounds contain at least one direct bond between a metal and carbon atom of an organic compound. Apart from learning the definition and classification of organometallic compounds, you are also going to learn about hapticity and structures of some organometallic compounds. Organometallic compounds have many commercial and pharmaceutical applications. In the next unit you will learn about metal carbonyls.

Organometallic chemistry can be viewed as a bridge between organic and inorganic chemistry.

Expected Learning Outcomes

After studying this unit you should be able to:

- ❖ define and classify organometallic compounds;
- ❖ understand the concept of hapticity; and
- ❖ describe the structures of methyl lithium, Zeise's salt, Ferrocene.

2.2 DEFINITION AND CLASSIFICATION

This section deals with the definition and classification of organometallic compounds. The organometallic compounds, by definition are those compounds that contain at least one metal-carbon (M-C) bond, where M may

also represent non-metals like B(boron), Si(silicon), P(phosphorus) or As (arsenic). The ligands involved are organic compounds and may also include CO(carbonyl) but not CN^- (cyanide), CH_3COO^- (acetate) (as the metal is bound to nitrogen/oxygen) etc. Compounds like $\text{Ti}(\text{OEt})_4$, $\text{Ca}(\text{NMe}_2)_2$ are not organometallic compounds but $\text{C}_6\text{H}_5\text{Ti}(\text{OEt})_3$, $\text{Fe}(\text{C}_2\text{H}_5)_2$, $(\text{C}_2\text{H}_5)_2\text{Zn}(\text{OAc})_2$ are organometallic compounds. Carbides, cyanides and carbonates are excluded. Metal carbonyls belong to the category of organometallics, which involve transition metals with low oxidation numbers. The first organometallic compound discovered was Zeise's salt, but discovery of ferrocene (π complex) was a landmark in the discovery of organometallic compounds.

Now, a question arises here, what are the differences between the organometallic compounds and organic compounds? They are the following:

S. No.	Organometallic compounds	Organic compounds
i)	The M–C bonds are mostly polar than the C–C bond.	C–C bond is not polar.
ii)	The other elements have possibility of using higher <i>d</i> orbitals and thus expanding their octet e.g., SiR_4 .	Carbon cannot expand its octet.
iii)	Presence of lone pairs of electrons on M may impart donor ability in alkyls or aryls, as in $\text{P}(\text{C}_2\text{H}_5)_3$, $\text{S}(\text{CH}_3)_2$ etc.	Does not have donor property.
iv)	When M is electron deficient or coordinatively unsaturated, the organometallic compounds may develop Lewis acid character as in BR_3 or ZnR_2 . The compound thus acts as Lewis base which is known as its carbanion character. But the compound is not ionic.	Cannot have Lewis acid character.

You have learnt about coordination compounds in the fourth semester of CBCS, in the BCHCT 137 course. So, a question may arise in your mind that what are the differences of organometallic and coordination compounds? Well, they are the following:

S. No.	Coordination Compounds	Organometallic Compounds
i)	Generally soluble in water	Soluble in hydrocarbon
ii)	They are not sensitive to air	They are air sensitive
iii)	They have high melting point ($> 250^\circ\text{C}$)	They have low melting point

Next, we will discuss that main stream of organometallics which are dominated by the nature of the M–C bond. We will learn their classification depending upon the nature of their M–C bond. Let us discuss them one by one.

- (a) Firstly, we have those organometallics where the M–C bond is a conventional σ -bond. This sort of σ -bonded organometallics belong to the main group chemistry. But if you compare them with the σ -bonded organometallics of transition metals, you will see that the latter are less stable.

- (b) Secondly, the organometallic compounds may be formed by σ -donor and π -acceptor ligands like carbon monoxide.
- (c) Thirdly, organometallics may be formed by π -electron donors for example, the olefins and other π -systems.
- (d) Lastly are those organometallic compounds which are formed of highly electropositive metals and are mostly ionic. They form a separate class.

Organometallic generally denotes a compound in which organic groups are directly linked to the metal through at least one carbon atom.

But, here you should note that the transition metal organometallic compounds have immense variety in their structures and bonding types. This is because transition metals can utilize *s*, *p* and *d* orbitals in bonding. Each orbital type can either donate or accept electron density. Just as in the bonding in coordination compounds, the *d* orbitals on the metal match the orbitals in organometallics to interact with *s* and *p* orbitals on the organic species. Unlike conventional transition metal complexes, the central metal atom in an organometallic compound is often in a very low oxidation state. Due to this flexibility in bonding and the ability to transfer electron density, transition metal organometallic compounds play a crucial role in the chemical industry as catalysts. In Fig. 2.1 a portion of the periodic table is given and the different types of bonding that are possible with most electropositive metals (the alkali metals), the *d*-block transition elements and main group elements are shown. It should be noted that there is no clarity regarding the nature of metal-carbon bonding in alkaline earth compounds and have been marked with * in Fig. 2.1.

In your previous BCHCT-137 course, in the Units 1, 2 and 3 you have learnt about transition elements.

In the same course, Units 4 and 5 dealt with coordination compounds.

Li	Be											B			
Na	Mg											Al	Si		
K	Cs*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
Rb	Sr*	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te
Cs	Ba*	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po
Fr	Ra*	Ac													

Covalent electron
deficient structures

Ionic

d-block Transition elements form complexes with both anionic σ donor ligands and with anionic and neutral π donor ligands. Electron deficient structures known.

Main Group Elements form volatile covalent compounds with anionic σ donor groups

Fig. 2.1: Types of bonding in organometallic compounds.

Organometallic compounds are utilised extensively for producing pharmaceuticals, agrichemicals, flavours, fragrances, semiconductors, and ceramic precursors in the coming days. Organometallic catalysts thus help in reducing fuel use in chemical processes thereby saving petroleum reserves of the earth.

2.2.1 Ionic Organometallic Compounds

The lanthanoids, actinoids and metals of groups 1 and 2, which have electronegativity less than one are highly electropositive metals. So their organometallic compounds are predominantly ionic. However, those of Li, Be, Mg have appreciable covalent character. These compounds are only coloured when the colour is derived from the organic nucleus which have conjugated double bonds. They are reactive towards air and water, non volatile solids and are insoluble in hydrocarbon solvents. They are very reactive and prepared in ethereal solvent. Their stability and reactivity is determined by the stability of the carbanion. Compounds containing $(C_nH_{2n+1})^-$ anion are not stable and difficult to isolate. If the electron density of the carbanion is delocalized, stable salt-like compounds are obtained. Such compounds are also highly reactive, for example $(C_5H_5)^- Na^+$ and $(C_5H_5)_2Ca^{2+}$ where the negative charge is delocalized over the π electron density. Examples of simple organometallic compounds are $LiCH_3$ for group 1 metals, $Be(CH_3)_2$ for group 2 and $B(CH_3)_3$ for group 13.

2.2.2 Covalent-Sigma Bonded Organometallic Compounds

σ -bonded organometallics are formed by most of the non-metals and also by metals of low electropositive character. The transition metals form fewer σ -bonded compounds and those are highly reactive. The M-C bond in these compounds may be regarded as a normal 2 centre-2 electron (2c-2e) bond and partial substitution of halogen or similar groups by organic groups may take place, as in Me_3SnCl , $MeSnCl_3$ etc. However, the M-C bond in these compounds also may have appreciable ionic character, though covalence predominates, example, tetraethyl lead $Pb(C_2H_5)_4$, organotin compound $((C_2H_5)_2SnI_2)$. The organic group is bound to the metal by a normal covalent, which is also referred to as a 2 centre-2 electron (2c-2e) bond. Such compounds are formed by elements which have electronegativity greater than one and less electropositive metals and may include metalloids and non metals. Often their bonds have some ionic character too.

You will understand later what is meant by η^2 and η^5 in section 2.3 on hapticity

Unlike the main group elements, transition elements form fewer simple alkyls or aryls. Such compounds are also mostly unstable under ordinary conditions and cannot be obtained by common methods. However, Pope and Peachy as early as in 1909 prepared the compound $(Me_2PtI)_4$. Stable alkyl and aryl compound are also known when other π -acceptor ligands are present (CO, PR_3 , alkynes, η^5 -Cp etc.) or with groups like $-CH_2Ph$, $-CH_2SiMe_3$, $-CH_2CMe_3$, 1-norbornyl etc. Stable Co-C bond is present in nature in vitamin B_{12} related compounds. Often due to coordinately unsaturated metal centres, the M-C σ -bonds are weak and such compounds decompose easily resulting in high reactivity.

2.2.3 Non Classical, Multicentre Bonding and π Complexes

In this section, you will learn about the non-classically bonded organometallics. The nature of bonding of these organometallic compounds cannot be done by conventional 2 centre-2 electron bond. The alkyls of Li, Be

and Al depict multicentre bonding type. Further examples of such non-classically bonded compounds will be found in the transition metal compounds of alkenes, alkynes and other ring systems.

Example $[(\eta^5 - \text{C}_5\text{H}_5)_2\text{Fe}]$, ferrocene $[\text{PtCl}_3(\eta^2 - \text{C}_2\text{H}_2)]$ Zeise's salt

The non classically bonded compounds may be divided into two classes as following:

- (i) Organometallic compounds having bridging alkyls. e.g. dimeric trialkylaluminium Al_2R_3 and polymeric dimethylberyllium $(\text{BeMe}_2)_n$ or diethylmagnesium $(\text{MgEt}_2)_n$. The structure of dimethylberyllium is shown in Fig. 2.2.

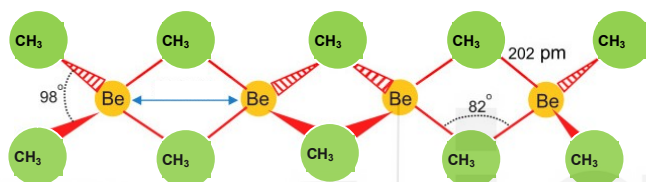


Fig. 2.2: Structure of dimethyl beryllium.

The structure of dimeric trialkyl aluminium is given Fig. 2.3 and the bridging and terminal methyls of trialkyl aluminium are shown in Fig. 2.4.

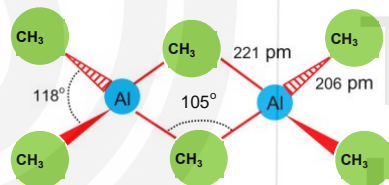


Fig. 2.3: Structure of dimeric trialkylaluminium.

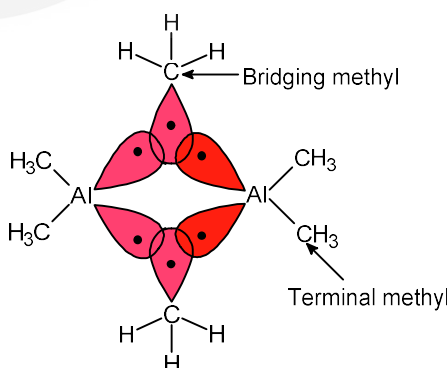


Fig. 2.4: The bridging and terminal methyl in trialkyl aluminium.

These compounds are characterized by presence of alkyl bridges. The metal is equidistant from the two metal atoms. The nature of bonding cannot be explained on basis of 2c-2e bond as the bridging C cannot be simultaneously bonded to two metal atoms and three substituents- H(hydrogen) or R(alkyl) . The bonding is explained on basis of Molecular

Orbital Theory (MOT) in which a M-C-M bond is formed by use of sp^3 hybrid orbital on C and each one of the M atoms. You have previously learnt about the multicentre bonding in boron hydrides which arises out of electron deficiency. Here also for similar reasons, multicentre bonding takes place.

In case of dimeric compounds of aluminium trialkyls, two types of Al-C bonds are noted, the terminal Al-C bonds are 2c-2e bonds while the bridging bonds are three centre – two electron (3c-2e) bonds. They are characterized by different bond lengths. It may be noted, that aluminium chloride is dimeric but all Al-Cl bonds are 2c-2e. Li alkyls also display multicentre bonds.

- (ii) π -bonded organometallics: These are transition metal complexes with unsaturated organic compounds where there is interaction between π orbital of the organic ligands and the d and p orbitals of metal atom. Compounds with alkenes, alkynes and cyclic compounds, having delocalized π orbital fall under this category. Examples of such ligands are alkene, butadiene, allyl, cyclopentadiene, benzene. Some important compounds are ferrocene $\text{Fe}(\text{C}_5\text{H}_5)_2$, dibenzylchromium $\text{Cr}(\text{C}_6\text{H}_6)_2$ and Zeises's salt $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$. Some common ligands which you will find in organometallic compounds are listed in Table 2.1.

Table 2.1: Some common ligands in organometallic chemistry

Formula	Name	Abbreviation
CO	Carbonyl	
CH_3	Methyl	Me
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$	n-Butyl	^nBu
$(\text{CH}_3)_3\text{C}$	Tertiary-butyl	^tBu
$[\text{C}_5\text{H}_5]^-$	Cyclopentadienyl	Cp
C_6H_5	Phenyl	Ph
C_6H_6	Benzene	
$(\text{C}_6\text{H}_5)_3\text{P}$	Triphenylphosphine	PPh_3
H		
F, Cl, Br, I		
CN		
$\mu\text{-F, Cl, etc.}^*$		
$\mu\text{-CO}$		
PR_3, PX_3		
NO		

* μ denotes bridging (already you have learnt about this prefix in Unit 4 (Section 4.4) of BCHCT 137.

