DIOXYGEN COMPLEXES

A compound capable of adding molecular oxygen and giving it up reversibly is called an oxygen carrying compound.

$$\text{Compound} + O_2 \rightleftharpoons \text{Compound}\cdot O_2$$

These oxygen carrying compounds are usually transition metal complexes. The O_2 molecule and its two reduced species O_2^- and O_2^{-2} can act as ligands to transition metals. The oxygen carrying compounds are of two types natural oxygen carriers and synthetic oxygen carriers. The transition metal present in those complexes plays a vital role in the oxygen carrying properties of the system.

The natural oxygen carriers are hemoglobin, hemocyanin, hemerythrin. Hemoglobin is a complex compound containing iron atom inside a heme group (which in turn is attached to a protein). Hemocyanin is a complex compound containing copper. Lobsters and crabs have blue blood which is due to hemocyanin. Hemerythrin is an iron complex. certain marine worms have violet colour blood due to hemerythrin.

The other type of oxygen carriers i.e. synthetic oxygen carriers of cobalt and Iridium have been synthesised. Molecular oxygen reacts reversibly with some metal complexes and such reversible reactions are involved in the oxygenation of hemoglobin and myoglobin. Generally electron is transferred from metal to O_2 with the formal oxidation of metal and reduction of O_2 initially giving a superoxo complex.

$$L_xM^{+n} + O_2 \rightleftharpoons L_xM^{(n+1)+}\cdot O_2^{\bullet}$$

Ex: $Co^{II}(acacen) + O_2 + Me_2NCHO \rightleftharpoons Co^{(III)}(O_2)(acacen)(Me_2NCHO)$

But in certain cases we can have 2e transfers giving a peroxo complex.

Ex: trans $Ir^{(I)}Cl(CO)(PPh_3)_2 + O_2 \rightleftharpoons Ir(O_2)Cl(CO)(PPh_3)_2$

The reaction of a superoxo complex with a second metal can lead to a bridging μ-peroxo species, which in turn can be oxidised to μ-superoxo species.

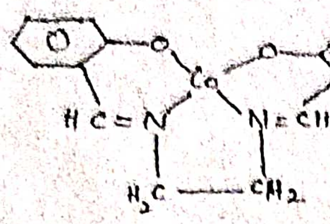
$$L_xM^{(n+1)+}O_2^- + L_xM^{+n} \rightleftharpoons L_xM^{(n+1)+}\underset{\text{peroxo complex}}{-(\mu-O_2^{-2})-}ML_x^{(n+1)+}$$

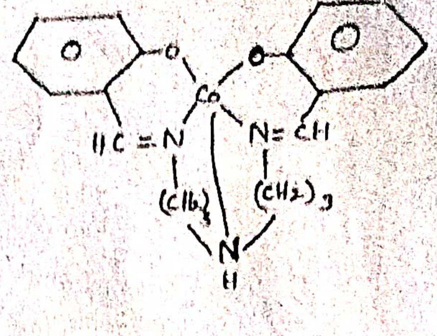
$$L_xM^{(n+1)+}-(\mu-O_2^{-2})-ML_x^{(n+1)+} \xrightleftharpoons[+e^-]{-e^-} L_xM^{(n+1)+}\underset{\text{Superoxo complex}}{-(\mu-O_2^-)-}ML_x^{(n+1)+}$$

The ammonical solutions of Co(II) salts on oxidation by air give brown salts called oxocobaltiates. Such oxidation at different conditions produce $\left[(H_3N)_5\overset{+3}{Co}-O_2^{-2}-\overset{+3}{Co}(NH_3)_5\right]^{+4}$ [Brown and diamagnetic] and $\left[(H_3N)_5\overset{+3}{Co}-O_2^{-}-\overset{+3}{Co}(NH_3)_5\right]^{+5}$ [green and paramagnetic]. The ammonical solution of Co(II) salt can also be oxidised by H_2O_2. These two complex ions cannot bind oxygen reversibly and hence cannot be used as oxygen carrier. The incapability of oxygen carrying capacity in these complexes is due to the existence of σ bond between oxygen and metal.

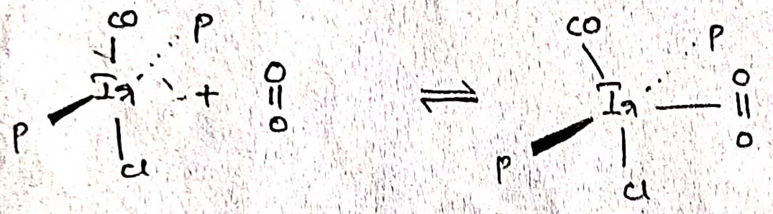
Hence any dioxygen complex to be oxygen carrier, the metal in the complex must bond to oxygen by a π bond

Have the certain cobalt chelates can behave as oxygen carriers. These two chelates are known to be able to reversibly carry oxygen both in the solid state and in solution.





Another well known oxygen carrier is an Iridium complex $[Ir(PPh_3)_2COCl]$. This compound does not react with O_2 as a solid, but in bezene solution it takes up one mole of oxygen(O_2) per iridium. As a result the colour of the compound changes from yellow to red.

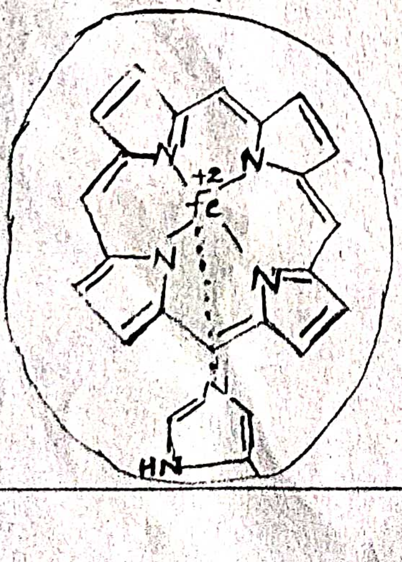


Hence it can be concluded that, oxygen carrying capability of a complex depends upon the reversible bonding of molecular oxygen.

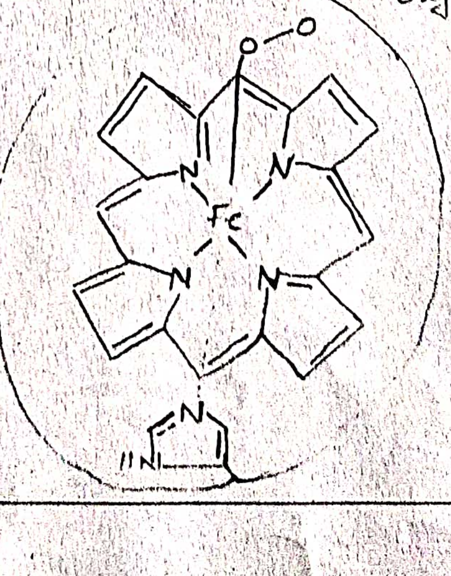
Structure of dioxygen complex:

Iron porphyrine play an important role such as transport and storage. In this the active site is defined by an iron centre co-ordinated by four nitrogen atoms provided by one heme group and fifth co-ordination by another base of protein chain

deoxyhemoglobin



oxyhemoglobin



In the deoxy form, the active site consists of an Iron (II) porphyrin encapsulated a water resistant pocket and bound through the imidazole group of histidine residue. he ferrous ion is 5- co-ordinated which allows the reversible binding of molecular oxygen in sixth co-ordination as shown above.

In the deoxy form the iron (II) atom is in the high spin states and lies about 0.5A' out of heme plane in the direction of the histidine group.

In the oxygenated form the iron (II) ion is in the low spin state and is nearly centred in the porphyrin plane. The dioxygen unit is bound in a bent fashion.

An important parameters that effects the oxygen binding ability is the acidity of the media, under acidic conditions the equilibrium between deoxy and oxy Hb is shifted in favour of the deoxygen process.

This pH dependence of dioxygen binding with hemoglobin is called as ~~Bohr~~ "Bohr effect". The dioxygen is ~~found~~ bound to the iron with an angle of ≅150° and an Fe-O bond length of ≅180pm.

