The monomer then interacts with alkene undergoing insertion to form an alkyl, which then undergoes hydrogenolysis. The reaction cycle is shown in Fig. 21.

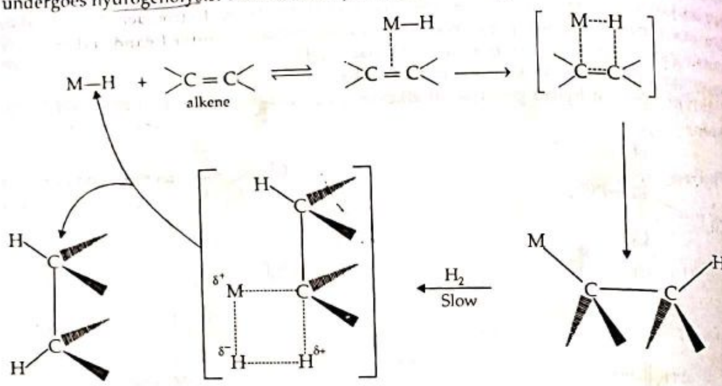


Fig. 21. Catalytic hydrogenation of alkene.

Alkenes appear to be hydrogenated in two steps and with selectivity.

In the absense of hydrogen the same compounds initiate polymerisation.

## METAL CARBONYLS

Carbon monoxide forms complexes with most of the transition metals in low oxidation states. These complexes are called ***metal carbonyls.*** In these complexes, the metal atoms are in their zero, low positive or negative oxidation states. Regarding metal carbonyls, there are three points of interest :

(*i*) Carbon monoxide is not considered a very strong Lewis base and yet it forms strong bonds to the metals in these complexes.

(*ii*) In these complexes, metal atoms are always in their low oxidation states, mostly zero, low positive or negative oxidation states.

(*iii*) About 99% of these complexes obey effective atomic number rule which accounts for their stability.

These complexes are of three types :

(*i*) *mononuclear*

(*ii*) *binuclear* and

(*iii*) *polynuclear carbonyls.*

Some metal carbonyls are also known to form important derivatives. Since these complexes contain metal atom in zero or low positive oxidation states, there does not seem to be attractive interactions between the metal and the ligands as is possible for the positively charged metal ion. It is the main characteristic of CO ligand that it can stabilize low oxidation states. This is due to the fact that it possesses vacant π-orbitals in addition to lone pairs. The formation of a sigma bond by the donation of a lone pair of electrons into the suitable vacant metal orbitals leads to excessive negative charge on the metal (in zero or negative oxidation state). To counter the accumulation of negative charge on the metal, a π-bond is formed by the back donation of electrons from the filled metal orbitals into the vacant π-type orbitals on the ligand. This also supplements the σ-bond. This ability of the ligand (CO) to accept electron density into vacant π orbitals is called **π-acidity**. Therefore, CO is also called a **π-acceptor** ligand and the metal carbonyls are referred as complexes of **π-acceptor (or π acid) ligands.**

### Preparation of metal carbonyls

There are a number of methods for the preparation of metal carbonyls. Some of these are given below :

**1. Direct synthesis.** The metal carbonyls can be prepared by the direct reaction of carbon monoxide with the finely divided metal. *For example,* nickel carbonyl is prepared by the direct reaction of finely divided nickel metal with CO at 25°C under one atmospheric pressure.

$$Ni + 4CO \xrightarrow{25°C} Ni(CO)_4$$

Ni, Fe, Mo.

Some other metal carbonyls are also prepared by the direct reaction at high temperatures and pressures.

$$Fe + 5CO \xrightarrow[100\text{ atm}]{200°C} Fe(CO)_5$$

$$Mo + 6CO \xrightarrow[250\text{ atm}]{200°C} Mo(CO)_6$$

**2. Reduction.** This is the most commonly used method for preparing metal carbonyls. In this method, the metal salts are reduced in the presence of CO. For example,

$$\underset{+3}{CrCl_3} + Al + 6CO \xrightarrow[C_6H_6]{AlCl_3} Cr(CO)_6 + AlCl_3$$

$$2CoCO_3 + 8CO + 2H_2 \xrightarrow[250\text{ atm}]{150°C} Co_2(CO)_8 + 2CO_2 + 2H_2O$$

$$WCl_6 + 3Zn + 6CO \xrightarrow[120°C]{AlCl_3} W(CO)_6 + 3ZnCl_2$$

$$VCl_3 + 4Na \xrightarrow[\text{Diglyme}]{CO} [Na(diglyme)_2]^+[V(CO)_6]^- + 3NaCl$$

$$\downarrow H_3PO_4$$

$$V(CO)_6 + H_2$$

$$RuI_3 + 5CO + 3Ag \xrightarrow[250\text{ atm}]{175°} Ru(CO)_5 + 3AgI$$

$$OsO_4 + 9CO \xrightarrow[350\text{ atm}]{250°C} Os(CO)_5 + 4CO_2$$

**3. Photolysis or thermolysis.** Higher carbonyls can be synthesised by photolysis or thermolysis of lower metal carbonyls.

$$2Fe(CO)_5 \xrightarrow{h\nu} Fe_2(CO)_9 + CO$$

$$3Os(CO)_5 \xrightarrow{h\nu} Os_3(CO)_{12} + 3CO$$

$$2Co_2(CO)_8 \xrightarrow{h\nu} Co_4(CO)_{12} + 4CO$$

**Reactions of Metal Carbonyls**

These are mostly air and moisture sensitives. Some common metal carbonyls and their physical states are given in Table 5.3.

The reactions of metal carbonyls are enormously varied. We discuss some of the important common reactions :

**1. Displacement reactions.** Metal carbonyls undergo displacement reactions in which one or more CO ligands may be displaced in contact with electron donors (Lewis bases) such as pyridine, phosphines ($R_3P$), isocyanides (RNC), *etc*. A molecule of CO is replaced by an electron pair donor. Therefore, a six electron donor (like benzene) could displace three CO molecules. Some of the common displacement reactions are :

$$Fe(CO)_5 + Ph_3P \longrightarrow Fe(CO)_4\,PPh_3 + CO$$

$$Fe(CO)_5 + 2Ph_3P \longrightarrow Fe(CO)_3\,(PPh_3)_2 + 2CO$$

$$Mo(CO)_6 \xrightarrow[-CO]{+Py} Mo(CO)_5\,Py \xrightarrow[-CO]{+Py} Mo(CO)_4\,Py_2 \xrightarrow[-CO]{+Py} Mo(CO)_3\,Py_3$$

$$Cr(CO)_6 + C_6H_6 \xrightarrow[-3CO]{} (C_6H_6)\,Cr\,(CO)_3$$

$$2Fe(CO)_5 + 2C_5H_6 \longrightarrow [(\eta^5-C_5H_5)\,Fe\,(CO)_2]_2$$

(Cyclopentadiene behaves as 5*e* donor)

$$Fe(CO)_5 + Me_3Si\,NC \longrightarrow (Me_3\,Si\,NC)\,Fe\,(CO)_4$$

$$Mo(CO)_6 + C_5H_5Na \longrightarrow Na\,[(\eta^5-C_5H_5)\,Mo(CO)_3]$$

Similarly, RC ≡ CR behaves as a 4 electron donor.