SAQ 1

- (i) Which is an organometallic compound (where M is a metal),
 C_2H_5-M-Br , $M-CN$ or $M-OR$?
- (ii) Decide whether each of the following compounds should be described as organometallic;
- (a) $B(CH_3)_3$ (b) $Fe(C_5H_5)_2$ (c) $Si(CH_3)_4$ (d) C_6H_5Ti
- (iii) With one example for each give the broad classification of organometallic compounds.

2.3 CONCEPT OF HAPTICITY

The classification of organometallic compounds is based on their bonding potentiality, commonly known as hapticity, which is symbolically represented as η^x , ($x = \text{one, two, three, } \dots$) or η -hapto bound (x is greek number, mono, di, tri, $\dots$). So x is the number of C atoms which coordinate to the metal and is referred to as hapticity. Thus we may define hapticity as the “number of carbon atoms within a bonding distance of metal atom or the number of carbon atoms through which an organic ligand is attached to a central metal atom. You will understand this better with the examples given in Fig. 2.5 and Table 2.2.

Greek word ‘haptein’ means to fasten’.

The group bridging two metal centres are given a prefix μ , as in $(Me_3Al)_2$; di- μ -methyl (tetramethyl) dialuminium.

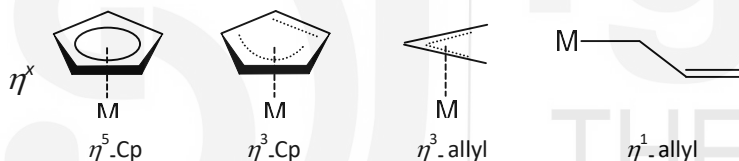
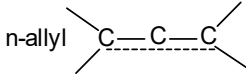
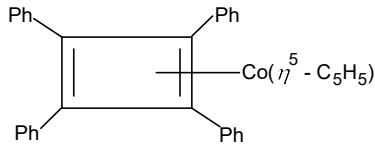


Fig. 2.5: Hapticity

Table 2.2: Classification of Organometallic Ligands and their Hapticities

Number	Examples of Ligands	Examples of Complexes
η^1 , monohapto	Alkyl (-R) Aryl (-Ar) Carbene ($=CH_2$) $\begin{array}{c} \text{OR}' \\ \\ =C \\ \\ R \end{array}$ = Cyclo Carbyne ($=CR$) Carbide (C)	LiC_2H_5 $Hg(C_6H_5)_2$ $[Ta(\eta^5-C_5H_5)_2(Me)(CH_2)]$ $[Cr(CO)_5(:C \begin{array}{c} \text{Ph} \\ \\ \text{Ph} \end{array})]$ $(\equiv Car)[Cr(CO)_4(\equiv CR)(Cl)]$ $Fe_5(C)(CO)_{15}$
η^5 , dihapto	Alkene $\left(\begin{array}{c} \diagup \quad \diagdown \\ \quad C=C \quad \\ \diagdown \quad \diagup \end{array} \right)$ Alkyne $-C \equiv C-$ Non-conjugated dienes are bis-dihapto	$(FC_2=CF_2)$ $Kl[Pt(\eta^2-C_2H_4)Cl_3]H_2O$ $[Pt(\eta^2-C_2Ph_2)(PPh_3)_2]$

η^3 - trihapto	n-allyl 	$[Ni(\eta^3 - C_3H_5)_2]$
η^4 - tetrahapto	Conjugated diene, cyclobutadiene	
η^5 - pentahapto	Cyclopentadiene, cyclopentadienyl derivatives	$[Fe(\eta^5 - C_5H_5)_2]$
η^6 - hexahapto	Arene (e.g. benzene, substituted benzene) cycloocta-1, 3, 5- triene)	$[Cr(\eta^6 - C_6H_6)_2]$
η^7 - heptahapto	Tropylium (cycloheptatrienyl)	$[V(\eta^5 - C_5H_5)(\eta^7 - C_7H_7)]^*$
η^8 - octahapto	Cyclooctatetraene	$[U(\eta^8 - C_8H_8)_2]$

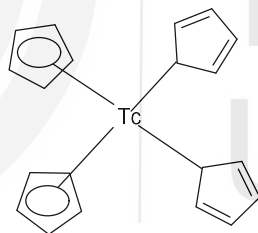
The bonding in CH_3Li consists of set of localized molecular orbitals. The symmetric combination of three Li 2s orbitals from CH_3 gives an orbital that can accommodate a pair of electron to form a 4c-2e bond.

SAQ 2

Give the hapticity of the cyclopentadienyl groups in

- i) $[Fe(C_5H_5)_2[(CO)_2]]$ complex (considering it obeys 18 electron rule)

ii)



2.4 STRUCTURES OF METHYL LITHIUM, ZEISE'S SALT AND FERROCENE

In this section, you will know about the structures of three organometallic compounds namely, methyl lithium, Zeise's salt and ferrocene.

Methyl lithium:

CH_3Li is the empirical formula for methyl lithium. In both solid and solution states it exists in oligomeric forms (IUPAC defines an oligomer as a substance composed of molecules containing a few of one or more species of atoms or groups of atoms (constitutional units) repetitively linked to each other). Tetrameric and hexameric forms of methyl lithium have been identified using spectroscopy. The tetrameric form in its simplified form is shown in Fig. 2.6 where, the four lithiums occupy alternate diagonal corners of the opposite

faces of the cube, forming a tetrahedron. The carbons of the methyl group occupy the four vacant corners of the cubes, which are also the alternate diagonal positions of the opposite faces of the cube. The structure of the tetramer is rather unusual. Each methyl C atom is above a face of the tetrahedron, and forms a triple bridge with the three Li atoms that are on the face of a tetrahedron. The structure is a distorted cube as indicated by its bond length measurements. The intramolecular Li-C distance is 231 pm. The C is not only bonded to three H atoms, but also to a Li atom in another tetrahedron (where the intermolecular Li-C distance is 236 pm. Thus the coordination number for the C atom is 7. In a similar way the coordination number of Li is also 7, made up by three Li in the tetrahedron, three C at the centres of faces of the tetrahedron, and one Li in another tetrahedron.

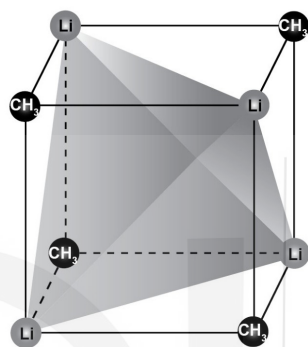


Fig. 2.6: Structure of Methyllithium.

Zeise's salt:

$[\text{Pt}(\eta^2 - \text{C}_2\text{H}_4)(\mu_2 - \text{Cl})_2\text{Cl}_2]^-$:- Potassium trichlorido(ethene)platinate(II)

Zeise's salt was the first organometallic compound which can be isolated in pure form (1825 by William Zeise). It is a square planar complex with 16 electrons and the structure of its anion is given in Fig. 2.7.

The Pt-Cl bond trans to the ethene group is significantly longer than the cis-Pt-Cl bonds. The four hydrogen atoms are away from the Pt atom. The carbon atoms of the ethene molecule are both at a same distance from the platinum atom. (The C-C distance, 137.5 pm, is slightly longer than the value found in free ethene (133.7 pm). C-C bond length increases in the complex. This is accompanied by a decrease in C=C stretching frequency in Zeise's salt. The C=C bond in Zeise's salt is perpendicular to the PtCl_3 plane so that the repulsion between hydrogen and chlorine atoms become least. Hence the bond from platinum to ethene goes through at the centre of C=C. The ethene molecule as a result gets deformed to allow the hydrogen atoms to move away from the rest of the ion.

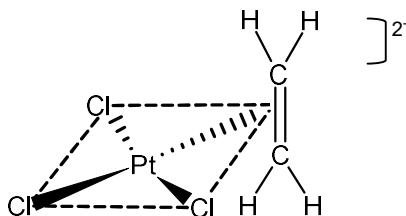


Fig. 2.7: Structure of anion of Zeise's salt.

Ferrocene

$[\text{Fe}(\eta^5 - \text{C}_5\text{H}_5)_2]$:- bis(η^5 -cyclopentadienyl) iron(II)

Ferrocene is known as a “sandwich” compound. It was discovered accidentally and independently by two independent groups of workers. It occurs as highly stable orange crystals with a melting point of 174 K. In solid state at low temperature, the rings are staggered. The rotational barrier is very small, with free rotation of the rings. At extremely low temperature, that is below 110 K, the cyclopentadienyl (Cp) rings are ordered and eclipsed. Each cyclopentadienyl (Cp) ring is aromatic. The two forms of ferrocene are shown in Fig. 2.8.

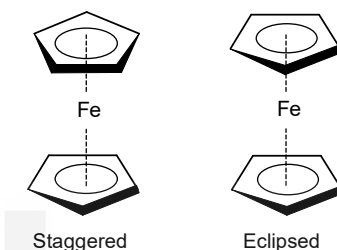


Fig. 2.8: Structure of Ferrocene.

Here, you must note that, these organometallic compounds where cyclopentadienyl group is involved are known as metallocenes. They have the pentahapto ligand and it forms compounds of the type $\text{M}(\text{C}_5\text{-H}_5)_n$, where M is the metal and n is its valency.

Before going further, try to answer the following SAQ.

SAQ 3

Compare the two possible structures of ferrocene.

The bonding in CH_3Li consists of set of localized molecular orbitals. The symmetric combination of three Li 2s orbitals with CH_3 gives an orbital that can accommodate a pair of electron to form a 4c-2e bond.

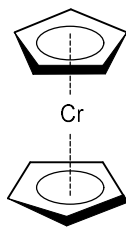
2.5 SUMMARY

In this unit, you have learnt about the basics of organometallic compounds including their definition and classification. The classification have been based on the nature of the metal carbon bonds and are of the types ionic, covalent -sigma bonded, non classical, multicentre bonding and π complexes. Thereafter the concept of hapticity have been discussed with suitable examples. Lastly we have discussed structures of methyl lithium, Zeise's salt and ferrocene. In the next unit you will be studying about the metal carbonyl compounds in detail.

2.6 TERMINAL QUESTIONS

1. Give the definition of an organometallic compound along with few examples.
2. Differentiate between ionic and covalent sigma bonded organometallic compounds giving suitable examples.
3. How can you classify organometallic compounds on the basis of hapticity?

4. Give the hapticity of the C_5H_5 ligand in the following compound.

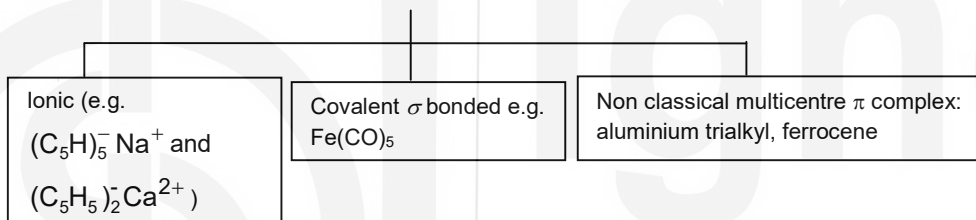


5. Give the structural formula and preparation of Zeise's Salt

2.7 ANSWERS

Self Assessment Questions

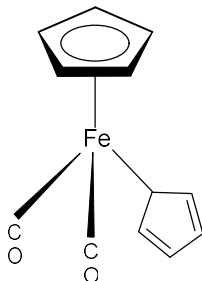
1. (i) $C_2H_5 - M - Br$ is an organometallic compound as it has a direct M-C bond
- (ii) a) Yes b) Yes c) Yes d) Yes. All of them have a direct M-C bond.
- (iii) Organometallic Compounds



2. (i) The two cyclopentadienyl groups in $[Fe(C_5H_5)_2[(CO)_2]]$ complex have different hapticities. One cyclopentadienyl function behaves as a pentahapto ligand whereas the other shows monohapto characteristic. The pentahapto and monohapto cyclopentadienyl groups act as six-and two-electron donors, respectively.

The resulting complex is very stable since it follows the 18-electron rule.

Fe(II)	=	$6e^-$
$2CO : 2 \times 2e^-$	=	$4e^-$
$(\eta^5-C_5H_5)^-$	=	$6e^-$
No. of electrons		$16e^-$
$(\eta^1-C_5H_5)^-$	=	$2e^-$
Total no. of electrons		$18e^-$



The correct composition of the complex may be written as $[Fe(\eta^1-C_5H_5)(\eta^5-C_5H_5)(CO)_2]$.

- (ii) From the structure drawn it is clear two of the cyclopentadienyl groups are pentahapto and one is monohapto, i.e. ($\eta^5 - \text{C}_5\text{H}_5$) ($\eta^1 - \text{C}_5\text{H}_5$) Ti.

3.	Sl. No.	Staggered Ferrocene	Eclipsed Ferrocene
	1	Occurs at low temperature	Occurs at extremely low temperature
	2	Less order	More order
	3	Structure is : Fig. 2.7(left)	Structure is Fig. 2.7(right)

Terminal Questions

- The organometallic compounds, by definition are those compounds that contain at least one metal-carbon (M-C) bond, where M may also represent non-metals like B(boron), Si(silicon), P(phosphorus) or As (arsenic). Example: Zeise's salt and ferrocene

S. No.	Ionic organometallics	σ bonded organometallics
1	The lanthanoids, actinoids and metals of groups one and two, which have electronegativity less than one are highly electropositive metals. So their organometallic compounds form ionic compounds.	σ -bonded organometallics are formed by most of the non-metals and also by metals of low electropositive character. The transition metals form fewer σ -bonded compounds and those are highly reactive.
2	They are reactive towards air and water, non volatile solids and are, insoluble in hydrocarbon solvents. They are very reactive and prepared in ethereal solvent.	
3	example $(\text{C}_5\text{H}_5)^- \text{Na}^+$ and $(\text{C}_5\text{H}_5)_2\text{Ca}^{2+}$	example $\text{Pb}(\text{C}_2\text{H}_5)_4$, $((\text{C}_2\text{H}_5)_2\text{SnI}_2)$

- Hapticity
- η^6 (that is hexahapto ligand)
- $[\text{Pt}_2(\eta^2 - \text{C}_2\text{H}_4)(\mu_2 - \text{Cl})_2\text{Cl}_2]$: Potassiumtrichloro(ethane)platinate(II)
Zeise's salt was the first organometallic compound which could be isolated in pure form (1825 by William Zeise). It is a square planar complex with 16 electrons and the structure of its anion is given in Fig. 2.7.