DINITROGEN COMPLEXES

Molecular nitrogen, N_2 isoelectronic with both CO and nitrosyl ion (NO^+). There are numerous complexes of CO and NO^+ and for many years no dinitrogen complex was known. This is attributed to the lack of polarity of N_2 and a resultant inability to behave as a π-acceptor.

The first dinitrogen complex was identified in 1965, resulted from the reduction of $RuCl_3(aq)$ by hydrazine hydrate. This is also synthesised by the reaction of N_2 with $[Ru(NH_3)_5H_2O]^{+2}$

$$[Ru(NH_3)_5H_2O]^{+2} + N_2 \longrightarrow [Ru(NH_3)_5N_2]^{+2}$$

Strong nucleophilicity of N_2 was shown by the displacement of water and the same is observed in the formation of bridged complex

$$[Ru(NH_3)_5N_2]^{+2} + [Ru(NH_3)_5H_2O]^{+2} \longrightarrow [Ru(NH_3)_5N_2Ru(NH_3)_5]^{+4} + H_2O.$$

Nitrogen complexes are usually made by reduction of halide complexes using sodium amalgam or other chemical reductants in an atmosphere of N_2

$$[Ru(NH_3)_5Cl]^{+2} \xrightarrow[H_2O]{Zn/Hg} [Ru(NH_3)_5H_2O]^{+2} \xrightarrow[N_2]{100\,atm} [Ru(NH_3)_5N_2]^{+2} + H_2O.$$

This dinitrogen complex ion can be isolated as its chloride.

The cation of the type $[(H_3N)_5Ru-N_2-Ru(NH_3)_5]^{+4}$ in which nitrogen molecule acts as a bridge can be obtained by the action of Zn amalgam on $[Ru(NH_3)_5Cl]^{+2}(aq)$ in the presence of nitrogen. It is also obtained as a by product in the $[Ru(NH_3)_5(H_2O)]^{+2}-N_2$ reaction.

Some dinitrogen complexes can be prepared by the direct uptake of gaseous nitrogen at atmospheric pressure in the presence of reducing agents and tertiary phosphine and arsines.

$$Co(acac)_3 + 3Ph_3P + N_2 \xrightarrow{Al(iso\,C_4H_9)_3} [Co\,H\,N_2(PPh_3)_3]$$

$$FeCl_2 + 3PEtPh_2 + N_2 \xrightarrow[EtOH]{NaBH_4} Fe\,H_2N_2(PEtPh_2)_3$$

$$OsCl_3(AsR_3)_3 + N_2 \xrightarrow[THF]{Zn/Hg} OsCl_2N_2(AsR_3)_3$$

Dinitrogen complexes can also be prepared by the reaction of nitrogen containing complexes with nitrous acid.

$$[Os(NH_3)_5N_2]^{+2} + HNO_2 \longrightarrow cis[Os(NH_3)_4(N_2)_2]^{+2} + 2H_2O.$$

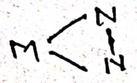
The most stable dinitrogen complexes are those of ruthenium, osmium and Iridium. Because the dinitrogen complexes of these metals do not decompose even at 100-200°c

Structure and Bonding:

There are two structural posibilities for terminal dinitrogen ligands and two for bridged cases.

M—N—N
end on terminal

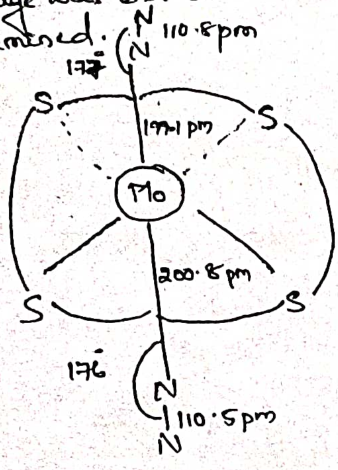
M—N—N—M
end on bridged

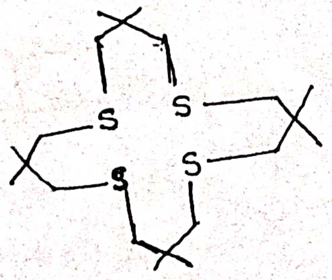


Side on terminal

Side on bridged.

x-ray study of ruthenium-dinitrogen complex indicated that the nature of Ru-N-N linkage was end-on. Structure for bis(dinitrogen) crown ~~ether~~ thioether complex was determined.





$Me_8[16]ane\,S_4$

The results for the complex are typical and shows that N_2 greatly resembles 'CO' in its bonding to metals. Back donation of electron density from metal to π^* (antibonding) orbitals is also confirmed from the short Mo-N bond which is more similar in length to Mo-CO than to the $Mo-NH_3$ bond in ammine complexes. The mean N-N bond length (110.65 pm) is slightly greater than that found in molecular nitrogen. This suggests weakening of nitrogen-nitrogen triple bond from the donation of electron density into the π^* orbital of N_2. No example of side on binding by N_2 has been reported in non-bridging complexes.

Evidences. Raman stretching frequency of free N_2 is 2331 cm^{-1}. upon co-ordination this vibration becomes IR active and shifts to lower frequency. For example, strong N-N stretching bands appear at 2105 cm^{-1} for $[Ru(NH_3)_5(N_2)]Cl_2$ and at 1955 and 1890 cm^{-1} for trans-$Mo(N_2)_2Me_8[16]ane\,S_4$.

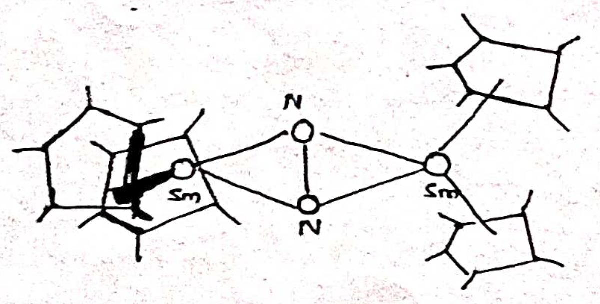
So metal-ligand bonds in carbonyl and dinitrogen complexes are very similar. But CO has superior π-accepting ability than N_2 due to this carbonyl dinitrogen complexes are unstable. When dinitrogen functions as bridging ligand, it usually exhibits end on co-ordination.

Eg: $[(H_3N)_5Ru-N_2-Ru(NH_3)_5]^{+4}$.

The superior π accepting ability of CO also accounts for the instability of carbonyl dinitrogen complexes. Both $Cr(CO)_5N_2$ and cis $Cr(CO)_4(N_2)_2$ have been investigated at low temperatures, but decompose when warmed. If some of the carbonyls are replaced with phosphines then there can be sufficient electron density which enhances the stability. For example $Mo(CO)_3(PCy_3)_2N_2$ can be isolated at room temperature.

$$Mo(CO)_3(PCy_3)_2 + N_2 \longrightarrow Mo(CO)_3(PCy_3)_2N_2$$

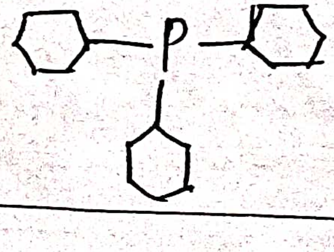
Recently, a dinitrogen complex of samarium (f-block metal) has been reported. In this complex molecular nitrogen functions as a side-on bridging ligand. This complex is obtained from the reaction of $Sm(C_5Me_5)$ and N_2. In this complex the two samarium atoms and two nitrogen atoms are in a planar arrangement and N-N bond distance (108.5 pm) is shorter than that found in free N_2



The significance of the transition metal dinitrogen complex is based on the capability of reducing the molecular nitrogen to ammonia and regenerating the nitrogen absorbing species. The reduction of molecular nitrogen to ammonia is known as nitrogen fixation. There are certain enzymes in nature which convert atmospheric nitrogen into ammonia. Nitrogenase is one such enzyme which is involved in nitrogen fixation.