$$Co_2(CO)_8 + RC \equiv CR \xrightarrow[-2CO]{} Co_2\,(CO)_6\,(RC \equiv CR)$$

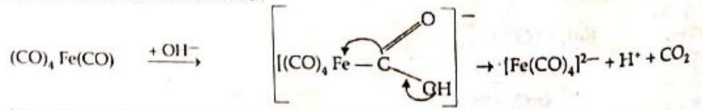
**2. Formation of carbonyl anionic complexes.** The metal carbonyls can be converted into anions known as carbonylate ions by the following methods :

(*i*) Metal carbonyls react with bases to give carbonylate ion

$$Fe(CO)_5 + OH^- \xrightarrow[KOH,\ MeOH]{} [Fe(CO)_4]^{2-} + H^+ + CO_2$$

$$Fe_2(CO)_9 \xrightarrow[Et_4NI]{} (Et_4N)_2\,[Fe_2(CO)_8]$$

The reaction is believed to proceed by nucleophilic attack of $OH^-$ ion on the carbon atom of a carbonyl group followed by the electron transfer to the metal atom and formation of carbon dioxide which is converted into carbonate as :



In some cases, the mechanism is more complicated.

(*ii*) Reduction of metal carbonyls with reducing agents produce carbonylate anions. The

TABLE 3.

Common known metal carbonyls

| Group | V A | VI A | VII A | VIII A | | |
|---|---|---|---|---|---|---|
| 3*d* series | $V(CO)_6$<br>Blue green crystals<br>70°(d)<br>Octahedral<br>Paramagnetic (one electron) | $Cr(CO)_6$<br>golden<br>white crystals<br>130° (d)<br>Octahedral | $Mn_2(CO)_8$<br>golden yellow crystal<br>(m.p. 152-155°C) | $Fe(CO)_5$<br>yellow liquid<br>mp – 20°,<br>b.p. 103°<br>trigonal biphyamidal<br>$Fe_2(CO)_9$<br>Orange yellow crystals 100° (d)<br>$Fe_3(CO)_{12}$ Green crystals 140° (d) | $Co_2(CO)_8$<br>orange cyrstals<br>m.p. 51°<br>$Co_4(CO)_{12}$<br>Black crystals | $Ni(CO)_4$<br>colourless<br>liquid<br>mp –25°, bp 42°<br>tetrahedral |
| 4*d* series | | $Mo(CO)_6$<br>white crystals<br>180° (d)<br>Octahedral | $Tc_2(CO)_{10}$<br>white crystals<br>160° (d) | $Ru(CO)_{10}$<br>colourless<br>liquid<br>mp –22°<br>$Ru_3(CO)_{12}$<br>yellow orange crystals<br>m.p. 150° | $Rh_4(CO)_{12}$<br>Red orange<br>crystals<br>150° (d) | |
| 5*d* series | | $W(CO)_6$<br>white crystals<br>180° (d)<br>octahedral | $Re_2(CO)_{10}$<br>white crystals<br>m.p. 177° | $Os(CO)_5$<br>colourless<br>liquid<br>m.p. – 15°<br>trigonal bipyramidal<br>$Os_3(CO)_{12}$<br>yellow crystals<br>m.p. 224° | $Ir_4(CO)_{12}$<br>yellow powder<br>210° (d) | |

reduction is carried out by alkali metal amalgams, hydride reagents and Na / K alloy in basic solvents including liquid ammonia.

$$Co_2(CO)_8 \xrightarrow[THF]{Na/Hg} 2Na[Co(CO)_4]$$

$$Cr(CO)_6 \xrightarrow[THF]{Na/Hg} Na_2[Cr(CO)_5]$$

$$Mn_2(CO)_8 \xrightarrow[THF]{KH} 2K[Mn(CO)_5]$$

$$Re_2(CO)_{10} \xrightarrow[THF]{NaBH_4} Na_2[Re_4(CO)_{16}]$$

$$Cr(CO)_6 \xrightarrow{NaBH_4} Na_2[Cr_2(CO)_{10}]$$

$$V(CO)_6 + Na \xrightarrow{NH_3(l)} Na^+ [V(CO)_6]^-$$

(*iii*) Many substituted carbonyl anions can be obtained by displacement of carbon monoxide from a metal carbonyl.

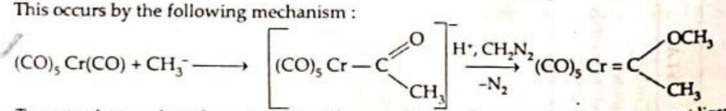
$$\overset{+}{Me_4N}\overset{-}{I} + Mo(CO)_6 \longrightarrow Me_4N[Mo(CO)_5I] + CO$$

$$Mo(CO)_6 + \overset{+}{Na}\overset{-}{B_3H_8} \longrightarrow Na[Mo(CO)_5\, B_3H_8] + CO$$

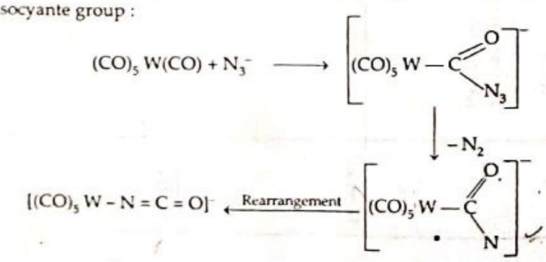
(*iv*) Metal carbonylate anions can be prepared by the reaction with $CH_3$ or $C_6H_5$ radicals.

$$(CO)_5\,Cr(CO) + CH_3^- \longrightarrow (CO)_5\,Cr = C(OCH_3)(CH_3)$$

This occurs by the following mechanism :



Tungsten hexacarbonyl reacts with azide according to above mechanism to convert ligand CO to an isocyante group :



**3. Formation of cationic carbonyl complexes.** These may be obtained in the formation of complex ides by the reaction of carbon monoxide and a Lewis acid such as $AlCl_3$ or $BF_3$. *For example,*

$$Mn(CO)_5Cl + CO + AlCl_3 \longrightarrow [Mn(CO)_6]^+ [AlCl_4]^-$$

$$Re(CO)_5Cl + AlCl_3 + CO \longrightarrow [Re(CO)_6]^+ [AlCl_4]^-$$

$$Fe(CO)_5 \xrightarrow{HCl,\, BCl_3} [FeH(CO)_5]^+ + [BCl_4^-]$$

**4. Formation of metal-metal bonds.** The metal-metal bonds can be formed by powerful reducing ents or by simple elimination reaction :

$$2Mo(CO)_6 + 2NaBH_4 \longrightarrow Na_2[Mo_2(CO)_{10}]$$

$$Mn(CO)_5Br + Li\,Mn(CO)_5 \xrightarrow{-Li\,Br} (CO)_5\,Mn - Mn(CO)_5$$

## BONDING IN METAL CARBONYLS

Carbon monoxide has one lone pair of electrons on both the carbon and the oxygen atom. In metal rbonyls, the CO molecule bonds itself to the metal atom through its carbon end as M ⟵ CO. herefore, the metal carbonyls are regarded as organometallics. The CO ligand can bind to the ansition metals in three different ways as shown in Fig 22.