UNIT 3

METAL CARBONYL COMPOUNDS-I

Structure

3.1	Introduction	3.5	Properties of Mononuclear and Polynuclear Carbonyl of 3d Metals
	Expected Learning Outcomes		
3.2	EAN Rule and 18 Electron Rule (as applied to Carbonyls)	3.6	Summary
3.3	Preparation - Direct Combination, Reductive Carbonylation	3.7	Terminal Questions
3.4	Structure (Based on VB Approach) and Properties	3.8	Answers

3.1 INTRODUCTION

In the previous unit, you were introduced to organometallic compounds. In this unit you will study metal carbonyl compounds. The details of EAN (Effective Atomic Number) Rule and 18 Electron Rule as applied to carbonyls will be discussed. This will be followed by preparation of metal carbonyls through direct combination and reductive carbonylation. Finally the structure of metal carbonyls and their properties with special reference to mononuclear and polynuclear carbonyls of 3d metals will be dealt with.

In the next unit, you will learn more about metal carbonyl compounds specially their bonding and IR stretching frequency data. So in this way, you will be learning all about the metal carbonyl compounds through units 3 and 4 of this course.

Expected Learning Outcomes

After studying this unit you should be able to:

- ❖ understand EAN Rule and 18 Electron Rule as applied to carbonyls;

- ❖ describe the preparation of metal carbonyls through direct combination and reductive carbonylation;
- ❖ understand the structure of metal carbonyls based on Valence Bond approach; and
- ❖ describe the properties of mononuclear and polynuclear carbonyl of 3d metals.

3.2 EAN RULE AND 18 ELECTRON RULE (AS APPLIED TO CARBONYLS)

Sidgwick first tried to explain bonding in transition metal complexes. He then extended octet theory of Lewis to coordination compounds.

The first carbonyls discovered were those of iron, cobalt and nickel. Their formulae, as well as the formulae of their carbonyls were derived later. A large number of metal carbonyls, including many anionic and cationic species, nitrosyl, hydrogen, and halogen-substituted metal carbonyls and small metal cluster carbonyls, conform to the **18 electron rule**. This rule can also be formulated in terms of the total number of electrons around the metal in which case this number is usually found to be 36, 54, or 86, corresponding to the atomic numbers of the noble gases Kr, Xe, and Rn. The metals are then said to have the effective atomic number of the noble gases, or to obey the **EAN rule**. Because the pseudo-noble gas valence shells of Kr, Xe, and Rn contain 18 electrons, it is simpler just to count valence shell electrons.

EAN is referred to as Effective Atomic Number. Complexes of transition metals with π -acid ligands, and their organometallic compounds generally obey the EAN rule. The central metal atom appears to have acquired the configuration of a noble gas by transference or sharing of electrons. The total number of electrons which the metal ion appears to have around itself is called the EAN of the metal and when this equals 36(Kr), 54(Xe) or 86(Rn) the EAN rule is said to be followed. Well, you can also say that when the metal achieves an outer shell configuration of $(n-1)d^{10}ns^2np^6$, there will be 18 electrons in the valence shell and a closed stable configuration. This is known as the 18 electron rule which has the advantage of being the same for all rows in the periodic table so that you need not remember the atomic numbers of all noble gases. This is another way of saying that all the bonding capacity of the metal is utilised. This rule allows the systematization of much of the structural chemistry of transition metal organometallic compounds. The transition metal complexes studied earlier are classical complexes and contain metal in the oxidation states + 2 or more and involve ligands which are N or O donors or halides. However in organometallic compounds, particularly the carbonyls where the EAN rule is followed, the metal is in low oxidation state, may be zero or even negative.

You know that when bonds are formed the orbitals involved should be matched in energy. This is noted in the middle of the series and for metals in low oxidation state. Increasing the oxidation state changes the slope of the binding energy versus atomic number line and increases their separation. So for sufficiently positive oxidation state (greater than or equal to 2), the EAN rule does not hold. Within its region of applicability the rule is a reliable guide to molecular structure and stoichiometry.

In certain cases molecules having 16 valence electrons seem to be equally stable. This is specially true for metals at the right corner of the transition series, i.e. Rh, Pd, Ir, Pt. These elements have the least tendency to be six coordinate and Ir(I), Pt(II) form many four-coordinate species.

In most cases the maximum coordination number is 6 and if each ligand donates a pair of electrons, then the metal must have d^6 configuration to follow 18 electron rule. Structure of such complexes are found to be roughly octahedral. Metals with d^8 system need 5 electron pairs and the expected geometry is trigonal bipyramidal or square pyramid whereas metals with d^{10} configuration need 4 electron pairs and form tetrahedral or square planar complexes. In case of 16 electron species they are generally square planar and are invariably based on d^8 metal ions. (VSEPR & Valence Bond Theory may be recapitulated from BCHCT-131, Units 7 and 8).

The rule is used to predict the existence and number of metal-metal bonds. Most stable metal carbonyls obey the rule. The steps to **calculate the EAN** of metal carbonyl compounds is given below:

1. Firstly, you must count the number of electrons in the valence shell of the metal atom. Depending on the charge of the metal in the complex, you have to add or subtract electrons.
2. Secondly, you have to check the number of electrons the organic ligand formally contributes to the valence shell of the atom (in case of CO each terminal ligand contributes two electrons and each bridging ligand contributes one electron to each metal).
3. Next, if any conventional ligands are present then check the number of electrons contributed to valence shell by them.
4. Each M-M bond donates one electron to each metal. So find out how many electrons donated by metal-metal bonds (M-M) in complexes.
5. You must add all electrons checked in steps 1 to 4. This gives the EAN.

Metals with odd atomic number cannot satisfy the EAN (18 electron) rule by simple addition of CO ligands, since the resultant entity will always have an odd number of electrons no matter how many CO molecules are added. There are several options open to these metals by which the 18 electron rule can be satisfied. The simplest is the addition of one electron by a reducing agent to form a carbonylate anion $[M(CO)_n]^-$.

There are some stable compounds with electrons other than 18. In such compounds, the factors such as CFSE (you have already studied about CFSE or the Crystal Field Theory in the previous course of CBCS, namely BCHCT-137, Units 6 & 7) and nature of M-C bonding contribute to the stability of the compound. Some of the metal carbonyl compounds of d block (Groups 9 & 10) obey 16 electron rule. $V(CO)_6$ has 17 electrons and is therefore called 17electron- species. It readily completes 18 electron configuration by accepting an electron from reducing agent. $V(CO)_6$ is the only odd electron carbonyl which does not dimerise. If it dimerises the coordination number of V will be 7 which is not favourable. This is because it would then produce steric hindrance. Ligand-ligand repulsion overcomes a weak V-V bond.

Alternatively, the electron deficient species can bond covalently with an atom or group which also has a single unpaired electron available, for example, H or Cl: $\text{HM}(\text{CO})_n$ or $\text{M}(\text{CO})_n\text{Cl}$. Finally if no other species is available with which to react, two moieties each with an unpaired electron can dimerize with resultant pairing of odd electrons. The pairing of the odd electron on each metal atom in the diamagnetic dimer results in a M-M bond. For example, $\text{Mn}(\text{CO})_5$ has 17-electrons. Two molecules 'share' their odd electron, in order to form a Mn-Mn bond. Consequently each Mn becomes an 18 electron species as shown below:

Mn	7e ⁻	Co	9e ⁻
5CO	10e ⁻	4CO	8e ⁻
Charge	1e ⁻	charge	1e ⁻
$[\text{Mn}(\text{CO})_5]^-$	18e ⁻	$[\text{Co}(\text{CO})_4]^-$	18e ⁻

The electron count shown above is for the neutral atom method. In the oxidation state procedure, each metal would be considered as an M^+ species with additional electron, so in this case there would be no entry for the overall charge.

The dimeric species, $\text{Mn}_2(\text{CO})_{10}$ and $\text{Co}_2(\text{CO})_8$, also are stable and are diamagnetic. If it is assumed that each compound has a metal-metal single (two-electron) bond, the electron count yields a total of 18 for each metal:

2Mn	14e ⁻	2Co	18e ⁻
10CO	20e ⁻	8CO	16e ⁻
Mn-Mn	2e ⁻	Co-Co	2e ⁻
$[\text{Mn}_2(\text{CO})_{10}]$ or 18e ⁻ /Mn	36e ⁻	$\text{Co}_2(\text{CO})_8$ or 18e ⁻ /Co	36e ⁻

So you see, for each such counting of total number of electrons, we follow the same method. Let us understand the 18 electron rule with the help of more examples:

Example 3.1: $\text{Fe}_2(\text{CO})_9$

2 Fe	16 e ⁻
9 CO	18 e ⁻
Fe – Fe bond	2e ⁻
Total Number of electrons	36
Electron for each Fe	36/2 = 18

Example 3.2: $\text{Ni}(\text{CO})_4$

Ni	10 e ⁻
4 CO	8 e ⁻
Total Number of electrons for $\text{Ni}(\text{CO})_4$	18

Example 3.3: $\text{Fe}(\text{CO})_5$

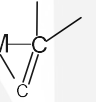
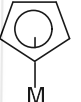
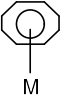
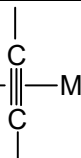
Fe	8 e ⁻
5 CO	10 e ⁻
Total Number of electrons for $\text{Fe}(\text{CO})_5$	18

Example 3.4: Using the 18 electron rule as a guide find the value of n in $\text{Co}_2(\text{CO})_n$

2 Co	18 e
n CO	$2n$ e
Co-Co	2 e
Thus $18 + 2n + 2 = 36$	
$2n = 16 : n = 8$	
So the formula is $\text{Co}_2(\text{CO})_8$	

Table 3.1: Contributions of ligands to electron counting

Terminal ligands	Neutral atom electron count	Oxidation state electron count
Carbonyl (M-CO)	2	2
Thiocarbonyl (M-CS)	2	2
Phosphine (M-PR ₃)	2	2
Amine (M-NR ₃)	2	2
Dinitrogen (M-N≡N)	2	2
Dihydrogen $\text{M}-\begin{array}{c} \text{H} \\ \\ \text{H} \end{array}$	2	2
Alkene $\text{M}-\begin{array}{c} \diagup \text{C} \diagdown \\ \\ \text{C} \end{array}$	2	2
Alkyne* $\text{M}-\begin{array}{c} \diagup \text{C} \diagdown \\ \equiv \\ \text{C} \end{array}$	2	2
Isocyanide (M-CNR)	2	2
Nitrosyl, bent ($\text{M}-\ddot{\text{N}} \begin{array}{c} \diagup \\ \text{O} \end{array}$)	3	2
Nitrosyl, linear (M-N≡O)	1	2
Halogen (M-X)	1	2
Hydrogen (M-H)	1	2

Alkyl (M-R)	1	2
 Acyl (M-C(=O)-R)	1	2
Aryl (M-C-R)	1	2
Amide (M-NR ₂)	1	2
Phosphide (M-PR ₂)	1	2
Alkoxide (M-OR)	1	2
Thiolate (M-SR)	1	2
Carbene = alkylidene (M=CR ₂)	2	4
Carbene = alkylidene (M=CR)	3	6
η^1 -Allyl M - 	1	2
η^3 -Allyl M - 	3	4
η^3 -Enyl M - 	3	4
η^1 -Cyclopentadienyl M - 	1	2
η^5 -Cyclopentadienyl 	5	6
η^6 -Benzene 	6	6
η^7 -Cycloheptatrienyl 	7	6
η^8 -Cyclooctatetraenyl 	8	10
Bridging ligands Carbonyl [M - (CO) - M]	2	2
Halogen (M -X- M)	3	4
Alkyne M -  - M	4	4
Hydrogen (M - H - M)	1	2

Alkyl [M– (CR ₃) – M]	2	2
Amide [M – (PR ₂) – M]	3	4
Phosphide [M– (PR ₂) –M]	3	4
Alkoxide [M – (OR) – M]	3	4

* Sometimes counted as a four-electrons donor if it functions as a π donor.

Table 3.2: Details of some common ligands found in organometallic compounds

Ligand	Formal charge	Electrons donated
H	-1	2
F, Cl, Br, I	-1	2
CN	-1	2
μ -F, Cl, etc.	-1	4
CO	0	2
μ -CO	0	2
PR ₃ , PX ₃	0	2
CH ₃ , C ₂ H ₅ , etc.	-1	2
μ -CH ₃	-1	2
NO	0	2
η^5 -[C ₅ H ₅] ⁻	-1	6
η^6 -C ₆ H ₆	0	6

SAQ 1

- Identify the 3d metal in M₂(CO)₉ assuming it obeys 18 electron rule.
- Find the number of metal-metal bonds in Fe₃(CO)₁₂ and Co₄(CO)₁₂
- Find the charge of the complex [Fe(CO)₄]^{x-}

3.3 PREPARATION - DIRECT COMBINATION, REDUCTIVE CARBONYLATION

In this section you will study the preparation of metal carbonyls by various method and we will use T for temperature and P for pressure.