Cy - cyclohexyl ligand.

$P(Cy)_3 - P(C_6H_{11})_3$



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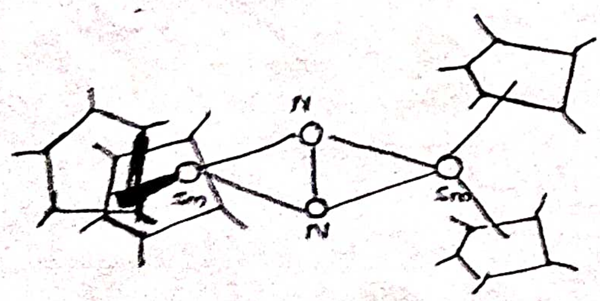

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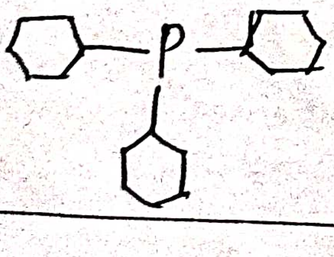


METAL NITROSYLS

The coordination compounds in which NO molecule is attached to a metal atom or ion as NO^+ ion are known as metal nitrosyls. The attachment of NO^+ to metal takes place through Nitrogen atom. In metal nitrosyls NO^+ acts as a ligand. Several types of metal nitrosyls are

(a) Metal nitrosyl carbonyls: The coordination compounds which contain both NO^+ and CO as ligands are known as metal nitrosyl carbonyls

Eg: $[\overset{2-}{Fe}(\overset{+}{NO})_2(CO)_2]$, $[\overset{-}{Co}(\overset{+}{NO})(CO)_3]$ etc.

(b) Metal Nitrosyl halides: The coordination compounds which contain both NO^+ and X^- (halide ion) as ligands are known as metal nitrosyl halides.

Eg: $[\overset{-}{Co}(\overset{+}{NO})_2X^-]$, $[Ni(\overset{+}{NO})X]$, $[\overset{-}{Fe}(\overset{+}{NO})_2I]$ etc.

(c) Metal nitrosyl thiocomplexes: This sort of metal complexes can only be given by Fe, Co, Ni

Eg: $M^+[\overset{-}{Fe}(\overset{+}{NO})_2S]^-$, $M^+[\overset{-}{Ni}(\overset{+}{NO})_2S]$ etc.

(d) Metal nitrosyl cyano complexes:

Eg: $[Mn^+(NO^+)(CN)_5]^{-3}$, $[\overset{+2}{Fe}(\overset{+}{NO})(CN)_5]^{-2}$ etc.

(e) Miscellaneous metal nitrosyl complexes:

Eg: $[\overset{+}{Co}(\overset{+}{NO})(NH_3)_5]^{+2}$, $[Co^+(\overset{+}{NO})(NO_2)_5]^{-3}$ etc.

Preparation of Metal nitrosyls:

(i) Metal nitrosyl carbonyls can be obtained by the action of nitric oxide on metal carbonyls.

$$[Fe(CO)_5] + 2NO \xrightarrow{95^\circ c} [Fe(CO)_2(NO)_2] + 3CO.$$

$$[Co_2(CO)_8] + 2NO \xrightarrow{40^\circ c} 2Co(CO)_3(NO) + 2CO.$$

$$[Fe_3(CO)_{12}] + 6NO \xrightarrow{85^\circ c} 3Fe(CO)_2(NO)_2 + 6CO.$$

(ii) Metal nitrosyl halides can be prepared in two ways:

(a) They can be prepared by the action of NO on metal halides in the presence of suitable metal (Co, Zn etc.) which acts as a halogen acceptor.

$$CoX_2 + 4NO + Co \longrightarrow 2[Co(NO)_2X]$$

$$2NiI_2 + 2NO + Zn \longrightarrow 2[Ni(NO)I] + ZnI_2$$

(b) They can be prepared by the action of halogen on nitrosyl carbonyls

$$2[Fe(CO)_2(NO)_2] + I_2 \longrightarrow 2[Fe(NO)_2I] + 4CO.$$

(iii) Sodium nitroprusside can be prepared in two ways

(a) It can be prepared by the action of $NaNO_2$ on $Na_4[Fe(CN)_6]$

$$Na_4[Fe(CN)_6] + NaNO_2 + H_2O \longrightarrow Na_2[Fe(CN)_5(NO^+)] + 2NaOH + NaCN.$$

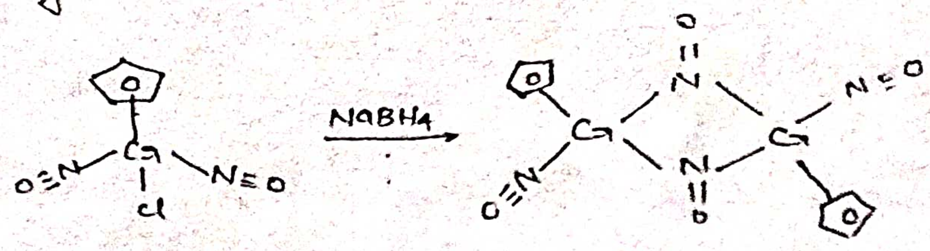
(b) Sodium nitroprusside can also be prepared by the action of nitric oxide on $Na_4[Fe(CN)_6]$ in acidic condition.

$$2Na_4[Fe(CN)_6] + H_2SO_4 + 3NO \longrightarrow 2Na_2[Fe(NO)(CN)_5] + 2NaCN + Na_2SO_4 + \frac{1}{2}N_2 + H_2O.$$

(iv) Metal nitrosyls complex of Iridium can be prepared by the action of $NO^+BF_4^-$ on Vaska's complex.

$$[Ir(PPh_3)_2COCl] + NO^+BF_4^- \longrightarrow [Ir(PPh_3)_2CO\,NO\,Cl]^+BF_4^-$$

(v) Although the nitrosyl group generally occurs as a terminal ligand, bridging nitrosyls are also known.



The final product contains bridging as well as terminal nitrosyl groups. It is also evidenced with IR frequencies ν (terminal NO) = 1672 cm^{-1} and
ν (bridging NO) = 1505 cm^{-1}

Properties of metal nitrosyls:

(i) Substitution reaction: In metal nitrosyl carbonyls the CO group can be substituted by ligands like PR_3, CNR, Phen etc.

$$Fe(CO)_2(NO)_2 + 2L \longrightarrow Fe(L)_2(NO)_2 + 2CO$$ where L can be PR_3, CNR

(ii) Action of halogens: Metal nitrosyl carbonyls on treatment with halogens give metal nitrosyl halides.

$$2[Fe(CO)_2(NO)_2] + I_2 \longrightarrow [Fe(NO)_2I]_2 + 4CO.$$

The metal nitrosyl halides reacts with other ligands to form mononuclear complexes.

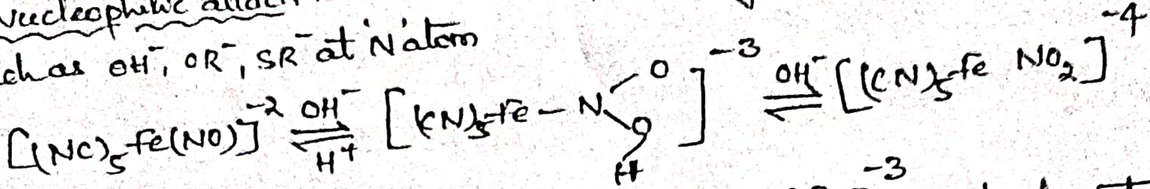
(a) $[Fe(NO)_2X]_2 + 2L \longrightarrow 2[Fe(NO)_2XL]$

Iron nitrosyl halide reacts with K_2S and then with CH_3Cl to form dark red compounds which are called Roussin's salts

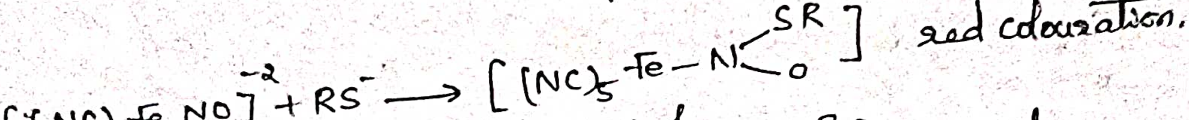
$$[Fe(NO)_2I]_2 \xrightarrow[-2KI]{+2K_2S} K_2[Fe(NO)_2S]_2 \xrightarrow[-2KCl]{+CH_3Cl} [Fe(NO)_2(SCH_3)]_2$$

(iii) Due to differences in the electronic structures of linear, bent and bridged 'NO' groups, considerable differences in their chemical reactivity can be expected. Generally, linear MNO groups are attacked by nucleophiles while bent ones, with a lone pair on 'N' are susceptable to electrophilic attack.