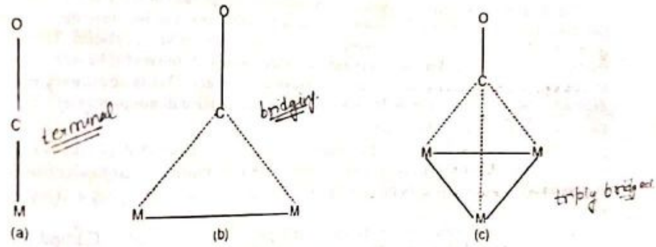


**Fig. 22.** Different ways of bonding of CO with metal atom.

(*a*) It can act as terminal ligand.
(*b*) It can act as bridging ligand.
(*c*) It can act a tripiy bridging ligand.

The common of all is the terminal carbonyls. In all cases M—C—O groups are linear.

**Bonding in Linear M—C—O groups**

We know that the Lewis acidity of CO is very small. The tendency of CO to form very large number of complexes in low oxidation states of the metals is quite astonishing. The high stability of metal carbon bond in metal carbonyls is due to the multiple nature of M—CO bond. There is much evidence also for this fact.

In terms of resonance, the bonding in metal carbonyls may be represented as :

$$\overset{-}{M}—\overset{+}{C} \equiv O \longleftrightarrow M = C = \ddot{O}:$$

However, the best explanation for bonding can be given in terms of molecular orbital theory as given below :

Carbon monoxide has a triple bond with lone pair of electrons on both C and oxygen atom as $\boxed{:C \equiv O:}$

(*i*) There is a dative overlap of the filled orbital of carbon (of CO) and suitable empty orbital of the metal forming a dative sigma bond (M ← CO).

This is shown in Fig. 22 (*a*).

(*ii*) There is a π-overlap involving donation of electrons from filled metal *d*-orbitals into vacant anti-bonding $\pi^*$ molecular orbitals. This results into the formation of M ⟶ CO bond. This is also called ***back donation*** or ***back bonding*** [Fig. 20 (b)].

The bonding in metal carbonyls is shown in Fig.20. In these figures, the shaded orbitals represent filled orbitals.

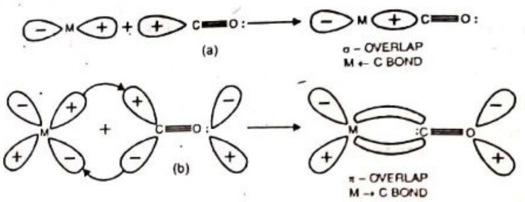


Fig. 23. Representation of bonding in metal carbonyls.

The formation of σ dative bond tends to increase the electron density on the metal atom. At the same time, the formation of π bond from metal to carbon tends to decrease the electron density on metal. Then the formation of π bond increases the strength of M—CO bond. This accounts for the *fact that CO is a very weak Lewis base towards non-transition metal halides like $BX_y$, $AlX_y$ etc. but forms very strong complexes with transition metals. This is obviously because of the drift of π electron density from M ⟶ C which increases the σ donor power of CO.*

**Evidence in support of Bonding**

1. The formation of back bonding from metal to CO molecule results in decrease in electron density on metal. This is supported by the dipole moment studies. It has been observed that the dipole moment of M — C bond is only very low about 0.5D suggesting a close approach to electronegativity.

2. The back bonding from metal to CO is expected to increase M — C bond strength with corresponding weakening of C ≡ O. This is due to the fact that electrons from back bonding fill the anti-bonding MOs of CO. As a result, the bonding ability of CO will decrease. Therefore, as the M—C bond becomes stronger, the C ≡ O bond becomes weaker. Therefore, the multiple bonding should be evidenced by the shorter M—C bond as compared to M—C single bonds and longer C—O bonds as compared to normal C ≡ O triple bonds. It has been observed that the bond length in CO molecule is 1.128Å and in metal carbonyls, it is of the order of 1.15Å. This small increase is justified but it is very small (0.02Å) and cannot give strong evidence. Therefore, bond length measurements of CO does not provide significant information because in the range of bond orders (2 – 3) concerned, CO bond length is relatively insensitive to bond order. The direct measurement of M—C single bonds is also difficult because zerovalent metals do not form such compounds.

However, to understand the extent to which the metal - carbon bonds get shortened in these compounds, an indirect method of measurement of bond distances can be applied. This can be done by measuring the length of M—CO bonds in the same molecule in which some other single bond M—X also exists. Using the known covalent radius of X, and using covalent radius of C to be 0.70 Å (when C is *sp* hybridised) or 0.77Å (when C is $sp^3$ hybridised) then the length for a single M—CO bond in this molecule can be calculated and compared with the observed value.

This procedure may be illustrated by considering the example of Mo(dien) $(CO)_3$ [dien = $NH(CH_2CH_2NH_2)_2$] where there is a single Mo—N bond because amine N atom has no orbitals available for π bonding.

When the covalent radius of $sp^3$N (0.70Å) is subtracted and the covalent radius of C (0.70Å) is added, then the length of single Mo—CO bond should be 2.32Å.

Bond length of Mo—CO

= (Bond length of Mo—N) — (Covalent radius of $sp^3$N) + (covalent radius of *sp* C)

= 2.32 – 0.70 + 0.70 = 2.32Å

However, the observed bond length is 1.94Å which shows that there is an extensive M—C π back bonding.

**Vibrational spectra of metal carbonyls**

Infrared spectroscopy has given valuable support for bonding in metal carbonyls. These studies provide information regarding bond orders of M—C and C ≡ O bonds. The decrease in C—O bond order or force constant is estimated by studying the CO stretching frequency in infrared spectroscopy. The infrared spectra is characterised by frequency of vibration, which is related to force constant (k) as

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}\ s^{-1}$$

free CO = 2150

ter CO = 2125-185

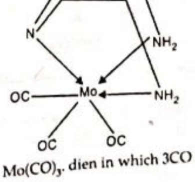
where μ is reduced mass of bonded atoms with mass $m_1$ and $m_2$ and is given as

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

The force constant is a measure of bond strength. The larger the force constant, the stronger the bond and higher the vibrational frequency. For example, a triple bond has higher force constant and therefore higher frequency than a double bond (C ≡ C : 2200 $cm^{-1}$ and C = C : 1650 $cm^{-1}$). In infrared spectrum the CO frequencies are generally very strong and therefore, can be conveniently used to study the force constant or bond strength of CO bond in different bonding situations.

Free CO has a infrared stretching frequency of 2143 $cm^{-1}$. In the case of terminal carbonyl groups in neutral molecules, the CO frequency has been found to be 2125—1850 $cm^{-1}$. This suggests that the bond strength of CO has decreased or the M—C bond strength has increased. This is only possible if there is back bonding from filled metal *d*-orbitals to the antibonding orbitals of CO.

Now, when some changes are made that should increase the extent of back M—C bonding, the CO frequencies are shifted to even lower values. For example, if some CO groups are replaced by ligands with low or negligible back accepting capacity, then the remaining CO groups accept the $d\pi$ electrons from the metal to a greater extent in order to prevent accumulation of negative charge on the metal atom. This will result into decrease in the bond strength of CO which is indicated by lowering in CO frequency. For example, consider the complex $Mo(CO)_3$ diene in which three CO groups of $Mo(CO)_6$ have been replaced by diethylene triamine $HN(CH_2CH_2NH_2)_2$, dien (a tridentate). This complex has three CO groups only relative to 6 in $Mo(CO)_6$ to accept the back donation from metal because the ligand containing N atom has no ability to accept back bonding. This will reduce the bond strength of CO to greater extent and consequently the CO stretching frequency is lowered to greater extent (1760 $cm^{-1}$) as compared to 2004 $cm^{-1}$ in $Mo(CO)_6$.