Preparation of Carbonyls

The known carbonyl of the 3d series are given in Table 3.3:

Table 3.3: Binary carbonyls of the 3d series

V(CO) ₆	Cr(CO) ₆	Mn ₂ (CO) ₁₀	Fe(CO) ₅		Ni(CO) ₄
			Fe ₂ (CO) ₉	Co ₂ (CO) ₈	
			Fe ₃ (CO) ₁₂ Co ₄ (CO) ₁₂		

The two general methods of preparation of simple carbonyls are:

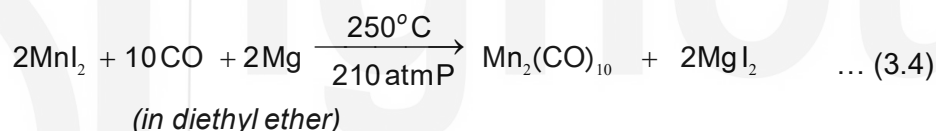
- (i) Direct reaction of metal with CO. This is possible for Fe, Ni and Co and are given below.



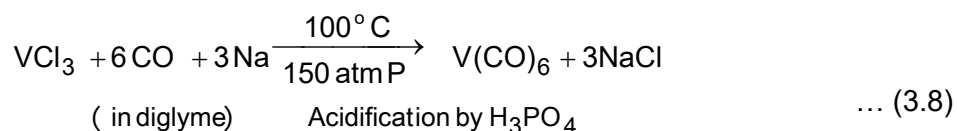
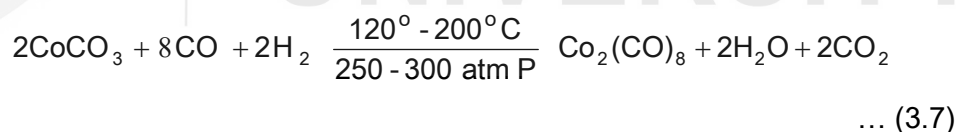
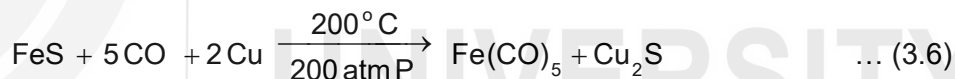
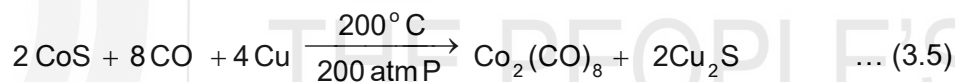
The extreme ease of thermal decomposition of $\text{Ni}(\text{CO})_4$ is the basis of Mond's process for purification of Ni.

- (ii) Reductive Carbonylation

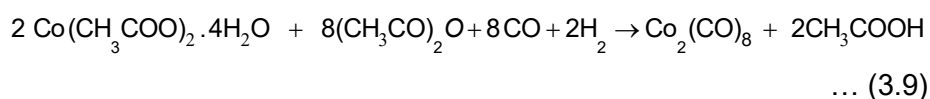
Here, reduction of a metal salt takes place in presence of a reducing agent and are given in the equations 3.4 to 3.9. The reducing agents may be Mg, Ag, Cu, Na, LiAlH_4 and even H_2 .



diglyme is diethylene glycol dimethyl ether.

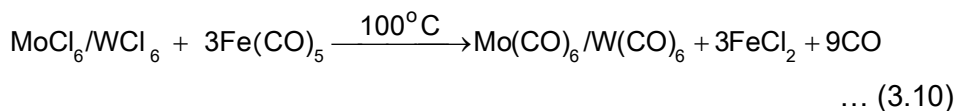


A synthetic method for making carbonyls from metal salts involves reduction of an acetate hydrate by H_2 in presence of CO and sufficient acetic anhydride to convert water of hydration to acetic acid.



- (iii) Some carbonyls may be obtained from other carbonyls

The preparation of mononuclear carbonyls of molybdenum and tungsten from iron pentacarbonyl is shown in Eq. 3.10.



The carbonyl group in iron pentacarbonyl is very easily replaced by chloride and thus different metal carbonyls may be obtained. Of course, the yield is not very good, but increasing the pressure may improve the yield.

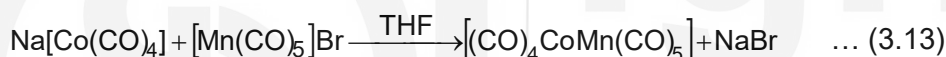
Methods of preparation of polynuclear carbonyls depend on the particular metal. Eq. 3.11 gives the method of photolysis (irradiation with ultraviolet (UV) light) of the lower metal carbonyl $\text{Fe}(\text{CO})_5$ in glacial acetic acid whereby the higher metal carbonyl $\text{Fe}_2(\text{CO})_9$ is obtained.



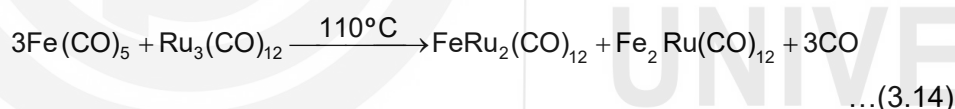
Photolysis of $\text{Os}(\text{CO})_5$ with UV light gives $\text{Os}_3(\text{CO})_{12}$



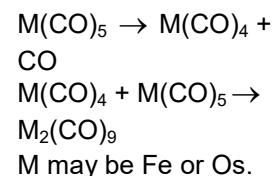
Heteronuclear carbonyls may be synthesised by methods as depicted in Eq. 3.13 and 3.14. In Eq. 3.13 an anionic metal carbonyl reacts with a metal carbonyl halide of a different metal and forms a heteronuclear metal carbonyl incorporating both the metals.



Eq. 3.14 show the formation of heteronuclear metal carbonyl by heating a mixture of two metal carbonyls in the appropriate temperature whereby there is loss of carbon monoxide.



The reaction in Eq. 3.11 may take place in two steps:



SAQ 2

- Give the reaction for the photolysis of osmium pentacarbonyl.
- Give two examples of preparation of metal carbonyls by reductive carbonylation.

3.4 STRUCTURE (BASED ON VALENCE BOND APPROACH) AND PROPERTIES

In this section you are going to study the structure of metal carbonyls based on valence bond approach. Look at Fig. 3.1, where the valence bond representations of CO and the MCO fragment are given.

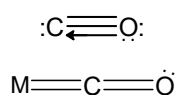


Fig. 3.1: Valence bond representations of CO and the MCO fragment.

The valence bond theory involves the concept of hybridization. The carbon and oxygen atoms in CO are sp hybridized with the following electronic configurations;

$$\text{C (ground) state} = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$$

$$\text{C (hybridized state)} = 1s^2, (sp_x)^2, (sp_x)^1, 2p_y^1, 2p_z^0$$

$$\text{O (ground state)} = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^2$$

$$\text{O (hybridized state)} = 1s^2, (sp_x)^2, (sp_x)^1, 2p_y^1, 2p_z^2$$

The σ bond is formed from the overlap of one half-filled sp_x -hybridized orbital of carbon atom and half-filled sp_x -hybridized orbital of the oxygen atom, while sp_x -hybridized lone pairs on both atoms remains non-bonding in nature. As shown in Fig.3.2, apart from this, the sidewise overlap of the orbitals which are namely the half filled $2p_y$ orbitals, and the dative or coordinative interaction of fully filled $2p_z$ orbital of oxygen with empty $2p_z$ orbitals of carbon result in two π bonds between.

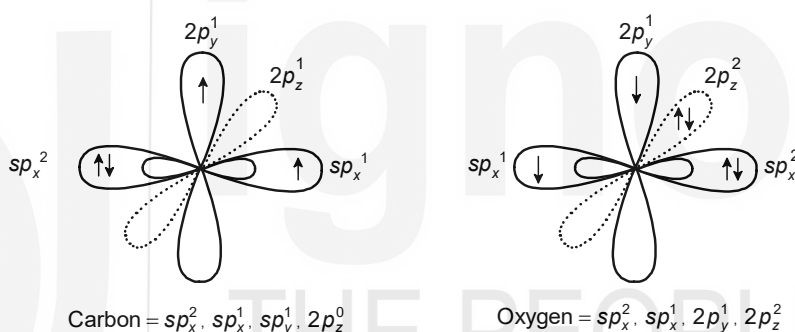


Fig. 3.2: Orbitals of C and O atoms.

Hence according to this model, the bonding within the CO molecule can be described as shown in Fig.3.3 below:

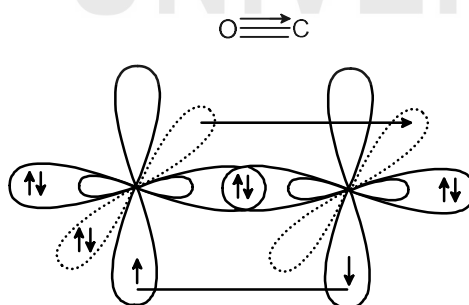


Fig. 3.3: Bonding within the CO molecule

Now, let us look at the metal-carbonyls where the central metal atom or ion furnishes the required number of empty hybrid orbitals to give the suitable orientation required to accept the electron pair from surrounding ligands. For example, in $[\text{Cr}(\text{CO})_6]$ the chromium atom undergoes a d^2sp^3 hybridization and furnishes six empty hybrid orbital of equivalent shapes and the same energy.

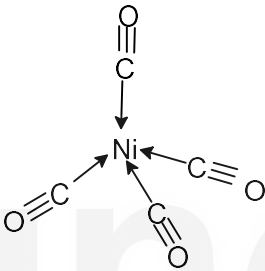
We start with the simplest carbonyls, that is the monomeric carbonyls. They have symmetrical structures with linear M-C-O links. In all the structures the CO ligands similar to the electron-pair in the VSEPR theory (BCHCT-131,

Unit-7) take the most distance positions. You can confirm the structures by various spectroscopic techniques.

VSEPR (Valence Shell Electron Pair Theory) predicts electrons which are confirmed by X-ray diffraction:

Ni(CO)_4 (Nickel tetracarbonyl) has the tetrahedral shape. It has linear Ni-C-O bonds, with the bond length of Ni-C equals to 150 pm, bond length of C-O equals to 115 pm (slightly longer than C-O in CO=112.8 pm). The tetrahedral shape is due to sp^3 hybridized nickel. The compound is diamagnetic with all the electrons being paired. The details of the structure of Ni(CO)_4 based on the valence bond approach is shown in Table 3.4.

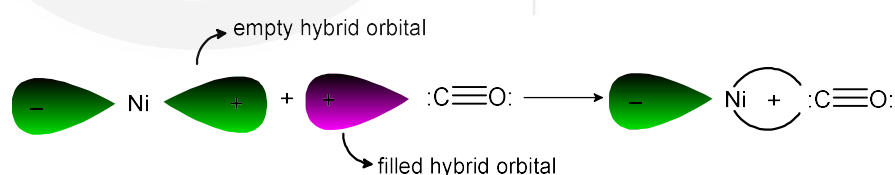
Table 3.4: Structure of Ni(CO)_4 based on Valence Bond approach

Ni atom	$3d$ ↑↓ ↑↓ ↑↓ ↑ ↑ $4s$ ↑↓ $4p$	 Fig. 3.4: Structure of Ni(CO)_4
	$3d$ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ $4s$ $4p$	
Ni(CO)_4	$3d$ ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ $4s$ xx $4p$ xx xx xx	

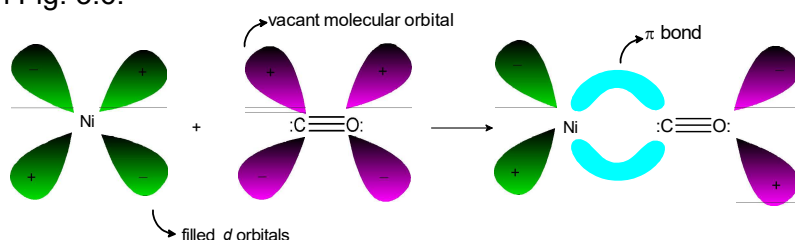
sp^3

xx denotes electron pair from CO

The empty sp^3 hybrid orbitals on Ni overlaps with filled orbital of CO forming Ni-CO σ bond as shown in Fig. 3.5.

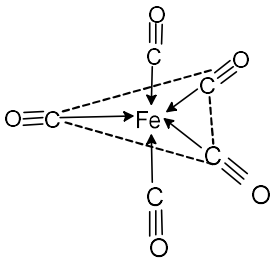


The negative charge on Ni which forms as a result of accumulation of electron density of σ bond formation is counterbalanced by formation of a back bond by overlap of filled orbitals of nickel with vacant π^* molecular orbital of CO as shown in Fig. 3.6.



$\text{Fe}(\text{CO})_5$ has TBP (trigonal bipyramidal) shape, the axial and equivalent bond lengths are marginally different as shown by X-ray diffraction. The details of the structure of $\text{Fe}(\text{CO})_5$ based on valence bond approach is given in Table 3.5.

Table 3.5: Structure of $\text{Fe}(\text{CO})_5$ based on valence bond approach

Fe	3d ↑↓ ↑ ↑ ↑ ↑ 4s ↑↓ 4p	 Fig. 3.7: Structure of $\text{Fe}(\text{CO})_5$
Fe in $\text{Fe}(\text{CO})_5$	3d ↑↓ ↑↓ ↑↓ ↑↓ 4s 4p	
$\text{Fe}(\text{CO})_5$	3d ↑↓ ↑↓ ↑↓ ↑↓ xx 4s xx 4p xx xx xx	

Rearrangement

dsp^3

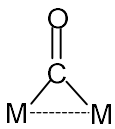
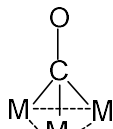
xx denotes electron pair from CO

Similarly it can be shown that $\text{Cr}(\text{CO})_6$ has octahedral structure. As CO groups bring electrons in pairs it is clear that when the metal has odd number of octahedral structure any mononuclear species will have an unpaired electron.