(a) Nucleophilic attack: Linear "NO" complexes in general interacts with nucleophiles such as OH^-, OR^-, SR^- at 'N' atom



$$[(NC)_5Fe(NO)]^{-2} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} \left[(CN)_5Fe-N\begin{smallmatrix}O\\ OH\end{smallmatrix}\right]^{-3} \overset{OH^-}{\rightleftharpoons} [(CN)_5Fe\ NO_2]^{-4}$$



$$[(NC)_5Fe\ NO]^{-2} + RS^- \longrightarrow \left[(NC)_5Fe-N\begin{smallmatrix}SR\\ O\end{smallmatrix}\right]^{-3}$$ red colouration.

This test is used to detect the thiols

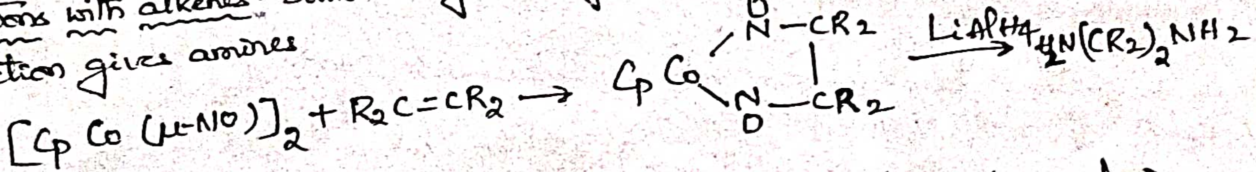
(b) electrophilic attack: Attack by H^+ & Me^+ may be at either N & O

$$(PPh_3)_3(CO)Cl\ Os(NO) \xrightarrow{HCl} (PPh_3)_2(CO)(Cl_2)Os-N\begin{smallmatrix}H\\ O\end{smallmatrix}$$

(iv) oxygenation: Some 'NO' complexes react with O_2

$$L_nMNO + \tfrac{1}{2}O_2 \rightleftharpoons L_nMNO_2$$

(v) Reactions with alkenes: Some bridged nitrosyls react with alkenes, finally on reduction gives amines



$$[CpCo(\mu\text{-}NO)]_2 + R_2C=CR_2 \rightarrow CpCo(ON-CR_2)(ON-CR_2) \xrightarrow{LiAlH_4} H_2N(CR_2)_2NH_2$$

(vi) Reduction: Reduction of L_nMNO by boro & alumino hydrides & other reducing agents can give species with H-M-NO units that can be further reduced to amines.

$$FeCl(NO)_3 \xrightarrow{Al} Fe_2(NO)_4(\mu\text{-}NH_2)_2$$

$$[RuCl(Py)_4NO]^{+2} \xrightarrow{Zn/H^+} [RuCl(Py)_4(NH_3)]^{+} + H_2O.$$

Many 'NO' species can of course undergo reversible $1e^-$ reductions such as

$$[(Et_2)(NCS)_2Mo(NO)_2] \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Et_2(NCS)_2Mo(NO)_2]^-$$

Properties of Sodium nitroprusside [$Na_2[Fe(CN)_5NO^+]$]:-

(i) Sodium nitroprusside is crystalline in nature and the crystals are ruby red in colour and are easily soluble in water.

(ii) To a solution containing sulphide ion, if freshly prepared sodium nitroprusside solution is added, a purple or violet colouration is produced. This is due to the formation of $Na_4[Fe^{+2}(CN)_5(NO^+)S]$ and formation of this complex confirms the presence of sulphide ion. [S^{-2} ion]

$$Na_2S + Na_2[Fe^{+2}(CN)_5(NO^+)] \longrightarrow Na_4[Fe^{+2}(CN)_5(NO^+)(S^{-2})]$$

violet or Purple colour.

(iii) The diamagnetic nature of $[Fe(CN)_5(NO)]^{-2}$ confirms the presence of NO as NO^+ ion in the complex.

(iv) On treatment with alkali sodium nitroprusside is converted to sodium ferrocyanide.

$$6Na_2[Fe(CN)_5NO] + 14NaOH \longrightarrow 5Na_4[Fe(CN)_6] + Fe(OH)_2 + 6NaNO_2 + 6H_2O.$$

(v) Silver nitrate on treatment with sodium nitroprusside produces a flesh coloured complex

$$2AgNO_3 + Na_2[Fe(CN)_5NO] \longrightarrow Ag_2[Fe(CN)_5NO] + 2NaNO_3$$

(vi) Alkali sulphites on treatment with sodium nitroprusside produces rose red colour due to the formation of a complex

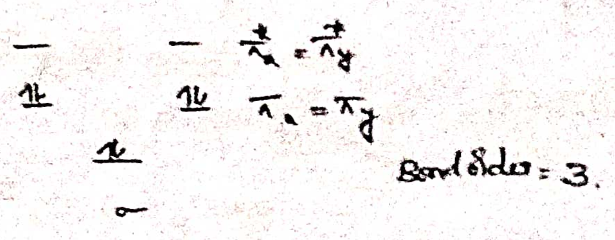
$$Na_2SO_3 + Na_2[Fe(CN)_5NO] \longrightarrow Na_4[Fe(CN)_5(NO)(SO_3)]$$

This test can be used to distinguish sulphites from thiosulphates because thiosulphates do not produce such complexes

Structure and Bonding:

The nitrosyl cation is isoelectronic with CO. They each have three bonding pairs between the atoms and lone pairs on both atoms.

NO^+ – $3+4-1 = 6$
CO – $2+4 = 6$



Bond Order = 3.

In NO molecule each atom is a potential donor. But the nitrogen co-ordinates preferentially, avoiding a large formal +ve charge on the more electronegative oxygen atom. In many respects NO^+ behaves similar to that of CO. However, in some important respect the nitrosyl group behaves in a manner not observed for carbon monoxide. In metal nitrosyl complexes, the nitrosyl ligand can exist either as a linear ligand or as a bent ligand. A bent nitrosyl ligand is an analogue of an organic nitroso group or

The NO group in Cl-N=O, where the nitrogen can be considered ~~to~~ be sp^2 hybridised and bears a lone pair. It is this lone pair that causes the nitrosyl group to be bent. Linear nitrosyl group is regarded as three electron donor and a bent nitrosyl group is regarded as one electron donor. In case of linear nitrosyl group, a nonbonding electron pair on nitrogen as well as the unpaired electron in the antibonding molecular orbital of NO are donated to metal atom of ion.

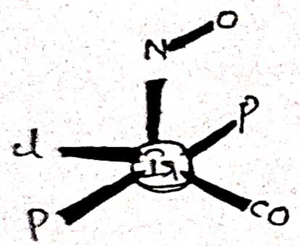
$$M + :N\dot{\equiv}O: \longrightarrow \overset{-2}{M}-\overset{+}{N}\equiv\overset{+}{O}: \longleftrightarrow \overset{-}{M}=\overset{+}{N}=\ddot{O}$$

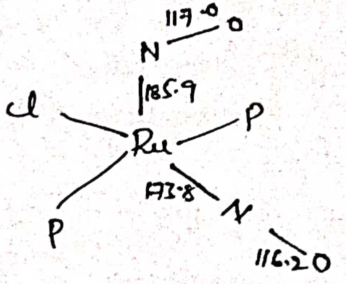
The ligand is viewed as a coordinated nitrosyl ion, NO^+ when linear and coordinated NO^- when bent.