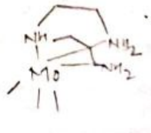


Fig. 24. Structure of diene $Mo(CO)_3$. dien in which 3CO groups are replaced by diene.

The oxidation state of the metal atom also affects the CO frequency in metal carbonyls in a way which suggests the back bonding tendency in M ⟶ C bond. If we have a negatively charged carbonylate anion such as $Co(CO)_4^-$ or $[Fe(CO)_4]^{2-}$, then there will be greater negative charge on the metal. As a result, we expect more π-back donation from metal to π orbitals of CO leading to further weakening of CO bond. As a result, CO frequency will be lowered. The higher the negative charge, the greater is the lowering. For example, when we go from $Cr(CO)_6$ to the iso electronic $V(CO)_6^-$ having more negative charge, the frequency has been found to be 1860 $cm^{-1}$ corresponding to the frequency found at 2000 $cm^{-1}$ in $Cr(CO)_6$.

On the other hand, the effect of positive charge on the metal complex will have reverse effect. With the positive charge on the metal atom, its back bonding tendency becomes lesser relative to neutral molecule. As a result, the weakening in CO bond will be less and consequently the lowering in CO frequency will also be less. For example, the CO absorption frequency in $Mn(CO)_6^+$ is at 2090 $cm^{-1}$ whereas its neutral isoelectronic molecule $Cr(CO)_6$ has CO absorption frequency at 2000 $cm^{-1}$.

Thus, it may be concluded that when changes are made which increases the extent of M—C back bonding, the CO frequencies are lowered to greater extent. On the other hand, when changes are made that decrease the extent of M—C bonding, the CO frequencies are lowered to lesser extent. [Moreover, in the case of isoelectronic series, the anionic complex has lowest CO frequency.] This fact may be illustrated by comparing the CO frequencies of isoelectronic ions as :

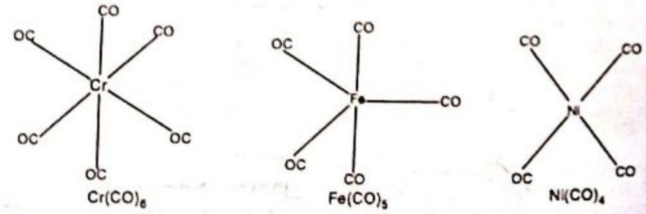
| Complex | CO stretching frequency | Complex | CO stretching frequency |
|---|---|---|---|
| $[Ni(CO)_4]$ | 2040 $cm^{-1}$ | $[Cr(CO)_6]$ | 2000 $cm^{-1}$ |
| $[Co(CO)_4]^-$ | 1920 $cm^{-1}$ | $[Mn(CO)_6]^+$ | 2090 $cm^{-1}$ |
| $[Fe(CO)_4]^{2-}$ | 1790 $cm^{-1}$ | $[V(CO)_6]^-$ | 1860 $cm^{-1}$ |
| $[Fe(CO)_6]^{2+}$ | 2204$cm^{-1}$ | | |

$\nu_{CO}$ = anion < neutral < cation

## STRUCTURE OF METAL CARBONYLS

### Mononuclear metal carbonyls

The mononuclear metal carbonyls have all terminal CO groups. The shapes are those expected from their formulae. For example, hexacarbonyls have regular **octahedral structures** (*e.g.* $Cr(CO)_6$, $V(CO)_6$), tetracarbonyls (*e.g.* $Ni(CO)_4$) have **tetrahedral structure**. The pentacarbonyls (e.g. $Fe(CO)_5$, $Os(CO)_5$) have **trigonal bipyramidal** shape. The shapes of some mononuclear carbonyls is shown below :



Structures of some mononuclear carbonyls.

### Binuclear metal carbonyls

The binuclear metal carbonyls have different types of structures. They show metal - metal bonding and bridging CO groups in their molecules. Their structures are described ahead :

(*i*) The binuclear metal carbonyls, $M_2(CO)_{10}$ where M = Mn, Ti or Re have metal-metal bonding their structures. Each metal has octahedral arrangement of CO groups. The structure of $Mn_2(CO)_{10}$ s shown in Fig. 25.

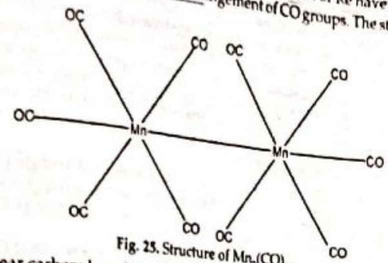


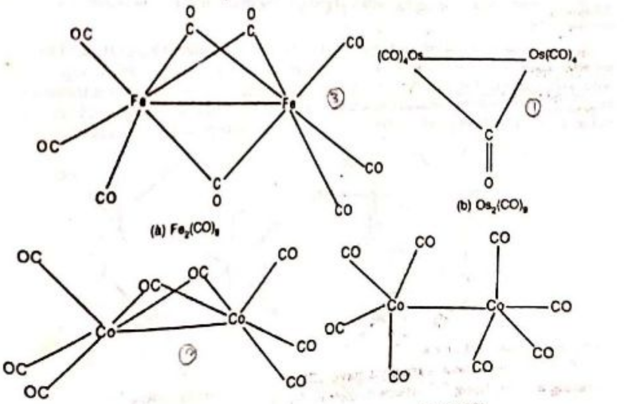
Fig. 25. Structure of $Mn_2(CO)_{10}$.

(*ii*) The binuclear carbonyls such as $Fe_2(CO)_9$, $Os_2(CO)_9$ and $Co_2(CO)_8$ have bridging carbonyl groups in addition to metal-metal bonds. Their structures are shown in Fig. 26.

$Fe_2(CO)_9$ has three bridging CO groups placed symmetrically around the Fe—Fe bond (Fig. 26 a). The metal-metal distance in $Fe_2(CO)_9$ is 2.46Å and each Fe atom is bonded to three terminal CO groups.

$Os_2(CO)_9$ has only one bridging carbonyl group and each Os atom has four terminal CO groups [Fig. 26 (b)].

$Co_2(CO)_8$ has two types of structure. In the solid state, there are two bridging carbonyl groups and each Co atom is bonded to three terminal CO groups. The two Co groups are bonded together by metal - metal bond. In solutions, $Co_2(CO)_8$ has Co—Co bond and each Co atom is bonded to four terminal CO groups as shown in Fig. 26 (*d*). This structure is found to exist in equilibrium with the bridged form in solutions of $Co_2(CO)_8$.



(a) $Fe_2(CO)_9$

(b) $Os_2(CO)_9$

(d) $Co_2(CO)_8$

(c) $Co_2(CO)_8$

Fig. 26. Structures of some binuclear carbonyls.

We have seen that in addition to terminal CO groups, there are some bridging carbonyl groups in binuclear complexes. The bridging CO groups are symmetrical and have equal M—C distances.