Binuclear Carbonyls.

These are characterized by presence of M-M bond. the CO ligand can fulfill three different structural functions and has three bonding modes each recognized by a characterized ν_{CO} stretching frequency and these are compiled in Table 3.6.

Table 3.6: Details of ν_{CO} stretching frequencies of metal carbonyls.

	$\text{O} \equiv \text{C}$	$\text{O} \equiv \text{C} \rightarrow \text{M}$		
	Free	Terminal μ_1	μ_2 -Doubly bridging (ketonic)	μ_3 -Triply bridging
ν_{CO} IR (cm^{-1}) (for neutral metal complexes)	2143	2120 - 1850	1850-1750	1730 - 1620

This is a useful distinction even though there are numerous borderline cases. In carbonyl anions, where because of extensive back bonding, the stretching frequency may fall below 1800 cm^{-1} although all carbonyl ligands are terminal. Terminal carbonyl groups are most common in binuclear carbonyls.

$\text{Mn}_2(\text{CO})_{10}$ has a structure composed of two staggered $\text{Mn}(\text{CO})_5$ units linked by an Mn–Mn bond. The Mn–Mn bond distance is 279 pm. Each Mn atom is linked to another Mn and 5 CO groups. There is no bridging carbonyl groups in between the two Mn atoms. The compound is diamagnetic, each Mn atom has coordination number 6 and is d^2sp^3 hybridised. The details of structure of $\text{Mn}_2(\text{CO})_{10}$ based on valence bond approach is given in Table 3.7.

Table 3.7: Structure of $\text{Mn}_2(\text{CO})_{10}$ based on valence bond approach

Free Mn atom	3d	4s	4p	Structure as in Fig. 3.8.
	$\uparrow \uparrow \uparrow \uparrow \uparrow$	$\uparrow\downarrow$	$\square \square \square$	
One Mn atom in $\text{Mn}_2(\text{CO})_{10}$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \times \times$ Mn-Mn bond $\uparrow$	$\times \times$	$\times \times \times \times \times \times$	
Another Mn atom in $\text{Mn}_2(\text{CO})_{10}$	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \downarrow \times \times$ d^2sp^3	$\times \times$	$\times \times \times \times \times \times$	

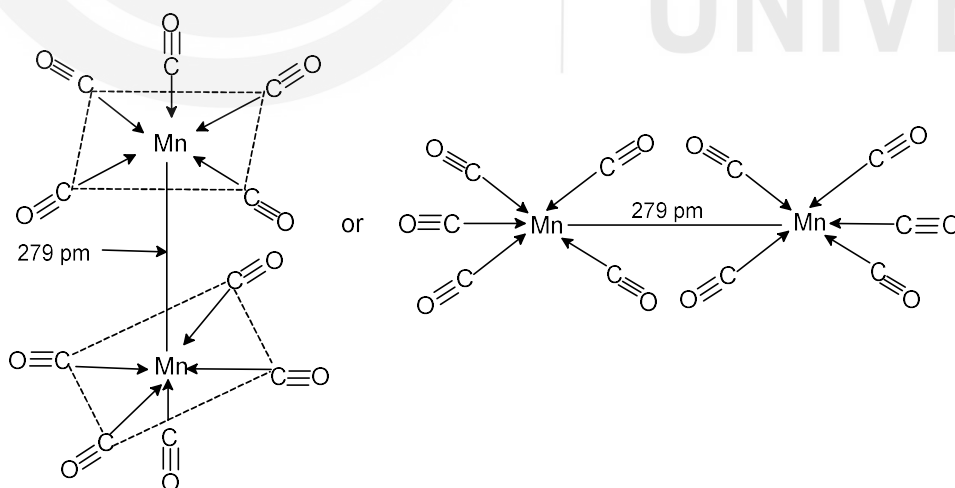
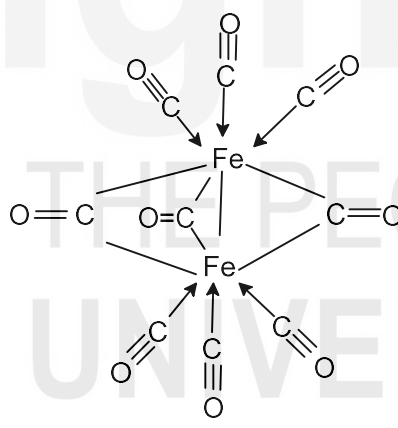


Fig. 3.8: Structure of $\text{Mn}_2(\text{CO})_{10}$ molecule. This structure in its simplified form is shown at the right hand side.

$\text{Fe}_2(\text{CO})_9$ has both bridging terminal CO groups. the molecule is diamagnetic and has short Fe-Fe distance indicating Fe-Fe bond (δ bond) (246 pm). Each Fe atom in linked to 3 bridging CO groups ($>\text{C}=\text{O}$) by a σ bond and 3 terminal CO groups coordinate bond. The bridging bonds are longer than terminal

bonds and coordination number of Fe is 7. The details of structure of $\text{Fe}_2(\text{CO})_9$ based on valence bond approach is given in Table 3.8.

Table 3.8: Structure of $\text{Fe}_2(\text{CO})_9$ based on valence bond approach

Fe	3d	4s	4p	Structure as in Fig. 3.9.
	$\uparrow\downarrow \uparrow \uparrow \uparrow \uparrow$	$\uparrow\downarrow$	$\square \square \square$	
One Fe in $\text{Fe}_2(\text{CO})_9$	3d	4s	4p	
	$\uparrow\downarrow \uparrow\downarrow \uparrow \uparrow \times \uparrow \times$	$\uparrow \times$	$\times \times \times \times \times \times$	
Another Fe in $\text{Fe}_2(\text{CO})_9$	3d	4s	4p	
	$\uparrow\downarrow \uparrow\downarrow \uparrow \times \uparrow \times$	$\uparrow \times$	$\times \times \times \times \times \times$	

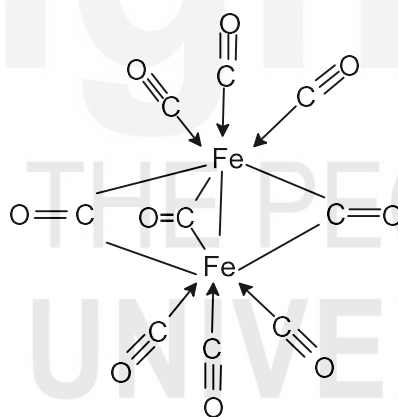


Fig. 3.9: Structure of $\text{Fe}_2(\text{CO})_9$

$\text{Co}_2(\text{CO})_8$ is an orange-brown crystalline solid soluble in alcohol, ether and CCl_4 . In solution the compound exists in two isomeric form, one having a bridged structure (Fig. 3.10a) and the other a non-bridged structure (Fig. 3.10b). The two isomers are in equilibrium with each other and are diamagnetic. X-ray structure of the crystal indicates a bridged structure in the solid state.

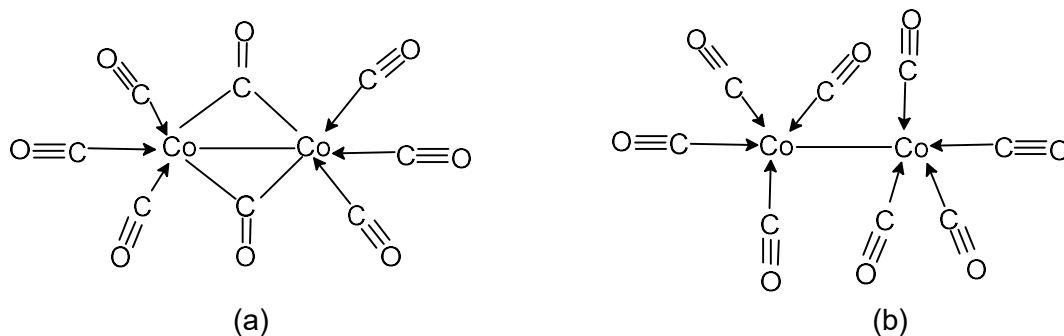


Fig. 3.10: Isomers of $\text{Co}_2(\text{CO})_8$

The total electrons can be counted in both structures as shown below:

Co	9 e ⁻
3 μ_1 CO	6 e ⁻
2 μ_2 CO	2 e ⁻
1 Co-Co	1 e ⁻
Total Number of electrons	18 e ⁻

Co	9 e ⁻
4 μ_1 CO	8 e ⁻
Co-Co	8 e ⁻
Total Number of electrons	18 e ⁻

The bridged structure Fig. 3.10a has 2 bridging CO groups; 3 terminal CO groups and Co-Co bond. Each Co atom is linked to another Co, 3 terminal and 2 bridging CO groups giving a coordination number of 6 indicating d^2sp^3 hybridization. The details of these are given in Fig. 3.10 and Table 3.9.

Table 3.9: Structure of $\text{Co}_2(\text{CO})_8$ based on valence bond approach

Free Co	3d	4s	4p
	$\uparrow\downarrow \uparrow\downarrow \uparrow \uparrow \uparrow$	$\uparrow\downarrow$	$\square \square \square$
One Co in $\text{Co}_2(\text{CO})_8$	3d	4s	4p
	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \uparrow$	xx	xx xx xx
	Co-Co bond		
Another Co in $\text{Co}_2(\text{CO})_8$	3d	4s	4p
	$\uparrow\downarrow \uparrow\downarrow \uparrow\downarrow \uparrow \downarrow$	xx	xx xx xx
	d^2sp^3		

3 vacant d^2sp^3 hybrid orbitals on each Co atom accept a lone pair of electrons donated by terminal CO groups forming 3 Co-CO bonds. Six such bonds are formed. One of the singly filled d^2sp^3 hybrid orbitals on one Co atom combines with another such orbital on another Co atom forming Co-Co bond. The remaining two singly filled hybrid orbitals on each Co accept one electron from bridging carbonyl groups. The non-bridged structure has one Co-Co bond and eight terminal carbonyl groups.

So in this section we have discussed the structures of various metal carbonyls and their relevant properties. Before going to the next section, please try the following SAQ.

SAQ 3

- Give the structure with valence bond approach for $\text{Fe}(\text{CO})_5$.
- How can you predict the number of metal-metal bonds in the isomers of $\text{Co}_2(\text{CO})_8$ assuming that it obeys 18 electron rule?

3.5 PROPERTIES OF MONONUCLEAR AND POLYNUCLEAR CARBONYL OF 3d METALS

This section will introduce you to the different properties of mononuclear and polynuclear carbonyls of 3d metals. Let us first discuss the physical properties. With the exception of mononuclear carbonyls of the iron group and $\text{Ni}(\text{CO})_4$, all known carbonyls are solids. Apart from $\text{V}(\text{CO})_6$ which is black green in colour, the mononuclear carbonyls are colourless and polynuclear carbonyls are coloured, where the colour becomes darker with increase in number of metal atoms. $\text{Fe}(\text{CO})_5$ is colourless (in some cases pale yellow) liquid, $\text{Fe}_2(\text{CO})_9$ forms golden yellow plates and $\text{Fe}_3(\text{CO})_{12}$ is very dark greenish black. Due to their covalent nature they are insoluble in water but soluble in organic solvents, like CCl_4 . Apart from $\text{V}(\text{CO})_6$ they are all diamagnetic.

Mononuclear metal carbonyl compounds take highly symmetric polyhedral coordination structures. Hexa-coordinate chromium, molybdenum, and tungsten hexacarbonyl, $\text{M}(\text{CO})_6$, assume a regular octahedral, penta-coordinate pentacarbonyliron, $\text{Fe}(\text{CO})_5$, a triangular bipyramid, and tetracarbonylnickel, $\text{Ni}(\text{CO})_4$, a regular tetrahedron coordination structure. The carbon atoms of carbonyl ligands coordinate to the metal, and the carbonyl moieties are oriented along the direction of the metal-carbon axis. Binuclear metal carbonyl $\text{Mn}_2(\text{CO})_{10}$ has an Mn-Mn bond joining two square pyramidal $\text{Mn}(\text{CO})_5$ parts (as shown in Fig. 3.8). In $\text{Fe}_2(\text{CO})_9$, two $\text{Fe}(\text{CO})_3$ sub-units are bridged by three carbonyl ligands (as shown in Fig. 3.9), and in $\text{Co}_2(\text{CO})_8$, two $\text{Co}(\text{CO})_3$ sub-units are connected by both three CO bridges and a Co-Co bond (as shown in Fig. 3.10).

There are a number of cluster metal carbonyl compounds with metal-metal bonds joining three or more metals, and terminal CO, μ -CO (a bridge between two metals), and μ_3 -CO (a bridge capping three metals) are coordinated to the metal frames. Many cluster carbonyls are formed by a pyrolysis reaction of mononuclear or binuclear carbonyl compounds. Typical metal carbonyl compounds and their properties are shown in Table 3.10.