The bent nitrosyl ligand was found in a derivative of vaska's complex

$$Ir(Ph_3P)_2(CO)Cl + NO^+BF_4 \longrightarrow [Ir(Ph_3P)_2\,CO\,NO\,Cl]^+BF_4^-$$

The product is square pyramidal with a bent nitrosyl group at the apical position. Other complex with bent M-NO is $[Ru(Ph_3P)_2(NO)_2Cl]^+$. This complex contains both linear and bent nitrosyl group.





To know whether the NO group is linear & bent, it is very necessary to know about the position of the lone pair of electrons. If there are available non bonding molecular orbitals on the metal (an electron poor system), the pair can reside in the non bonding MO of metal and allow the nitrogen to function as an sp σ donor with concomitant π back bonding. On the other hand if all the low-lying orbitals on the metal are already filled, the pair of electrons must occupy an essentially non-bonding orbital on the nitrogen, requiring trigonal hybridisation (sp^2) and a bent system.

The metal-nitrogen bond lengths in the ruthenium complex containing both types of nitrosyl ligands are in accordance with the expected values. In a linear system there is a short metal nitrogen bond (173.8 pm) indicating substantial π bonding. In a bent system there is long metal-nitrogen bond (185.9 pm) which essentially involves σ-bonding only. Where as NO bond lengths in bent and linear systems (ie 117.0 and 116.2 pm) are very nearly equal, indicate that both apical and basal arrangements of NO groups has a bond order in between two and three.

MAGNETIC PROPERTIES

Thermal energy and Magnetic property:

A number of J levels are possible for a multielectron system. The ground state J level will be decided by Hund's rule. The J levels of a given Russell-Saunders term together constitute a multiplet, and a given J level of the multiplet is called a component of the multiplet. The energy gap between two successive J levels is known as the multiplet width. Normally, the magnetic property of a substance originates from its ground state. In certain cases, the energy gap between successive J levels may be less i.e. the upper J levels may lie closer to the ground state. If ~~the~~ the J levels exist closely then the multiplet width is in the neighbourhood of kT, the thermal energy. In such a situation, the excited states may be significantly populated. The existence of population in higher energy state alters the magnetic moment of the substance. Therefore it is necessary to consider the population of the excited state while deriving the magnetic moment. Such a consideration leads to three distinct situations, namely (i) the multiplet width is large as compared to kT, (2) the multiplet ~~wid~~ width is small as compared to kT and (3) the multiplet width is comparable to kT.

(1) Multiplet width large as compared to kT:

Multiplet width will be larger than kT, only when L and S vectors interact strongly. The interaction of L and S vectors generate a resultant vector J. In this situation, J becomes a good quantum number such that the quantum numbers L and S no longer dictate the ultimate magnetic properties. Because of strong interaction between L and S vectors, the energy separation between successive J levels will be large. As a result, the lowest lying component (i.e. J level) alone is populated.

In this case, the magnetic moment can be calculated using formula

$$\mu_J = g\beta\sqrt{J(J+1)}$$

(2) Multiplet width small as compared to kT:

When the multiplet width is quite small as compared to kT, virtually all the J levels may be assumed to be populated.

In this case, the magnetic moment can be calculated using the formula

$$\mu_{L+S} = \sqrt{L(L+1)+4S(S+1)}\ \beta.$$

(3) Multiplet width comparable to kT:

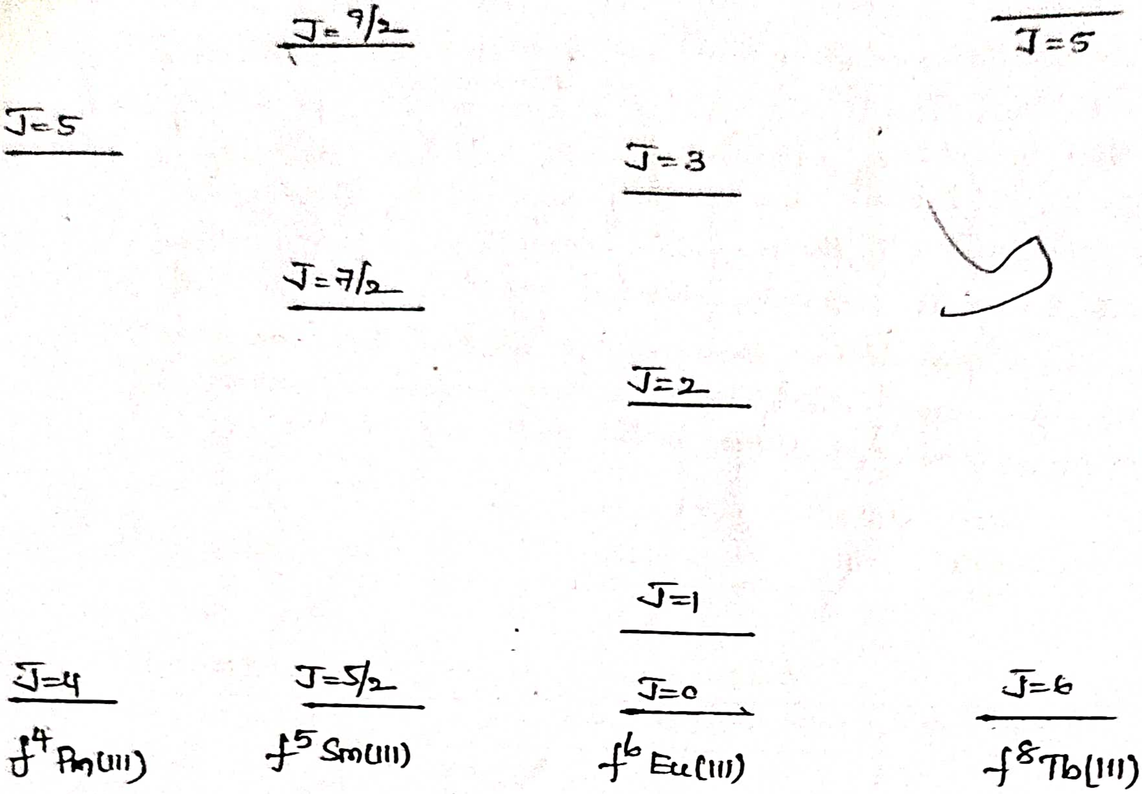
When the multiplet width is comparable to kT then the magnetic moments can be calculated using complicated formula.

Magnetic properties of Lanthanides and Actinides:

The fifteen lanthanides (lanthanum to lutecium) belong to the inner transition series. Among these lanthanides, the common oxidation state is +3. The trivalent lanthanides have the electronic configuration [Pd] $4f^n 5s^2 5p^6$ (n=0 to 14 from La to Lu). The magnetism in lanthanides arises from the 4f level. Since the 4f level is incompletely filled and is too far inside (i.e. effectively shielded by the filled 5s and 5p subshells) to be influenced by the surrounding coordinating ligand, a trivalent lanthanide complex functions as a free ion. The crystal field effect in a lanthanide is no more than about one-hundredth that observed in a first transition series metal ion. Also, in lanthanides, the spin-orbit coupling constant is quite high. As a result Lands vectors effectively couple to give the J vector. Therefore, J is a good quantum number for lanthanides. The magnetic moments for lanthanides can be calculated using the formula $\mu_J = g\beta\sqrt{J(J+1)}$. It should be noted that the $\mu_S = \sqrt{4S(S+1)}$ BM and $\mu_{L+S} = \sqrt{L(L+1)+4S(S+1)}$ BM does not apply except for the ions with the f^0, f^7 and f^{14} configurations. For these three configurations, L=0, so that the μ_J equation automatically reduces to the μ_S equation.