The bonding in bridging carbonyl groups may be regarded as 2 electron 3 centred overlap. It may be noted that the bridge occurs in conjunction with metal-metal bond. The carbon monoxide bridges in the absence of metal-metal bonds are unstable. Thus, the metal-metal bond is essential for the stability of the bridges. The stability of CO bridges depends upon the size of the metal atom. If the metal atoms are larger in size, the bridged structure become unstable relative to unbridged structures. Therefore, the relative stability of non bridged structures increases as the size of the metal atom increases. *For example*, the smaller Fe atom in $Fe_2(CO)_9$ has 3 bridging CO groups whereas bigger osmium in $Os_2(CO)_9$ has one bridging CO group.

The infrared spectral studies also help to show the presence of bridging CO group. The CO stretching frequency of bridging group is lower than the terminal CO group. *For example*, terminal CO groups in $Co_2(CO)_8$ absorbs in the range 2000 — 2100 cm$^{-1}$ whereas bridging CO groups have bands in the range 1886 – 1857 cm$^{-1}$.

It has been observed that in general, the CO frequencies for the terminal CO groups are in the range 1850 – 2150 cm and the frequencies for bridging CO groups are in the range 1750 – 1850 cm. Triply bridging CO groups have still lower CO frequencies in the range 1620 to 1730 cm in neutral molecules (Table 4).

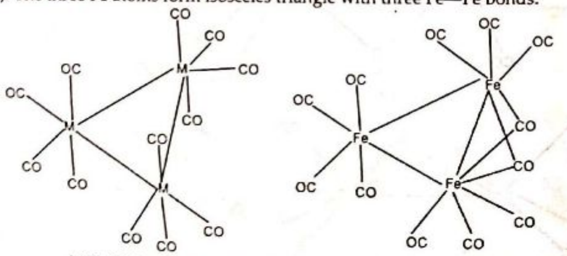
**Table 4. CO group frequency in different metal carbonyls.**

| Type of CO bond | ν(CO) cm$^{-1}$ |
|---|---|
| Uncoordinated | 2143 |
| Terminal | 2150 — 1850 |
| Doubly bridged | 1850 — 1750 |
| Triply bridged | 1730 — 1620 |

### Polynuclear metal carbonyls

The structures of polynuclear metal carbonyls are more complex. They contain metal- metal bonds and terminal and bridging carbonyl groups. The structures of some polynuclear carbonyl are discussed below :

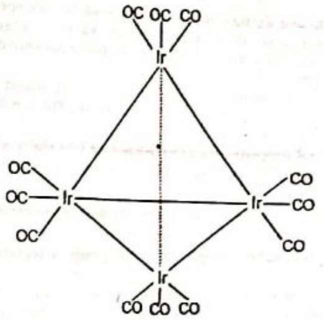
(*i*) Among the trinuclear carbonyls known at present, crystalline $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ have the structures as shown in Fig. 27 (*a*). In this structure, the metal atoms form an equilateral triangle with no bridging CO groups. All the 12 CO groups are terminal. The structure of trinuclear carbonyl, $Fe_3(CO)_9$ is different than that of $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$. It has two bridging CO groups as shown in Fig. 27 (*b*). The three Fe atoms form isosceles triangle with three Fe—Fe bonds.



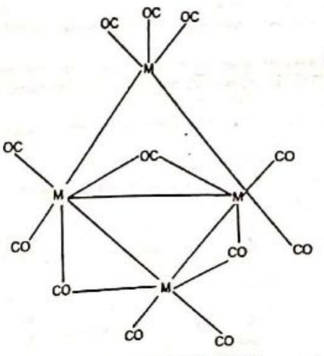
(a) $M_3(CO)_{12}$ (M = Os or Ru)　　(b) $Fe_3(CO)_9$ 12

Fig. 27. Structures of (a) $M_3(CO)_{12}$ [M = Os or Ru) and (b) $Fe_3(CO)_9$.

(ii) Tetracarbonyls having the formula $M_4(CO)_{12}$ where M = Co, Rh or Ir have similar tetrahedral arrangement of four metal atoms. In case of $Ir_4(CO)_{12}$, the structure is non bridged structure in which four $Ir(CO)_3$ terminal units have symmetrical arrangement of tetrahedron [Fig. 27 (*a*)]. On the other hand $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ have structure in which there are bridged CO groups also. Three triangular faces have terminal $M(CO)_2$ groups with one bridging CO group along each edge. The fourth triangular face is occupied by $M(CO)_3$ group [Fig. 28 (*b*)].



(c) $Ir_4(CO)_{12}$



(b) $M_4(CO)_{12}$ [M=Co, Rh]

Fig. 28. Structures of some tetranuclear carbonyls (a) $Ir_4(CO)_{12}$ and (b) $M_4(CO)_{12}$ [M = Co, Rh]

# BIOINORGANIC CHEMISTRY

## CONTENTS

- Essential and trace elements in biological processes.
- Metalloporphyrins with special reference to hemoglobin and myoglobin.
- Biological role of alkali and alkaline earth metal ions with special reference to $Ca^{2+}$.
- Nitrogen fixation.

Many biochemical reactions depend upon the presence of metal ions. These ions may be present in certain specific positions in biomolecules and may act to facilitate or inhibit the reactions occurring in the biological systems. **Bioinorganic Chemistry** is the branch of science which brings inorganic chemistry into life processes by recognizing the fundamental importance of life dependence on metal ions. In a simple way bioinorganic chemistry means the **study of the roles of metal ions in biology.**

This branch is a fast developing branch of Chemistry because of its importance in biological systems. The advances in bioinorganic chemistry have led to the understanding of biological systems and insight into the structures and mysteries that nature has. This has also helped us to synthesise and characterize new inorganic compounds which resemble those found in living systems.

## ESSENTIAL AND TRACE ELEMENTS IN BIOLOGICAL SYSTEMS

Bioinorganic chemistry means the inorganic elements in the chemistry of life. The studies of biochemical reactions occurring within living systems have shown that certain metal ions play a vital role in normal growth and functions of biological processes. The inorganic elements have many functions such as skeletal components of bones and teeth, as electrolytes in maintaining water balance in vascular system and tissues and in the prosthetic groups of many enzymes. The abundance of elements in human body, earth's crust and sea water is given in Table 1 :

Table 1. Chemical abundances of elements in human body, earth's crust and sea water

| *Composition of human body* | | *Composition of earth's crust* | | *Composition of sea water* | |
|---|---|---|---|---|---|
| H | 63% | O | 46.6% ✓ | H | 66% ✓ |
| O | 25.5% | Si | 27.7% | O | 33% |
| C | 9.5% | Al | 8.1% | Cl | 0.33% |
| N | 1.4% | Fe | 5.0% | Na | 0.28% |
| Ca | 0.31% | Ca | 3.6% | Mg | 0.033% |
| P | 0.22% | Na | 2.8% | S | 0.017% |
| Cl | 0.03% | K | 2.6% | Ca | 0.006% |
| K | 0.06% | Mg | 2.1% | K | 0.006% |
| S | 0.05% | Ti | 0.44% | C | 0.0014% |
| Na | 0.03% | H | 0.14% | Br | 0.0005% |
| Mg | 0.01% | C | 0.20% | | |

$H > O > C > N > Ca$

The inspection of Table 1 shows that all those elements which are appreciably abundant in human body (except phosphorus) are also abundant in sea water. Some of these elements are essential for life and maintenance of plants and animals. These elements may be present in la (bulk) or in small quantities (traces). Therefore, the elements may be classified as essential nonessential elements.