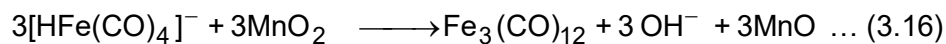
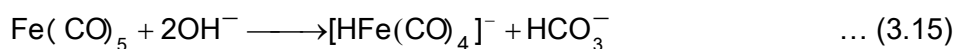
Table 3.10 : Metal carbonyl compounds and their properties

	5	6	7	8	9
4	$\text{V}(\text{CO})_6$ Black solid d.70°C	$\text{Cr}(\text{CO})_6$ White solid d. 90°C	$\text{Mn}_2(\text{CO})_{10}$ Yellow solid mp 154°C	$\text{Fe}(\text{CO})_5$ Yellow liquid bp 103°C	$\text{Co}_2(\text{CO})_8$ Red solid mp 51°C
5		$\text{Mo}(\text{CO})_6$ White solid sublime	$\text{Tc}_2(\text{CO})_{10}$ White solid mp 160°C	$\text{Ru}_3(\text{CO})_{12}$ Orange solid d.150°C	$\text{Rh}_6(\text{CO})_{16}$ Black solid d.220°C
6		$\text{W}(\text{CO})_6$ White solid sublime	$\text{Re}_2(\text{CO})_{10}$ White solid mp 177°C	$\text{Os}_3(\text{CO})_{12}$ Orange solid mp 221°C	$\text{Ir}_4(\text{CO})_{12}$ Yellow solid d.220°C

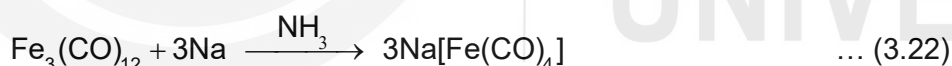
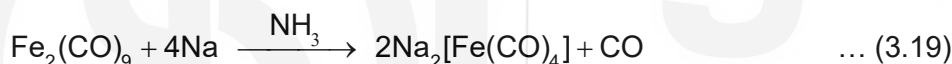
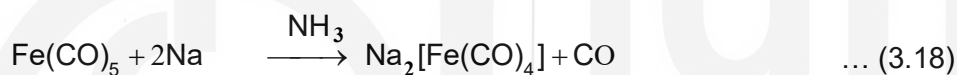
Next, you are going to learn about the chemical properties of metal carbonyls.

Reaction of carbonyls

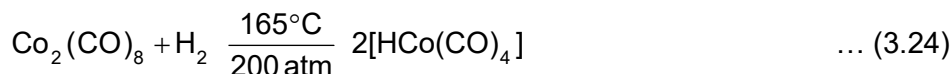
1. $\text{Fe}(\text{CO})_5$ when heated with alkali followed by oxidation with MnO_2 gives $\text{Fe}_3(\text{CO})_{12}$



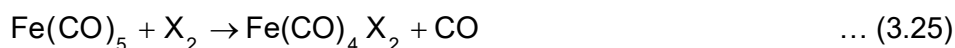
2. The most important reaction is formation of carbonylate anion by addition of alkali or reduction as shown in Eq. 3.17 to 3.22. If you look carefully in Eq. 3.17 you will see that the reaction of sodium hydroxide with a metal carbonyl is basically a nucleophilic attack by a hydroxide ion on the carbonyl group and thereby it gives a metal carboxylic acid complex, which further reacts with sodium hydroxide to form a hydrido anion.



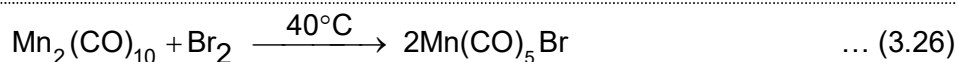
3. Formation of carbonyl hydrides takes place by reaction of metal carbonyls with H_2 is shown in Eq. 3.23 to Eq. 3.24.



4. Formation of carbonyl halides takes place by reaction of metal carbonyls with halogen. You will find the common reaction of metal carbonyls with halogens in Eq. 3.25 to 3.28.



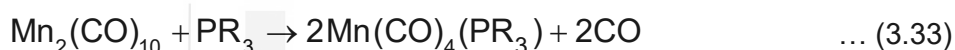
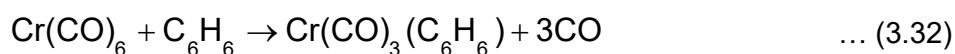
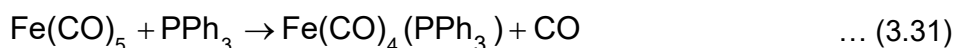
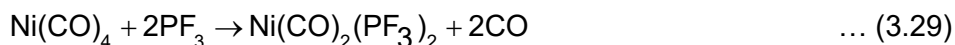
In Eq. 3.26, the halogen reacts to form lower carbonyl by causing cleavage in the metal-metal bond.



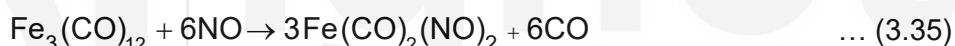
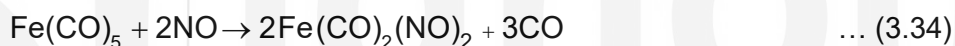
$\text{Co}_2(\text{CO})_8$ and $\text{Ni}(\text{CO})_4$ decompose in presence of halogens forming halides and is shown in Eq. 3.27 and Eq. 3.28.



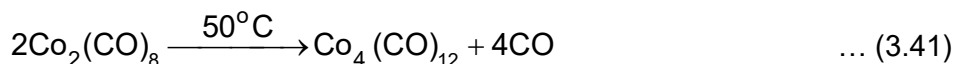
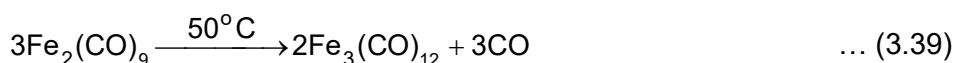
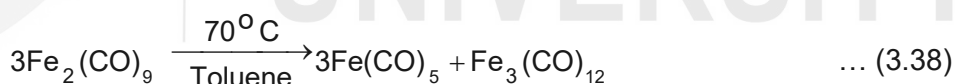
5. Displacement of CO by other ligands which are actually substitution reactions as shown in Eq. 3.29 to 3.33.



6. Formation of nitrosyl with NO take place as shown in Eq. 3.34 to 3.36.



7. Action of heat – This varies from case to case as shown in Eq. 3.37 to 3.42.



SAQ 4

- (i) Give the equation for formation of carbonyl hydrides with hydrogen for a carbonyl of cobalt.
-

- (ii) How can formation of nitrosyl complexes be formed from carbonyl complexes? Give any one suitable equation to show this.

3.6 SUMMARY

In this unit discussions about the EAN Rule and 18 Electron Rule as applied to carbonyls were done at first. Next the preparation of metal carbonyls through direct combination and reductive carbonylation were also taken up. The structure of metal carbonyls based on Valence Bond approach and properties were then discussed in detail. Lastly the properties of mononuclear and polynuclear carbonyl of 3d metals have been discussed. In the next unit you are going to learn more about the metal carbonyls.

3.7 TERMINAL QUESTION

1. Give the method of preparation of $\text{Fe}(\text{CO})_5$ from iron powder.
2. Show that $\text{Fe}_3(\text{CO})_{12}$ obeys 18 electron rule.
3. Explain the structure of $\text{Fe}_2(\text{CO})_9$ based on valence bond approach.
4. What is the carbonylate anion? Give any two reactions where its formation takes place from metal carbonyls.

3.8 ANSWERS

Self Assessment Questions

1. i) Let number of electrons on M = n $\therefore$ $2M = 2n$ electrons

M-M bond = 2 electrons

9 CO = 18 electrons

$$2n + 2 + 18 = 36 \quad 2n = 16 \therefore n = 8$$

As metal is in zero oxidation state it is Fe.

- ii) $\text{Fe}_3(\text{CO})_{12}$ Let number of Fe-Fe bonds = x ; each bond involve 2 electrons from Fe-Fe bond = $2x$

3 Fe	24 e^-
12 CO	24 e^-
electrons from Fe-Fe bonds	$2x$
Total number electrons	$24 + 24 + 2x = 54$
	$2x = 6 \therefore x = 3$

For $\text{Co}_4(\text{CO})_{12}$, similarly we can say,

4 Co	$(4 \times 9) e^-$
12 CO	24 e^-

electrons from Co-Co bonds	$2x$
Total number electrons	$36 + 24 + 2x = 72$
	$2x = 12 \therefore x = 6$

iii) Fe has 8 electrons. So we see,

$$8 + (2 \times 4) + x = 18 \therefore x = 2$$

$$= \text{Charge is } -2, [\text{Fe}(\text{CO})_4]^{2-}$$

2. i) Eq. 3.12

ii) Reductive carbonylation involves the reduction of a metal salt in presence of a reducing agent. The reducing agents may be Mg, Ag etc. Eq. 3.4 to 3.9 are examples. (any two examples with equations may be given)

3. i) $\text{Fe}(\text{CO})_5$ is TBP (details as in Table 3.5)

ii) $\text{Co}_2(\text{CO})_8$ has one metal-metal bond assuming it obeys 18 electron rule (calculations given below Fig. 3.10.)

4. i) Eq. 3.24

ii) Any equation, from Eq. 3.34 to Eq. 3.36

Terminal Questions

1. Eq. 3.1

2. Refer to Table 3.5. and extend it to $\text{Fe}_3(\text{CO})_{12}$.

3 Fe	3×8	$24 e^-$
12 CO	12×2	$24 e^-$
Total electron count		48

$$\begin{array}{lcl} \text{So number of metal-metal bonds (Fe-Fe) must be} & \rightarrow & 3 \times 2 = 6 \\ \text{Total electron count} & & 54 e^- \end{array}$$

Therefore 18 electron per Fe atom

3. Table 3.7

4. Carbonylate anion is the anion which has carbonyl (CO) in it. It is formed as shown in Equations. 3.17 to 3.22.

UNIT 4

METAL CARBONYL COMPOUNDS-II

Structure

4.1	Introduction	4.3	Use of IR Stretching Frequency Data(as evidence for Synergic Effect)
	Expected Learning Outcomes		
4.2	Bonding, π -acceptor Behaviour of Carbon Monoxide	4.4	Summary
	Synergic Effects (MO Diagram of CO)	4.5	Terminal Questions
		4.6	Answers

4.1 INTRODUCTION

You were introduced to metal carbonyl compounds in the previous unit. In this unit you will learn more about these compounds, the bonding in metal carbonyls will be discussed with reference to the molecular orbital diagram of carbon monoxide. You will learn about the π acceptor behavior of carbon monoxide and the concept of synergic effect. A brief introduction will be given to the use of IR stretching frequency data as an evidence to synergic effect.

Expected Learning Outcomes

After studying this unit you should be able to:

- ❖ understand bonding, π -acceptor behaviour of carbon monoxide with reference to MO diagram of CO;
- ❖ explain synergic effects; and
- ❖ understand the use of IR stretching frequency data(as evidence for synergic effect).

4.2 BONDING, π -ACCEPTOR BEHAVIOUR OF CARBON MONOXIDE

Bonding in Carbonyl Compounds

As mentioned earlier, the nature of the bonding between carbon monoxide and a transition metal is interesting. This bonding is also the reason why so many transition metal carbonyl compounds exist, why they are so stable, why they can exist in low oxidation states, and why main group carbonyls are very rare. Thus, we need to look at the bonding between transition metals and carbon monoxide in some detail.

In the previous course, BCHCT 131, Unit 9, you have learnt that the bonding in heteronuclear diatomic molecules can be shown with the help of a molecular orbital diagram. Because the effective nuclear charge differs between the constituent atoms, the orbital energies are lower for the atom with the higher effective nuclear charge. Fig. 4.1 shows a simplified molecular orbital diagram for the carbon monoxide molecule (a more sophisticated representation would mix in some 2s component to the bonding).

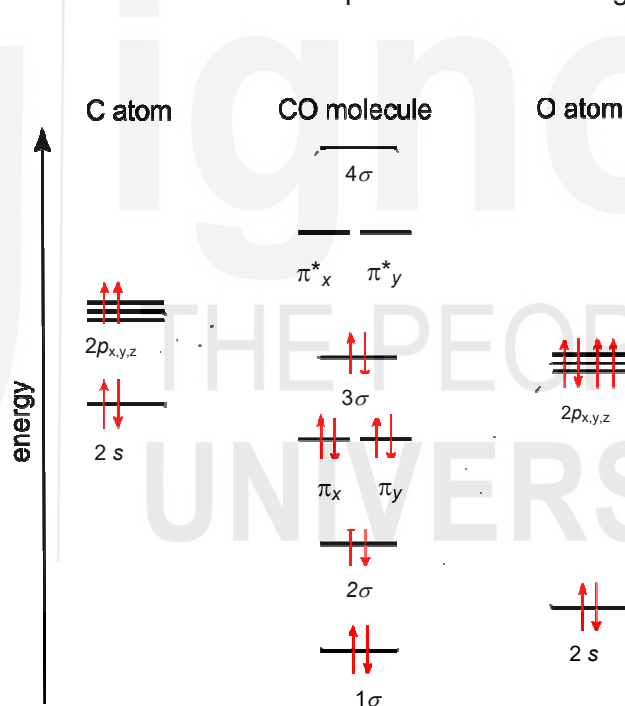


Fig. 4.1 : Molecular energy level scheme for CO.