The following table, includes the magnetic moments for the trivalent lanthanides, calculated using μ_J equation and determined experimentally. These two magnetic moments i.e. μ_J and μ_{exp} are in good agreement with each other for all the lanthanides except for Samarium (III) and Europium (III). The two lanthanides Sm(III) and Eu(III) do not obey the μ_J equation. The deviation exhibited by these two lanthanides can be explained by considering J levels and the possible energy separation between them. The study of J levels for Sm(III) and Eu(III) is studied in conjunction with that of Promethium (III) and Terbium (III).

The J values of these four ions are shown in the following figure.



The energy separation between the ground state and the first excited state is 5λ for Pm(III), 7/2λ for Sm(III), λ for Eu(III) and 6λ for Tb(III). Where λ is spin-orbit coupling constant and the value of which indicates the extent of spin-orbit coupling. The energy separation between these states in Eu(III) is close to kT. Therefore, at room temperature, the first excited state of Sm(III) and the first and even the second and third excited states of Eu(III) are populated. As a result, the magnetic moments for these ions cannot be calculated using μ_J equation and [illegible] are calculated using the complicated equation.

Actinides:

As in lanthanides, the f orbitals are incompletely filled in actinides. The 5f orbitals of the actinides are poorly shielded by the outer orbitals. It is because of this poor shielding, the 5f orbitals of the actinides are under a much greater crystal field effect than the 4f orbitals of the lanthanides. The crystal field effect in an actinide compound is about one-tenth that in a first transition series metal ion and at least ten times more than that in a lanthanide.

The Russell-Saunders coupling is not valid in actinides, instead j-j coupling is observed in the actinide compounds. The experimental magnetic moment of the actinides is less ~~that~~ than that of a lanthanide with similar electronic configuration. As the 5f orbitals are greatly affected by the crystal field, the orbital contribution for the magnetic moment may be quenched. The deviation in the magnetic moments exhibited by Plutonium (III) and Americium (III) can be explained in a similar way as that of Samarium (III) and Europium (III). The experimental and theoretical magnetic moments of some actinides compounds are shown in the following table.

TABLE 3.1 Magnetic properties of lanthanides

n $(4f^n)$	M^{3+}	L	S	Ground state term	g	μ_J (B.M.)	μ_{exp} (B.M.)
0	La	0	0	$^1S_0$		0	Diamagnetic
1	Ce	3	1/2	$^2F_{5/2}$	6/7	2.54	2.3–2.5
2	Pr	5	1	$^3H_4$	4/5	3.58	3.4–3.6
3	Nd	6	3/2	$^4I_{9/2}$	8/11	3.62	3.5–3.6
4	Pm	6	2	$^5I_4$	3/5	2.68	
5	Sm	5	5/2	$^6H_{5/2}$	2/7	0.84	1.5–1.6
6	Eu	3	3	$^7F_0$	1	0	3.4–3.6
7	Gd	0	7/2	$^8S_{7/2}$	2	7.94	7.8–8.0
8	Tb	3	3	$^7F_6$	3/2	9.72	9.4–9.6
9	Dy	5	5/2	$^6H_{15/2}$	4/3	10.63	10.4–10.5
10	Ho	6	2	$^5I_8$	5/4	10.60	10.3–10.5
11	Er	6	3/2	$^4I_{15/2}$	6/5	9.57	9.4–9.6
12	Tm	5	1	$^3H_6$	7/6	7.63	7.1–7.4
13	Yb	3	1/2	$^2F_{7/2}$	8/7	4.50	4.4–4.9
14	Lu	0	0	$^1S_0$	1	0	Diamagnetic

TABLE 3.3 Electronic structure of actinide elements

Element	Symbol	Atomic number	Electronic structure
Actinium	Ac	89	$6d^17s^2$
Thorium	Th	90	$6d^27s^2$
Protactinium	Pa	91	$5f^16d^27s^2$
Uranium	U	92	$5f^36d^17s^2$
Neptunium	Np	93	$5f^57s^2$
Plutonium	Pu	94	$5f^67s^2$
Americium	Am	95	$5f^77s^2$
Curium	Cm	96	$5f^76d^17s^2$
Berkelium	Bk	97	$5f^86d^17s^2$
Californium	Cf	98	$5f^{10}7s^2$

The electronic structure of the remaining actinides is not shown because their magnetic properties are not known with certainty.

TABLE 3.4 Experimental (μ_{exp}) and theoretical (μ_J) magnetic moments of some actinide compounds

n (f^n)	Ion	Russell-Saunders term symbol	Compound	μ_J (B.M.)	μ_{exp} (B.M.)
1	U^{5+}	$^2F_{5/2}$	UCl_5	2.54	1.7
	Np^{6+}	$^2F_{5/2}$	NpF_6	2.54	2.0
2	U^{4+}	$^3H_4$	$[N(CH_3)_4]_2UCl_6$	3.58	2.2
	Pu^{6+}	$^3H_4$	PuF_6	3.58	0.6
	Np^{5+}	$^3H_4$	$NpO_2(C_2O_4H)\cdot 2H_2O$	3.58	3.2
3	Np^{4+}	$^4I_{9/2}$	$KNpF_5$	3.62	2.9
4	Pu^{4+}	$^5I_4$	$[N(CH_3)_4]_2PuCl_6$	2.68	1.8
5	Pu^{3+}	$^6H_{5/2}$	PuF_3	0.84	1.2
6	Am^{3+}	$^7F_0$	AmF_3	0	1.6
7	Cm^{3+}	$^8S_{7/2}$	CmF_3	7.94	7.9

Spectral Properties of Lanthanides & Actinides.

Electronic spectra:

Generally metal ion complexes exhibit four types of electronic spectra

(1) Legand field spectra:

This spectra is due to the electronic transitions totally within the metal ion. These transitions may be between one d-orbital and other d-orbital or from one f-orbital to other f-orbital.

(2) Legand to Metal charge transfer:

This occurs due to the transition of electron from Molecular orbital located on the legand to the non-bonding or antibonding molecular orbital located on the metal ion.

(3) Metal to legand charge transfer:

This occurs due to the transition of electron from an antibonding or non-bonding orbital on the metal to the antibonding orbital located on the legand.

(4) The intraligand transitions:

The intraligand transitions are observed when an electron transition takes place from one ligand orbital to another orbital.

All the electronic transitions are not allowed. Some restrictions are imposed on the electronic transitions interms of selection rules from the knowledge of quantum mechanics.

(a) Spin selection rule:

According to spin selection rule, transitions are allowed between those levels for which $\Delta S = 0$ i.e. levels with same spin multiplicity

(b) Laporte selection rule:

According to this rule transitions occur only between the levels with $\Delta l = \pm 1$ i.e. the transitions in a given set of d or f orbitals are forbidden if the molecule or ion has a centre of symmetry.

Electronic spectra of lanthanides and actinides

The absorption spectrum of a lanthanide or an actinide complex results from the Laporte forbidden f–f transitions. The 4f orbitals of the lanthanides are deep seated and are therefore not exposed to the surrounding coordinating ligands. An electronic transition between the J states leads to a weak, sharp, line like band. The broadening of a band usually depends on the vibrational effects of the ligands surrounding the metal ion. However, the influence of ligands on the 4f orbitals of lanthanides is minimum and hence the f–f transitions are observed as narrow bands. In case of d-d transitions of transitional metal ions complexes, broad absorption bands are observed. The line like band in lanthanides become narrower as the temperature decreases.

However, if the 4f electron is excited to outer levels, which are under the influence of surrounding ligands, results in strong and broad absorption bands. A broad electronic spectral band in a lanthanide complex can also result from an L→M charge transfer transition. The electronic spectrum of a lanthanide complex is remarkably insensitive to a change in the environment of the lanthanide ion.