## ESSENTIAL ELEMENTS

The essential elements may be defined as **those elements which are required for the mainten of life of plants and animals.** These are indispensible and the absence of these elements result death or a severe malfunction of the organism. However, this rigorous criterion cannot always satisfied and this led to broader definition of essentiality. ***An element may be considered essent when its deficient intake produces an impairment of function and when the restoration of physiolog levels of that element relieves the impaired function or prevents impairment.*** This means that organism can neither grow nor completes its life cycle without the essential elements.

The elements which donot play any positive role in biological systems **are non essenti elements.** Obviously, determining the essentiality of an element is very difficult.

**The criteria for an essential elements are :** b ①

(i) the element is present in tissues of different elements at comparable **concentrations.**

(ii) A physiological deficiency or abnormality appears when the **element is withdrawn** from t diet

(iii) The deficiency or abnormality can be relieved or prevented by the addition of th element.

(iv) The abnormalities are accompanied by specific biochemical changes which can be remed or prevented when the deficiency is checked.

(v) A specific biochemical function is associated with a particular element.

Thus, essential elements are indispensible for the growth and normal functioning of anim and plants.

The essential elements may further be divided into two broad groups :

(i) Bulk elements or (ii) Trace elements

(i) **Bulk elements** are the elements which are found in higher concentrations.

(ii) **Trace elements** are those which are needed in very low concentrations.

It may be noted that it is very difficult to define the limits of **beneficial** or detrimen oncentrations. This may vary from organism to organism. The essential **element may become** 'to t higher than normal concentration. For example, selenium is an essential element in mammals, ne of the serious problem is the poisoning of live stock from eating plants that concentrates th lement. The essential bulk or trace elements required by every animal or plants are listed in Ta . There are about 30 elements which are recognized as essential to life. These are classified into ulk or structural elements, five macro minerals and 19 trace elements. These different types lements present in human body are also shown in Fig. 1 in the order of their percentages.

**Table 2 Classification of essential elements.**

| ***Bulk Structural elements*** | ***Macrominerals elements*** | ***Trace elements*** | ***Ultratrace elements*** |
|---|---|---|---|
| Hydrogen (H),<br>Carbon (C),<br>Nitrogen (N),<br>Oxygen (O),<br>Phosphorus (P)<br>and Sulphur (S) | Sodium (Na),<br>Potassium (K),<br>Magnesium (Mg),<br>Calcium (Ca),<br>Chlorine (Cl) and<br>$PO_4$, $SO_4$. | Iron (Fe),<br>Copper (Cu)<br>and Zinc (Zn) | Nonmetals : **Fluorine (F), Iodine** (I), Selenium **(Se), Silicon (Si),** arsenic (As), **Boron (B)**<br>**Metals : Manganese (Mn),** Molybdenum (Mo), **Cobalt (Co),** Chromium (Cr), **Vanadium (V),** Nickel (Ni), **Cadmium (Cd), Tin** (Sn), Lead (Pb), **Lithium (Li).** |

Not all the elements given in Table 2 as essential bulk or trace are required by **every animal or plant.** For example, $Na^+$ is of vital importance to higher animals but it is not **essential for many** bacteria and most plants except blue green algae. On the other hand, only some **higher plants have** been found to require aluminium, boron or vanadium. Similarly, molybdenum is **essential to only** those organisms which derive their nitrogen from inorganic sources. A number of **non essential trace** elements may be considered as *non nutritive* and *nontoxic* but some like $Ag^+$, $Hg^{2+}$, $Pb^{2+}$, *etc.* **are highly** toxic. Similarly, selenium is essential in trace amounts for some animals but **proves to be toxic in** higher concentrations. It may be noted that even some essential elements may **prove to be toxic if** consumed in larger amounts.

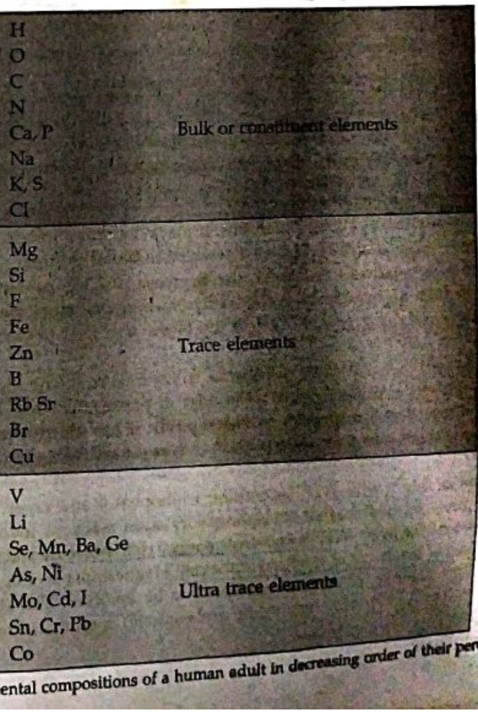


**Fig. 1.** Elemental compositions of a human adult in decreasing order of their percentages.

## ESSENTIAL BULK ELEMENTS

$K^+$, elecb $K^+$

The main essential bulk elements are :

**Potassium and Sodium**

**Potassium** is found almost universally as the principal inorganic cation present in mos cells. It is essential to almost all organisms except blue green algae. It is the major cat intracellular fluid and plays an important role in ***nerve action*** and ***function of the heart***.

**Sodium** is the major cation of extra cellular fluid in animals. Like potassium ion, sodi is also important in ***nerve functioning in animals***. It is the major component of vertebrate plasma. The main role of these cations alongwith $Cl^-$ anion is the ***osmotic regulation*** of bod tissue fluids. $K^+$ and $Na^+$ ions also serve as essential activating ions for specific ***enzyme ac*** These cations with $Ca^{2+}$ and $Mg^{2+}$ ions are also important in the preservation of the ***integrity*** ***cell membranes*** and in the normal activity of excitable tissues.

**Calcium and Magnesium**

**Calcium and magnesium are present as carbonates and phosphates in the skeletal struc** mammals as about 99% of $Ca^{2+}$ and 70% $Mg^{2+}$. Calcium is essential for all organisms and in cell walls, bones and some cells as structural component. In human blood, $Ca^{2+}$ is presen in the plasma in which about 50% is in ionic form and remaining is present in combinatio nondiffusable form) with serum protein. The important minerals in biological structural ma containing calcium are given in Table 3.