For the carbon monoxide molecule, the highest-energy occupied molecular orbital (HOMO) is a σ_{2p} orbital essentially derived from the high-energy 2p carbon and oxygen atomic orbitals. We assume this orbital resembles a lone pair on the carbon atom. The lowest-energy unoccupied molecular orbitals (LUMOs) are the π^*_{2p} antibonding orbitals. Oxygen has a greater effective nuclear charge than carbon so the atomic orbitals of oxygen are lying much deeper than those of the carbon atoms. As a result oxygen atoms contribute more to the charge for the bonding MOs. But the carbon atom has more contribution towards the antibonding molecular orbitals. You can see from the MO energy level diagram in the Fig. 4.1 that the bonding MOs are all occupied fully and result in triple bond to the carbon monoxide molecule. There is one lone pair available in the carbon atom which may be donated to the metal

centre. Again, the predominant contribution comes from the $2p$ atomic orbitals of carbon, so they too, are focused around the carbon rather than around the oxygen atom. Approximate shapes of these orbitals are shown in Fig. 4.2.

In Fig. 4.2 you can see the overlap of the end of the σ HOMO of the carbon monoxide with an empty d orbital of the metal; that is, the carbon monoxide is acting as a Lewis base and donating a pair of electrons to the metal that acts as a Lewis acid. This donation of electron density is through carbon as the HOMO is a carbon like orbital.

This leads to high electron density on the metal. Imagine six ligands simultaneously donating electrons to a metal centre, which, if is in a low oxidation state, will already be electron rich. Six CO ligands are simultaneously donating electrons to a metal via the overlap of the HOMO of CO with an empty d or hybrid orbital of the M. This leads to formation of σ bond between M and CO. Thus there is need to delocalize this electron density. This simultaneous bonding is called 'back bonding' or synergic bonding. This is achieved by an overlap of a filled d orbital on the metal with the π^* LUMO of the carbon monoxide (Fig. 4.1). These two orbitals have the correct symmetry to allow this interaction, and thus the electron density is removed from the metal centre back onto the carbonyl ligand to some extent. This results in charge transfer. This additional bond is a $d\pi-p\pi$ bond. So, the carbon monoxide is said to be a σ donor and a π acceptor, and the metal is a σ acceptor and a π donor. Thus, there would be a flow of electrons from the carbon monoxide to the metal through the σ system and a flow (back bonding or synergic bonding) through the π system in the reverse direction. This synergic effect leads to a strong, short, almost double covalent bond between the metal and carbon atoms.

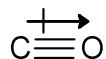
According to this representation of the bonding, electrons would be "pushed" into the π antibonding orbital of the carbon monoxide. An increased occupancy of antibonding orbitals would lead to a reduction of the bond order below its value of three in the free carbon monoxide molecule. Experimental measurements have shown that, indeed, the carbon-oxygen bonds in these carbonyl compounds is longer and weaker than that in carbon monoxide itself (discussed in detail in Sec. 4.3). This is good evidence for the validity of the molecular orbital bonding model. As added evidence, nearly all stable neutral metal carbonyl compounds are found in the middle transition metal groups (Groups 6 to 9), where the metal has some d electrons available for donation into the carbonyl π system but few enough that other d orbitals remain empty and capable of accepting electron pairs from carbonyl ligands.

Other ligands can bond to transition metals in this way, for example, alkenes and phosphines, but they are not as good π acceptors as carbon monoxide.

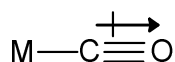
Metal atoms in metal carbonyls have low oxidation states which may be negative, zero or low positive. Then how do the metal carbonyls remains stable in such low oxidation states? Well, it is due to the concerted bonding effect which actually involves a sigma bond between the metal and carbon. This sigma bond is formed by the overlap of sp hybrid orbital of carbon and a vacant orbital of the metal atom. So sp^3 hybrid orbital of Ni in $Ni(CO)_4$, dsp^3 hybrid orbital of $Fe(CO)_5$ and d^2sp^3 hybrid orbital of Cr in $Cr(CO)_6$ has this type

of bonding. Simultaneously, π bonds are formed when the filled d orbitals of the metal atoms overlap with the vacant antibonding orbitals of CO groups. this sort of bonding is illustrated in the Figs. 4.2a and 4.2b.

Next, you see that in free CO, the electrons are polarized in the direction of the more electronegative oxygen. It is found that, the electrons in the π orbitals are concentrated in the vicinity of the oxygen atom and not of the carbon.



When transition metal cation is there with CO, it reduces the polarization in the C-O bond as it attracts the bonding electron.



So the electrons in the positively charged complex are more equally shared by the carbon and the oxygen. This results in a stronger bond and so the C-O stretch is in higher-energy.

Simple carbonyl contains terminal CO groups which bonds through C and not O. You should note that, it behaves as electron pair donor and acceptor through C and not O despite O being more electronegative. CO is a σ donor Lewis base and also a π acceptor Lewis acid. The σ donation from $\text{L} \rightarrow \text{M}$ and π back donation from $\text{M} \rightarrow \text{L}$ is together known as synergic. Spectroscopic study indicated that CO is present as a part of the molecule. However, polynuclear carbonyls may contain bridging CO. In carbonyls, the sigma bonding is reinforced by additional σ bonding which stabilizes complexes and very low oxidation states of metal. Many carbonyl compounds have metal in a zero oxidation state. The very low oxidation states are not found with sigma-bonding ligands such as H_2O and NH_3 .

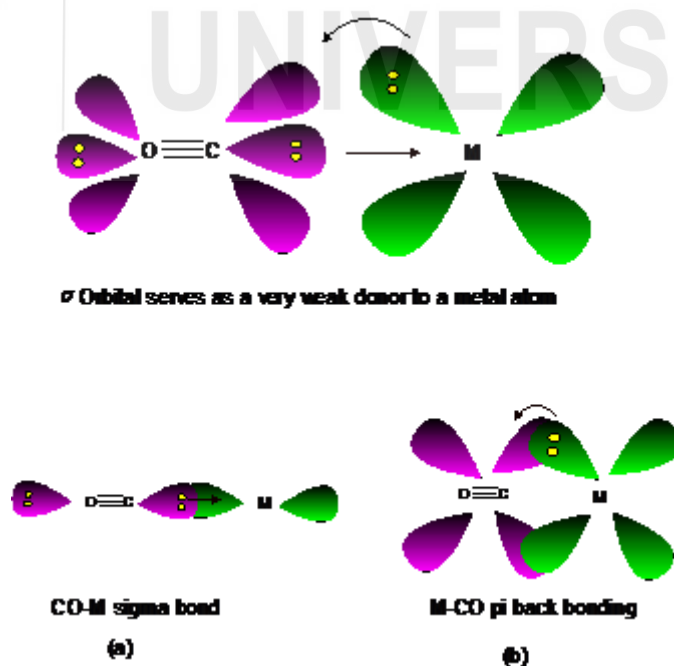


Fig. 4.2: Synergic bonding in metal carbonyls.

The resulting covalent bond between metal and carbon atoms is not only strong, short but almost double.

SAQ 1

- i) What is synergic effect with respect to carbon monoxide?
 - ii) What may be a very good evidence that the MO bonding model of CO holds good.
 - iii) In CO, which is the HOMO and which is the LUMO?
 - iv) Why does the filled d orbital on the metal overlap with the π LUMO of the carbon monoxide for metal-carbonyl complexes.
-

4.3 USE OF IR STRETCHING FREQUENCY DATA (AS EVIDENCE FOR SYNERGIC EFFECT)

In this section, you are going to learn about use of IR stretching frequency data as an evidence for synergic effect. It is easier to obtain IR spectra and are useful to follow reactions.

Evidence for Synergic Bonding

Infrared spectroscopy is a useful tool for investigating the structures of carbonyl compounds. The stretching frequency of the (carbon-oxygen) $C \equiv O$ bond vibrates around 2143 cm^{-1} in the gaseous state. The vibration frequency in carbonyl compounds lies within the range $2100\text{--}1700\text{ cm}^{-1}$, depending on the structure and nature of other ligands present. This region is not having bands that arise from organic groups.

Now, let us see if we can validate the synergic bonding model with the help of IR spectroscopy. If such a bonding exists then the length and strength of the $C - O$ bond should change as electrons are placed into the π^* orbital. This makes the bond weaker and longer and it should vibrate at a lower frequency. The same is observed experimentally too, the $C \equiv O$ bonds in carbonyl compounds do vibrate at lower frequencies than gaseous carbon monoxide does. This gives evidence for synergic bonding.

Here you should note that the $C-O$ stretching frequency is very sensitive to the electronic environment around the metal. Take the case of a metal carbonyl where high electron density is localized on the metal. This will lead to an increase in the extent of the back bonding as this will reduce the electron density. There after electron density in the π^* orbital increases. This results in decrease in bond order and thereby increase in bond length which causes a decrease in the $C-O$ stretching frequency.

Next, look at the IR stretching frequencies of the following complexes:

$[Ni(CO)_3PMe_3]$ 2064 cm^{-1}

$[Ni(CO)_3PPh_3]$ 2069 cm^{-1}

$[Ni(CO)_3PF_3]$ 2111 cm^{-1}

The methyl groups on PMe_3 show a positive inductive effect in the first of the three complexes given above. An inductive effect is the shifting of electrons in

a bond in response to the electronegativity of nearby atoms. In this case, electron density will be towards the metal, thus back bonding increases and forms stronger M-C bonds. Thus a weaker C-O interaction results and lower infrared stretching frequency takes place. By contrast, fluorine in PF_3 is electron withdrawing and will remove electron density from the metal. This leads to a reduction in the extent of back bonding required, and so the C-O bond remains stronger and shorter, indicated by the higher stretching frequency.

Now let us remember some facts regarding effective nuclear charge here. For multielectron atoms, where the ns orbitals, which penetrate most, have the highest increase in effective nuclear charge. So, the energy of ns orbitals drops much below the corresponding energies of the np or the nd atomic orbital. But, the situation changes when the $3d$ orbitals get filled up with some electrons. The $4s$ orbital occupies much space so it is far more penetrating than the $3d$ orbital. Thus the effect of the positive nuclear charge is much more in $4s$ than that of $3d$ and the energy of $4s$ orbital falls and it becomes more stable than that of $3d$.

Next, look at the carbonyls of Ni, Co and Fe given in Table 4.1. The central metal in all of these species has eight d electrons. However, the effective nuclear charge increases from iron to nickel (you have already studied these in previous course BCHCT 137, Units 1 & 2). Thus the residual negative charge of the metal is greater for iron than for nickel. As the negative charge on the complex increases, the metal has a higher electron density to give away and so the back bonding is increased. As a result, the electron density in the π^* will be increased, and the bond between the carbon and oxygen weakens and vibrates at a lower frequency.

Look at Table 4.1, where the infrared stretching frequencies of the isoelectronic and isostructural species like Ni(CO)_4 , $[\text{Co(CO)}_4]^-$ and $[\text{Fe(CO)}_4]^{2-}$ are given. The overall negative charge may be residing only on the metal. With increasing negative charge the electron density may be transferred much more easily from M to π^* orbital of CO. So the M-C bond order increases in the direction $\text{Ni-C}(1.33) < \text{Co-C}(1.89) < \text{Fe-C}(2.16)$. At the same time the C-O bond order decreases in the direction as shown in Table 4.2. As you learnt that back bonding depends very much on the electron density of the metal. So we can also predict the electronic characteristics of the metal centre. Extensive back bonding lowers the C-O bond order and thereby the C-O stretching frequency whereas for the positively charged complex, the opposite happens as shown in Table 4.1. In Table 4.1, you can see that IR stretching frequency changes when we move from Cr(CO)_6 to Ni(CO)_4 . This is because the structure changes from octahedral to tetrahedral.

Now let us observe what happens to the IR stretching frequencies in polynuclear carbonyls. Let us take the example of the neutral carbonyls where the IR stretching frequency ranges are $1800\text{--}1900\text{ cm}^{-1}$ for bridging CO and $1950\text{--}2150\text{ cm}^{-1}$ for terminal COs. A specific example can be taken for $\text{Co}_2(\text{CO})_8$ in the solid state where it shows IR stretching bands at 1857, 1886, 2001, 2031, 2044, 2059, 2071 and 2112 cm^{-1} . Even the C-O bond lengths are different for the two types of bonding as shown in Table 4.3.

Table 4.1: Infrared Stretching Frequencies of Neutral and Anionic Carbonyl Complexes

Metal carbonyl	Ni(CO)_4	$[\text{Co(CO)}_4]^-$	$[\text{Fe(CO)}_4]^{2-}$
ν_{CO}	2046	1883	1788 cm^{-1}
Metal carbonyl	$[\text{Mn(CO)}_6]^+$	Cr(CO)_6	$[\text{V(CO)}_6]^-$
ν_{CO}	2090	2000	1860 cm^{-1}

Table 4.2: C-O bond order of Neutral and Anionic Carbonyl Complexes

Metal carbonyl	Ni(CO)_4	$[\text{Co(CO)}_4]^-$	$[\text{Fe(CO)}_4]^{2-}$
C-O bond order	2.54	2.14	1.85

Table 4.3: Bridging and terminal C-O bond lengths of Polynuclear Carbonyl Complexes

Bridging C-O (μ_2 -CO) bond length	1218 pm
Terminal C-O M-CO bond length	117 pm

From the above studies, what can you conclude for the cases in Table 4.4 where the metal oxidation decrease? Well, the metal-carbonyl $\nu_{\text{(M-C)}}$ stretching frequencies will increase as the metal oxidation state decrease.

Table 4.4: Stretching frequencies of carbonyls

Metal carbonyl	$[\text{Mn(CO)}_6]^+$	Cr(CO)_6	$[\text{V(CO)}_6]^-$
$\nu_{\text{M-C}}$	416 cm^{-1}	441 cm^{-1}	460 cm^{-1}

The conclusions arrived at, on the effect of formal positive charge on the metal atom, is that there is no change in the strength of σ -bond between the carbon and oxygen as well as the meta and carbon. It is only the π -electron or π -electron density that is altered. It has been observed that the metal-carbon force constants in isoelectronic Re(CO)_6^+ and W(CO)_6 are almost equal, 2.76 and 273 m dyne/pm. The carbonyl stretching frequencies for the complexes are shown in Table 4.5, which are consistent with the above argument. But the near equality in M-C force constants in the hexacarbonyl suggest, and loss in π -bonding is compensated by improved σ -donation.