The actinide complexes (for example, the complexes of Am^{+3} and still heavier actinides) also exhibit narrow electronic spectral bands. Even those narrow bands are about ten times more intense than those of the lanthanide complexes. The electronic spectral bands of the complexes of Pu^{+3} and still lighter actinides are broad, similar to the broad bands observed in the transition metal complexes. This tendency in lighter actinides is due to the greater exposure of 5f orbitals and also due to the broadening effect of the vibrations of the ligands. In case of heavier actinides, the nuclear charge increases and hence the 5f orbital behave like 4f orbital of the Lanthanides, and as a result, the electronic spectral behaviour of the lanthanides and heavier actinides are comparable. Even in actinides the broad bands may also arise due to the charge transfer transitions.

Analytical applications of Lanthanides and Actinides:

1. Lanthanide and Actinide Complexes; $Ln(L\text{-}L)_3$ and $An(L\text{-}L)_3$, of sterically hindered β-diketones [eg. $Me_3C-\overset{O}{\overset{\|}{C}}-CH=\overset{O}{C}-CMe_3]^-$ are volatile. Though they have high molecular weight, they have measurable vapour pressure at temperatures below the boiling point of water. They have been used as antiknock additives, solventextraction and as homogeneous catalysts.

2. The Lanthanide complexes of β-diketonates have been used as NMR shift reagents. The proton NMR spectrum of ~~eth~~ cholestrol is greatly simplified in presence of $Eu(dpm)_3 Py)$. Similarly the ^1H-NMR spectrum of heptanol is also simplified with the use of these shift reagents.

3. To a solution containing oxalate ion, if cerous nitrate is added then a white precipitate of cerous oxalate is obtained. The precipitate is insoluble in water and dissolves slightly in dilute acids.

$$2\,Ce(NO_3)_3 + 3H_2C_2O_4 \longrightarrow Ce_2(C_2O_4)_3 + 6HNO_3$$

4. Ceric sulphate $[Ce(SO_4)_2]$ is a good oxidising agent. It is used in volumetric analysis as an oxidising agent for the titration of Fe^{+2}, $C_2O_4^{-2}$, NO_2^-, Mo^{+5} etc.

5. Thorium salts form white precipitate with ammonium hydroxide & sodium hydroxide, which is insoluble in excess of the reagent.

$$ThCl_4 + 4NH_4OH \longrightarrow Th(OH)_4\downarrow + 4NH_4Cl.$$

6. Thorium salt forms white precipitate with sodium thiosulphate & $K_4[Fe(CN)_6]$ in neutral & acidic medium

$$ThCl_4 + K_4[Fe(CN)_6] \longrightarrow Th[Fe(CN)_6]\downarrow + 4KCl.$$

7. Uranyl nitrate $[UO_2(NO_3)_2 \cdot 6H_2O]$ can be used for the volumetric determination of phosphate and Arsenate.

8. Uranyl acetate $[UO_2(CH_3COO)_2 \cdot 2H_2O]$ is a very important reagent in qualitative analysis. It can be used for the determination of phosphate and for detection of sodium and in the identification of K^+, Rb, Cs, NH_4^+, Mn, Zn, Fe, Ni, Co & Cu.

INTERHALOGEN COMPOUNDS

In addition to molecular halogen(i.e. X_2), a number of interhalogen compounds are known. The halogens react with each other to form interhalogen compounds under suitable conditions. The main reason for the formation of these compounds is the large electronegativity and size differences among halogens. Among these halogens fluorine being small and more electronegative forms a number of interhalogen compounds. All the known interhalogen compounds can be broadly divided into four types AX, AX_3, AX_5 and AX_7. The following is the table of various interhalogen compounds.

AX	AX_3	AX_5	AX_7
ClF	ClF_3		
BrF	BrF_3	ClF_5	
$BrCl$	$(ICl_3)_2$	BrF_5	
ICl			
IBr	IF_3	IF_5	IF_7
IF (unstable)	(unstable)		

In all the above type interhalogen molecules, never, there are more than two different interhalogens. The bond in these interhalogens is essentially of the covalent nature. These interhalogens can be prepared by the direct reaction between the halogens & by the action of a halogen on a lower interhalogen. The product formed depends on the condition.

(i) Direct combination:

$$Cl_2 + F_2 \text{ (equal volume)} \xrightarrow{200°C} 2ClF$$

$$Cl_2 + 3F_2 \text{ (excess } F_2) \xrightarrow{300°C} 2ClF_3$$

$$I_2 + Cl_{2\,(liquid)} \text{ (equimolar)} \longrightarrow 2ICl$$

$$I_2 + Cl_2 \text{ (liquid) (Excess } Cl_2) \longrightarrow (ICl_3)_2$$

$$I_{2(g)} + 7F_2 \xrightarrow{250-300°C} 2IF_7$$

$$I_{2(s)} + 5F_2 \xrightarrow{20°C} 2IF_5$$

(ii) Action of halogens over lower interhalogens:

$Cl_2 + ICl \longrightarrow ICl_3$

$ClF + F_2 \longrightarrow ClF_3$

The interhalogen compounds with higher valencies i.e. AX_5 and AX_7 type were largely formed by larger atoms such as Br and I with smaller atom fluorine. The interhalogen compounds are generally more reactive than the halogen. Because the A−X bond in interhalogens is a weaker bond than X−X in the halogens. The reactions of interhalogens are similar to those of halogens.

Properties:

I Hydrolysis of interhalogen compounds:

Hydrolysis of interhalogens result in the formation of halide and oxohalide ions. The oxohalide ion is always formed from the larger halogen present.

$ICl + H_2O \longrightarrow HCl + HOI$ (Hypoiodous acid)

$BrF_5 + 3H_2O \longrightarrow 5HF + HBrO_3$ (Bromic acid)

II Fluorination reaction:

Halogen fluorides are very reactive and act as strong fluorinating agents (ClF_3, BrF_3 and IF_3). Many metal oxides were fluorinated by these interhalogen fluorides.

$3UO_2 + 4BrF_3 \longrightarrow 3UF_4 + 2Br_2 + 3O_2$

ClF fluorinates many metals and non-metals.

$6ClF + 2Al \longrightarrow 2AlF_3 + 3Cl_2$

$6ClF + U \longrightarrow UF_6 + 3Cl_2$

$6ClF + S \longrightarrow SF_6 + 3Cl_2$

In certain cases these interhalogens can chlorinate and fluorinate simultaneously

$ClF + SF_4 \longrightarrow SF_5Cl$

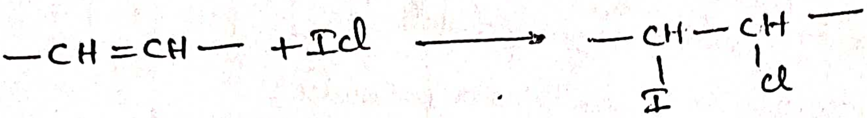
$ClF + CO \longrightarrow COFCl$

$ClF + SO_2 \longrightarrow ClSO_2F$

(III) Addition to Double bond:

Iodine monochloride (ICl) [Wij's reagents] & Iodine monobromide [Hanus reagent] can be used in the estimation of the iodine number of fats and oils. Iodine number is a measure of the number of double bonds i.e. the degree of unsaturation of the fat & oil.

The ICl solution is brown coloured and when it is added to an unsaturated fat the colour disappears.



$$-CH=CH- + ICl \longrightarrow -\underset{\displaystyle I}{\underset{|}{CH}}-\underset{\displaystyle Cl}{\underset{|}{CH}}-$$

The interhalogens also form addition compounds with alkali halides.

$$NaBr + ICl \longrightarrow Na^+[BrICl]^-$$ Polyhalide ion

$$KI + ICl \longrightarrow K^+[I_2Cl]^-$$

Interhalogens as Ionizing solvents:

These interhalogens can be used as non aqueous ionizing solvents.

$$3ICl \rightleftharpoons [I_2Cl]^+ + [ICl_2]^-$$

$$2BrF_3 \rightleftharpoons [BrF_2]^+ + [BrF_4]^-$$

$$2IF_5 \rightleftharpoons [IF_4]^+ + [IF_6]^-$$

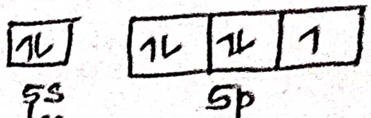
Those substances which produce $[BrF_2]^+$ ions are acids and $[BrF_4]^-$ ions are bases in the BrF_3 solvents.