**Table 3 Calcium containing minerals in biological structural materials.**

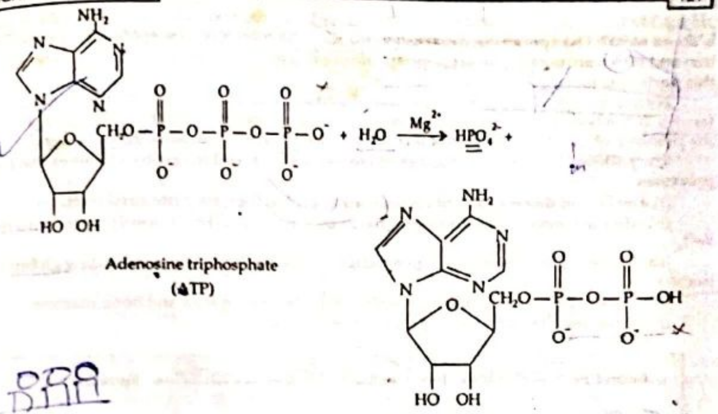
| Mineral | Formula | Organism | Location |
|---|---|---|---|
| Calcite | $CaCO_3$ | Birds | Egg shells |
| Argonite | $CaCO_3$ | Mollusks | Shells |
| Hydroxyapatite | $Ca_5(PO_4)_3(OH)$ | Vertebrates, mammals | Bones |

Calcium is necessary to all cellular organisms. It plays important role in **muscle cont** **and stabilization of certain enzymes.** It is also involved in **blood clotting.**

Though calcium is relatively harmless, the decrease of $Ca^{2+}$ content in blood d dietry deficiency or from an insufficiency of parathyroid hormone **may lead to a disease** **tetany**. On the otherhand, an excess of $Ca^{2+}$ in the blood **may lead to calcification** internal organisms.

**Magnesium** is also essential to all organisms. In contrast to distribution of $Ca^{2+}$ in of mammals, more $Mg^{2+}$ is present in red cells than in plasma. The $Mg^{2+}$ content of cells is relatively more. It is also present in **chlorophyll**. It has **electrochemical** and **activating functions**. $Mg^{2+}$ ions play an important role as an **activating ion in many** reactions.

The interaction of $Mg^{2+}$ with ATP (adenosine triphophate) and other nucleotides is important. It has been studied that all transphosphorylation reactions involving ATP p smoothly in the presence of $Mg^{2+}$. ATP is known as **energy rich molecule and is used as an** source to derive most of the chemical reactions of the cell. Magnesium plays significant role conversion and $Mg^{2+}$ complex of ATP is considered to be involved. The standard free change of hydrolysis of ATP to ADP (adenosine diphosphate) is estimated to be -31.0 kJ



Adenosine triphosphate (ATP)

Adenosine diphosphate (ADP)

It has been observed that the activating effect of $Mg^{2+}$ in transphosphorylation may be duplicated *in vitro* by Mn(II). In some other reactions $Mg^{2+}$ is duplicated by $Ca^{2+}$, $Co^{2+}$, $Zn^{2+}$ or $Ni^{2+}$.

**Phosphate**

The important reactions involving inorganic phosphorus compounds are the incorporation and release of phosphate groups in and from organic compounds and skeletal materials (bones). The important phosphate compounds are nucleotides, polynucleotides and phospholipids. The biochemcal importance of phosphate group is in metabolism of carbohydrates, fats, proteins and vitamins. The presence of phosphorus in bones and its function in regulation of pH of the blood are very important. The normal formation of bones depends upon the relative amounts of dietary phosphorus, and calcium in addition to vitamin D.

## ESSENTIAL TRACE ELEMENTS

The nineteen essential trace elements include three prominent biologically active metals : iron, copper and zinc. All the remaining essential elements are considered as ultratrace because they involve less than 10 mg in the adult human with the exception of fluorine and boron. The nutritional requirement for the **essential trace elements** is related to their participation in the action of various enzymes. The trace elements have important role in metalloenzymes. The trace elements are essential because they serve as required prosthetic groups in active sites and/or as coenzymes for indispensable metalloenzymes or metal-ion activated enzymes.

**Iron**

Among the trace elements, iron is one of the metals found in greatest abundance in biological systems in the form of porphyrin complexes or hemes such as **hemoglobin and myoglobin.** Of the total iron in the human body (about 4.3 g per 70 kg body weight), about 70% is present in hemoglobin and about 3% in myoglobin. Most of the remaining iron is stored as ferritin.

Ferritin is major iron storage protein in mammals but it is also found in plant chloroplasts and fungi. It is distributed mainly in the spleen, liver and bone marrow. It consists of a shell of protein (apoferritin) sub units surrounding a micelle of ferric hydroxide-oxide-phosphate, having the composition $Fe(OOH)_8 \cdot (FeOPO_3H_2)$. The iron content of ferritin varies from zero to about 23%. Apoferritin protein may be prepared from ferritin by reduction of ferric ions to ferrous ions at

$F(OH)_3$–O–Phosphate

ferritin — apoferritin

pH = 4.5 followed by removal of $Fe^{2+}$ ions by dialysis. The approximate formula weight of apo is about 46500. The apoferritin dissociates into about 24 sub units. The apoferritin protein ca iron and then transport it to an appropriate site to aid in the biosynthesis of other molecules invo this particular metal.

Ferritin has also been prepared in the laboratory which have the properties similar to na ferritin. It has been prepared by treatment of crystalline apoferritin with an inorganic Fe (II) s the presence of $O_2$. It is belived that ferritin is formed *in vivo* by an analogous process.

**The pathway of $Fe^{3+}$ from food stuffs to hemoglobin and to ferritin involves the follo processes :**

(i) The $Fe^{3+}$ of dietary material is reduced to $Fe^{2+}$ in the gastrointestinal tract.

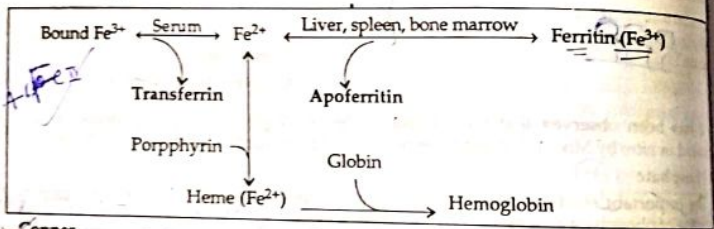
(ii) After absorption into the cells of the intestinal mucosa, $Fe^{2+}$ is incorporated into ferrit $Fe^{3+}$.

(iii) The $Fe^{2+}$ in mucosa is also converted to $Fe^{3+}$ plasma (bound by iron-binding globulin na *transferrin*).

(iv) Plasma $Fe^{3+}$ is in equilibrium with iron in the liver, spleen and bone marrow.

In the tissues, the following changes are believed to occur :

C'A + Fe II



## Copper

Copper is essential to all organisms and is a constituent of redox enzymes and hemocy Copper in hemocyanin is oxygen carrier and supplies oxygen to certain aquatic creatures and m enzymes. Copper containing *enzymes play an important role in the pigmentation of skin, functioni brain and in iron metabolism in body in hemoglobin formation*. Probably copper containing enz systems are involved in some steps. The deficiency of copper in human system develops an ane characterized not only by marked decrease in the total iron and heme content in blood and tiss but also by an increased amount of free porphyrin in the erythrocytes.

The excess of copper in human body is also harmful. A disease known as ***Wilson disease*** up the copper metabolism of human system in such a way that it absorbs excessive copper fr intestinal track and gets deposited in excess in the liver, kidney or brain. Patients suffering from t disease are treated with controlled doses of EDTA which forms a water soluble complex with Cu which get excreted through urine.

In higher concentrations, copper is highly toxic to invertibrates and moderately toxic to ot mammals also.

## Cobalt

Cobalt is also essential trace element which is essential for many organisms inclu mammals. It **activates** a number of **enzymes**. It is constituent of **vitamin $B_{12}$** which is required the formation of hemoglobin *in vivo*. However, it is highly toxic to plants and moderately toxi mammals when injected intravenously. Deficiency of cobalt in soil adversely affects the heal grazing animals. Adding cobalt salts to soil, improved their health.