Table 4.5: Stretching frequencies of different carbonyls

	$[\text{Re(CO)}_6]^+$	Co(CO)_6
$\nu_{\text{C-O}}$	2085 cm^{-1}	1978 cm^{-1}

While actually obtaining an IR spectra of a metal carbonyl, remember to take it in the vapour phase or in a non-interacting solvent such as hexane. This is because the medium does affect the number of bands and their width. Also, if the sample is in solid phase (eg. a KBr pellet), possibilities of intermolecular

vibrational coupling or pressure-induced molecular distortion may take place along with splitting of the bands.

You will be studying the basic principles of IR in Unit 11 of this course and its applications in small organic molecules in the Unit 12. Here we will now look at some sample IR spectra for simple metal carbonyls and try to conclude their structures from them. Look at the Fig. 4.3. How can the structure of solid $\text{Fe}_2(\text{CO})_9$ be inferred? You can see that the IR spectrum of $\text{Fe}_2(\text{CO})_9$ has strong bands in both the terminal and bridging regions. So it can be said that there are both types of CO groups in it, which is confirmed by X-ray studies.

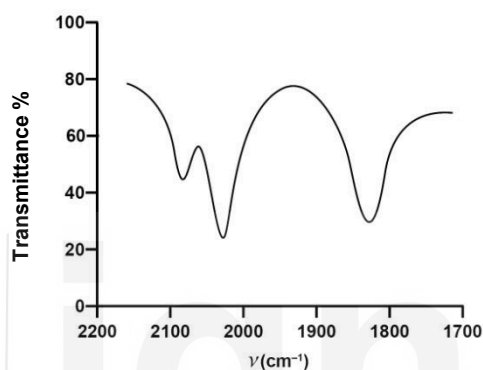


Fig. 4.3: The IR spectrum of $\text{Fe}_2(\text{CO})_9$

Next, let us look at the sample IR spectra given below in Fig. 4.4. There are two high-frequency terminal CO stretches and the bridging CO ligands has absorption in the lower frequency. But the two bridging CO groups are almost in the same line and thus a single band is observed even though the complex has a low symmetry and should have give two bands for the two bridging CO.

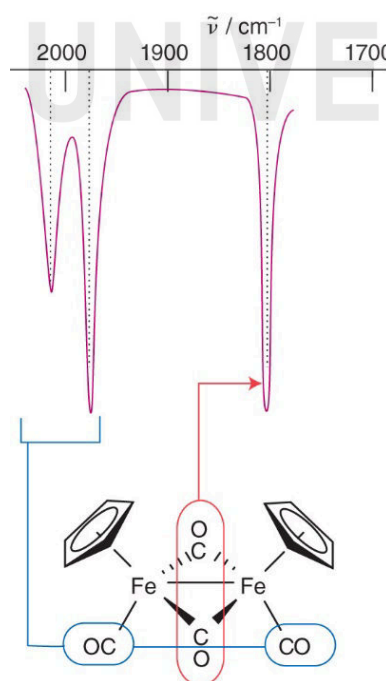
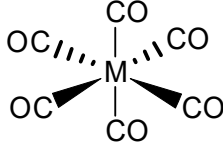
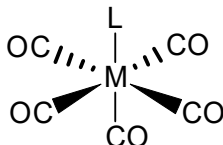
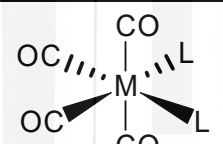
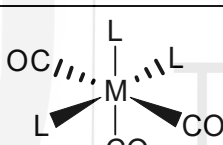
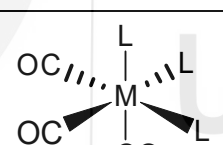
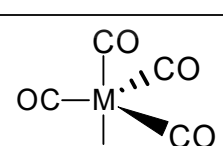
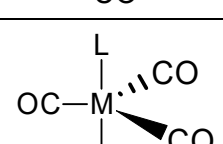
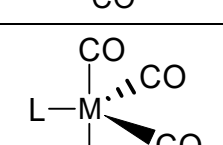
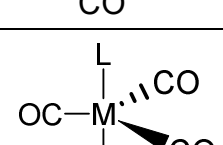


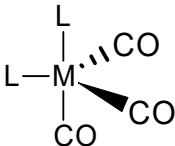
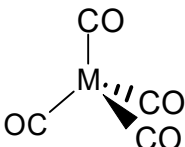
Fig. 4.4: The IR spectrum of $\text{Fe}_2(\text{Cp})_2(\text{CO})_4$

In Table 4.6 is given the relation between the structure of a carbonyl complex and the number of CO stretching bands in its IR spectrum.

The number of IR bands expected in the CO stretching region is based on formal selection rules, and in some cases fewer bands are observed.

Table 4.6: Relation between the structure of a carbonyl complex and the number of CO stretching bands in its IR spectrum

Complex	Isomer	Structure	No. of bands*
$[M(CO)_6]$			1
$[M(CO)_5L]$			3*
$[M(CO)_4L_2]$	<i>trans</i>		1
$[M(CO)_4L_2]$	<i>cis</i>		4**
$[M(CO)_3L_3]$	<i>mer</i>		3**
$[M(CO)_3L_3]$	<i>fac</i>		2
$[M(CO)_5]$			2
$[M(CO)_4L]$	<i>ax</i>		3***
$[M(CO)_4L]$	<i>eq</i>		4
$[M(CO)_3L_2]$	<i>trans</i>		1

$[M(CO)_3L_2]$	<i>cis</i>		3
$[M(CO)_4]$			1

*if the four fold array of CO ligands lies in the same plane as the metal atom, two will be observed.

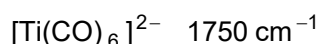
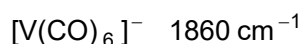
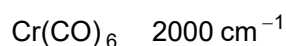
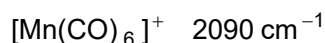
**if the *trans* CO ligands are nearly collinear, one fewer band will be observed.

***if the three-fold equatorial array of CO ligands is nearly planar, only two bands will be observed.

After the formula of a complex is established and we know that it has a CO ligand, we can look at the spectrum of the ν_{C-O} region. As Group Theory is beyond the scope of this course, we will just note here that the spectra would depend a lot on the local symmetry about the metal to which the carbonyls are attached. Also, the more symmetric the molecule, less the number of distinct bands are expected. So *trans* structure which is more symmetric has only one IR-active band compared to four for the *cis* compound. Then why are there some additional bands? Well, the ligand is not symmetric and as a result it lowers the overall symmetry of the molecule. So the symmetry around the metal is lowered as a result. So more bands appear. Also the dipole moment of the molecule is less for a symmetric vibration and increases when it is an asymmetric one. Now, intensity is proportional on the magnitude of the dipole change, so asymmetric vibrations give more intense absorptions.

SAQ 2

- Give the explanation of the relative position of the IR stretching absorptions in $[V(CO)_6]^-$ versus $Cr(CO)_6$.
- The C – O stretching frequencies in the IR spectra of certain metal carbonyl species are as follows:



The value for $CO(g)$ is 2143 cm^{-1} . Discuss.

4.4 SUMMARY

In this unit the details of metal carbonyl compounds specially their bonding, π -acceptor behaviour of carbon monoxide have been discussed. Also the

synergic effects including the MO diagram of CO alongwith the use of IR stretching frequency data as evidence for synergic effect have also been discussed in details. So with the help of Units 3 and 4 you have been able to study the details of metal carbonyl compounds. This is the last unit of this block and in the next block you will be studying about bioinorganic chemistry in details.

4.5 TERMINAL QUESTION

1. Explain the molecular energy level scheme for CO with a diagram.
2. Write the different possible structures for $\text{Mn}_2(\text{CO})_{10}$ and $\text{Co}_2(\text{CO})_8$. The ν_{CO} of the $\text{Mn}_2(\text{CO})_{10}$ is in the range 2044-1980 cm^{-1} , while $\text{Co}_2(\text{CO})_8$ /has it in the range 2071-2022 cm^{-1} , and at 1860 and 1858 cm^{-1} . What may be their possible structures?
3. $\text{Mo}(\text{py})_2(\text{CO})_4$ has two forms one – single CO structure another four. Give reason for this.
4. In a carbonyl complex with a linear OC-M-CO group, how will the CO stretching frequency change when a) one CO is replaced by triethyl amine b) a positive charge is put on the complex c) if the complex is given a negative charge.

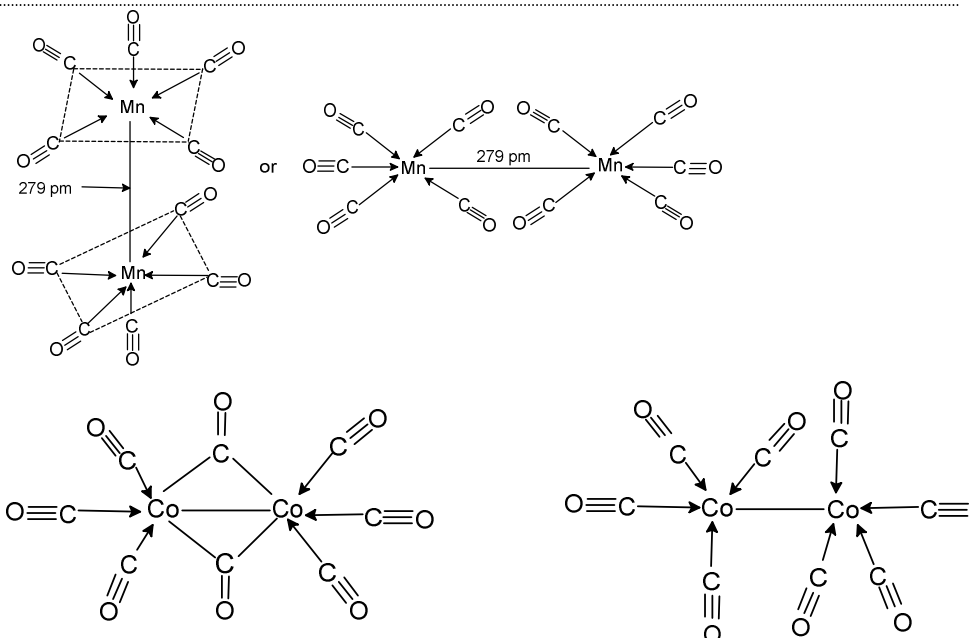
4.6 ANSWERS

1. i) CO is a σ donor and a π acceptor the metal is a σ acceptor and a π donor. Thus, there would be a flow of electrons from the CO to the metal, through the σ system and a flow (back bonding or synergic bonding) through the π system in the reverse direction.
 ii) Experimental measurements show that the carbon-oxygen bonds in the carbonyl compounds are longer and weaker than that in presenting CO. This provides good evidence that the MO bonding model of CO holds good.
 iii) In CO, the HOMO is a sigma $2p$ orbital. LUMO are the pi $2p$ antibonding orbitals.
 iv) As these two orbitals have the correct symmetry for overlap.
2. i) In $\text{V}(\text{CO})_6^-$, more negative charge have to be taken from the metal atom, so a band is found at about 1860 cm^{-1} . Whereas the one found at about 2000 cm^{-1} in $\text{Cr}(\text{CO})_6$. Where the negative charge is on the metal, the CO groups must accept more $d\pi$ electrons from the metal to prevent the accumulation of negative charge on the metal atom.
 ii) With increasing negative charge the electron density may be transferred much more easily from M to π^* orbital of CO and so the stretching frequency lowers.

Terminal Questions

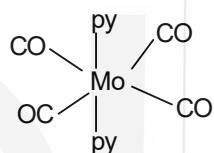
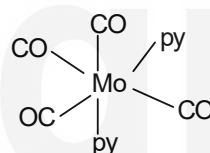
1. Section 4.3, Fig. 4.1

2.



3.

two isomers, bridged COs

 $1\nu_{\text{co}}$ stretching bond.

All four COs in different environment, so different stretching band.

4. a) The triethyl amine group will show a positive inductive effect. Electron density will be towards metal, back bonding increases and forms stronger M–C bonds. So the IR stretching frequency of CO will decrease.
- b) If positive charge, the reverse of a) will take place and frequency increases.
- c) With negative charge, same as in a).

Sources of Figures

Fig. 4.4: Weller et al, www.oxfordtextbooks.co.uk/orc/ichem6e

Sources of Tables

Table 3.1: Huheey et al, Inorganic Chemistry, 4th Edition, Table 18.1, Pearson)Table 4.6: Weller et al, www.oxfordtextbooks.co.uk/orc/ichem6e

Further Reading

1. James E Huheey, Ellen A Keiter, Richard L Keiter & Okhil K Medhi, Inorganic Chemistry (4th Edition), Pearson.
2. Cotton, Wilkinson, Gaus, Basic Inorganic Chemistry, 3rd Edition, John Wiley & Sons, India.

3. Ramaprasad Sarkar, General and Inorganic Chemistry, NCBA.
4. K. F. Purcell and J. C. Kotz, Inorganic Chemistry, Halt Saunders International Editions.
5. Vasishta Bhatt, Essentials of Coordination Chemistry, Elsevier.
6. Weller, Overton, Rourke and Armstrong, Inorganic Chemistry, 6th Edition, Oxford University Press.