## Lead

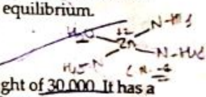
It has no known biological function. It is highly toxic to most plants and is a cummulative po

to mammals. It inhibits the synthesis of hemoglobin in mammals and is very toxic for central nervous system. One of the symptoms of lead poisoning is anemia.

## Zinc

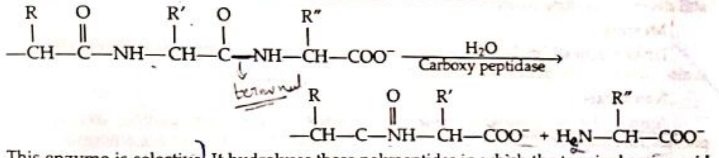
Zinc is an essential element for almost all organisms. It is used in more than 70 enzymes. It behaves as a Lewis acid in biochemical systems. It is soft acceptor as compared to other divalent cations like $Mg^{2+}$, $Ca^{2+}$ or $Mn^{2+}$ and therefore, acts as a stronger Lewis acid towards many biomolecules. The $Zn^{2+}$ complexes are also much more labile than the corresponding complexes of $Mg^{2+}$, $Ni^{2+}$, or $Mn^{2+}$ and the geometry of $Zn^{2+}$ complexes is facile as compared to those of $Mg^{2+}$, $Cu^{2+}$ or $Ni^{2+}$ complexes. Zinc containing enzyme carbonic anhydrase is vital for respiration in animals because it catalyses the normally slow carbonic acid- carbon dioxide reaction equilibrium.

$$CO_2\,(aq) + H_2O \underset{\text{anhydrase}}{\overset{\text{Carbonic}}{\rightleftharpoons}} H_2CO_3(aq)$$



The enzyme has one atom of zinc per molecule and has a molecular weight of 30,000. It has a common four coordinated environment around $Zn^{2+}$ in which three of the ligands are the immadazole nitrogens of three histidines and fourth is water molecule or hydroxide ion. The carbon dioxide hydration and dehydration of carbonic acid equilibrium is pH dependent.

**Carboxypeptidase** is also zinc containing enzyme having some 300 amino acid residues including three methionyl residues. Their functions are the catalytic hydrolysis of peptide bonds. Its activity is directed specially towards carboxyl terminal peptide bonds.



$$-\underset{|}{\overset{R}{CH}}-\overset{O}{\overset{\|}{C}}-NH-\overset{R'}{\overset{|}{CH}}-\overset{O}{\overset{|}{C}}-NH-\overset{R''}{\overset{|}{CH}}-COO^- \xrightarrow[\text{Carboxy peptidase}]{H_2O} -\overset{R}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-NH-\overset{R'}{\overset{|}{CH}}-COO^- + H_2N-\overset{R''}{\overset{|}{CH}}-COO^-$$

This enzyme is selective. It hydrolyses those polypeptides in which the terminal amino acid segment has an aromatic or a branch chain aliphatic substituent, R".

The deficiency of this enzyme may cause loss of appetite. It is only toxic in very large amounts. However, excess over doses may cause diarrhea and vomitting.

Cu ? P

## Selenium

Selenium is essential trace element for mammals and some higher plants. It is component of glutathione peroxidase. It is an essential constituent of some enzymes and protects biological systems against free radical oxidants, stresses and protects against heavy (soft) metal ions. It is moderately toxic to plants and highly toxic to mammals in higher or even in very low concentrations. Live stocks grown on selenium deficient pastures suffer from white muscle disease. However, if grazing in a soil having higher selenium concentration, they suffer from **central nervous system toxinosis.**

## Molybdenum

It is an essential trace element for all organisms with the possible exception of green algae. It is constituent of several enzymes which are used by nature for nitrogen fixation and nitrate reduction.

It is moderately toxic. Molybdenum excesses in biological systems may cause copper deficiency and is associated with gout like syndrome.

[illegible] liver pain [illegible] like arthritis.

## Chromium

It is an essential trace element which is present in adult human body in ultra trace amounts. It is involved in glucose metabolism and diabetes. Cr(III) and insulin both maintain the correct level of glucose in the blood. It is the component

It is highly toxic as Cr (VI) in which state it is carcinogenic.

## Manganese

It is essential to all organisms. It activates numerous enzymes. The Mn(II) enzyme produced in the liver converts nitrogenous waste products into urea which is carried by the blood to the ki which excrete it out into the urine.

The deficiency of manganese in soil inhibits plant growth and leads to infertility in ma which consume such plants.

**Nickel**

Nickel is an essential trace element for several hydrogenases and plant ureases (cla enzymes). Its deficiency in food slows down the functioning of the liver in chicks and rats rai deficient diet.

It is highly toxic to most plants and moderately toxic to mammals. It is carcinogenic if pre in higher concentrations in biological systems.

**Arsenic**

It is an ultra trace element in red algae, chick, rat, pig, goat and some mammals ind humans. Its deficiency in chicks results in depressed growth.

It is moderately toxic to plants and highly toxic to mammals when present in more than trace amounts.

**Cadmium**

This is an ultra trace element and has practically no significant use in living organisms. It i to all organisms. It is cummulative poison in mammals causing renal failure, hypertension, an and disorders of bone marrow.

**Mercury**

It has practically no biological function. It is highly toxic to fungi, green plants and anim is also cummulative poison for mammals.

**Nonmetals**

Among the nonmetals, the essential elements are hydrogen, carbon, oxygen, nitr phosphorus, sulphur, chlorine and iodine. Most of these are needed in trace amounts except C N and O which are abundant and are present in most of the chemicals in the living system.

**Phosphorus**

It is an important part of energy rich molecules, ATP and is an important component of the as apatite $Ca_5(PO_4)_3X$ where when X = OH, the **hydroxy apatite** is the major component of tissue in the skeleton of vertebrates. It is also strength ensuring material of the teeth. Partial for of fluorapatite, $Ca_5(PO_4)_3F$ strengthens the structure and makes it less soluble in the acid for from fermenting organic material in teeth.

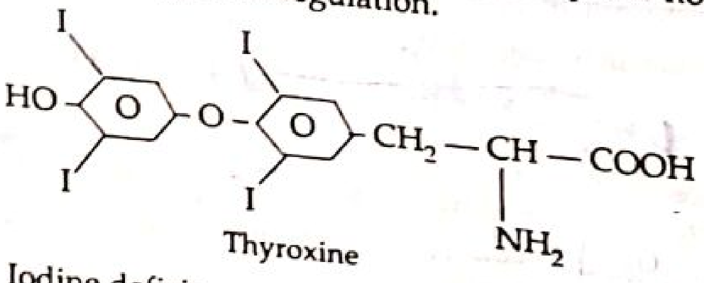
**Chloride**

$Cl^-$

It is the major anion commonly found within and without the cell. It is essential for higher and mammals as NaCl electrolyte. In HCl, it is essential in digestic juices. The deficiency of ch in infants can lead to impaired growth.

**Iodine**

It is an essential constituent of the thyroid hormone *e.g.* thyroxine which is impor metabolism and growth regulation.



Thyroxine

Iodine deficiency causes abnormal functioning of thyroid gland and causes goitre.