Structures:

AX type interhalogens structure:

The known interhalogens of this type are ICl, IBr, ClF, BrF etc. The general valence configuration of halogens is ns^2np^5. It is clear from this configuration that only one p-orbital is half filled. This half filled p-orbital of one halogen atom overlaps with the half filled p-orbital of other halogen, resulting in the formation of a covalent bond.

Electronic configuration of Iodine is ground state

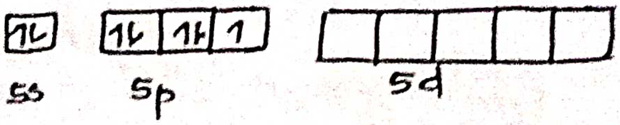


∴ AX type interhalogen compounds are linear molecules.

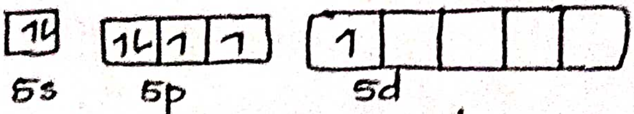
AX_3 type interhalogens structure:

The known interhalogens of this category are ClF_3, ICl_3, IBr_3, $BrCl_3$, BrF_3 etc. In ICl_3 molecule the central atom is iodine and whose configuration is $5s^2 5p^5$

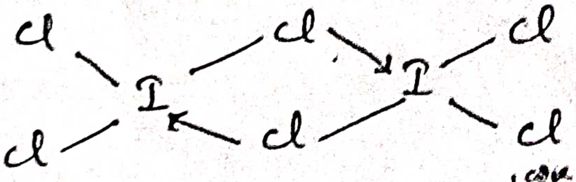
Ground state configuration of Iodine is



Excited state configuration of Iodine is

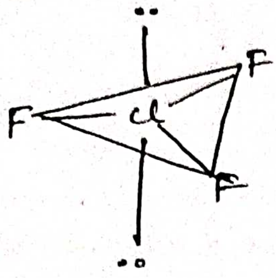


The central atom undergoes sp^3d hybridisation. The three unpaired electrons form bonds with three chlorine atoms. From the ~~[illegible]~~ hybridisation (sp^3d) the ICl_3 molecule should acquire trigonal bipyramidal structure. A structural study of ICl_3 ~~by~~ indicated that ICl_3 does not exists as monomer, rather exists as a dimer $(ICl_3)_2$. $(ICl_3)_2$ is a bright yellow solid.

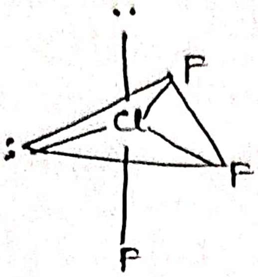


The terminal I-Cl bonds are normal single bonds of length 2.38Å and 2.39Å. The bridging I-Cl bonds are appreciably longer (2.68Å and 2.72Å).

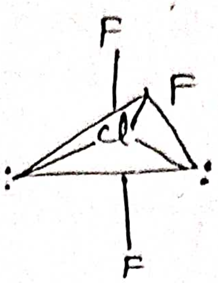
A structural study of ClF_3 by microwave spectroscopy and x-ray crystallography shows that the molecule is T-shaped, with bond angles of 87°40' which is close to 90°. In the molecule ClF_3, there two bonds are of one length and third bond has different bond length.



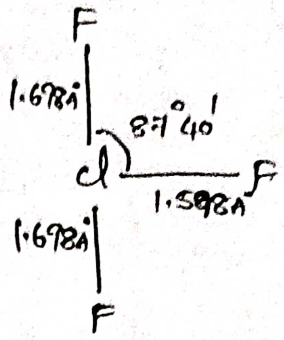
(1)



(2)



(3)

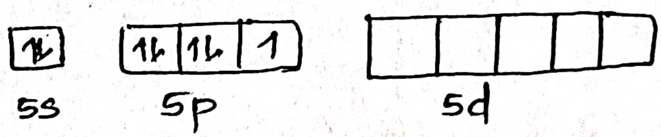


In a trigonal bipyramidal structure there two types of bonds, all the equitorial bonds are of one type with short bond length and apical bonds are of one type with longer bond lengths. In ClF_3 structure two bonds are of length 1.698A° and one bond of length 1.598A° which are quite ~~corrdt~~ consistent with structure (3) than with (1) & (2).

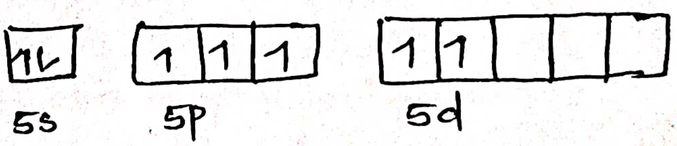
AX_5 type interhalogen structure:

The known interhalogens of this category are BrF_5, IF_5 etc. The central atom in IF_5 is iodine whose electronic configuration is $5s^2 5p^5$

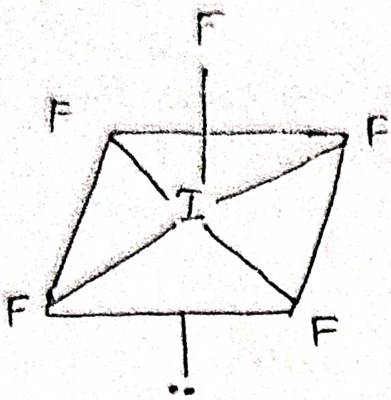
Ground state



Excited state



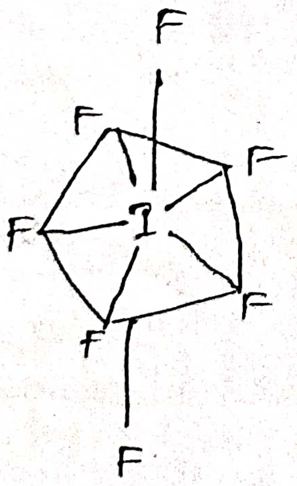
The central atom undergoes sp^3d^2 hybridisation. Out of the six hybrid orbitals five are half filled and one hybrid orbital contains a lone pair. The half orbitals form bonds with five fluorines.



The actual structure of IF_5 molecule is a square based pyramidal structure.

AX_7 type interhalogen structure:

The known interhalogen of this type is IF_7. In IF_7, the central atom Iodine undergoes sp^3d^3 hybridisation and hence the molecule has pentagonal bipyramidal structure.



Halogen oxides:

The compounds with oxygen show greater differences between the different halogens than any other class of compound. The difference is because of variation in size and electronegativities of halogens. Fluorine is small in size, lacks d-orbitals and is highly electronegative. In addition oxygen is less electronegative than Fluorine, but more electronegative than Cl, Br and I. Thus binary compounds of Fluorine and oxygen are fluorides of oxygen rather than oxides of fluorine. The other halogens are less electronegative than oxygen and thus form oxides. There is only a small electronegative difference between the halogens and oxygen, so the bonds are largely covalent.

Most of the halogen oxides are unstable. The iodine oxides are the most stable, than the chlorine oxides, but the bromine oxides all decompose below room temperature.

Fluorides of oxygen:

The two important fluorides of oxygen are OF_2 [oxygen difluoride] and O_2F_2 [dioxygen difluoride]

Oxygen difluoride [OF_2]: This is prepared by passing fluorine gas through sodium hydroxide solution.

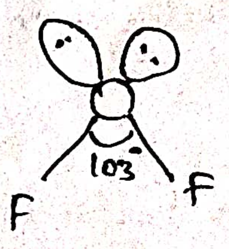
$$2NaOH + 2F_2 \longrightarrow OF_2 + 2NaF + H_2O$$

It is a pale yellow gas which is highly poisonous. It decompose in the presence of water to yield hydrogen fluoride.

$$H_2O + F_2O \longrightarrow 2HF + O_2$$

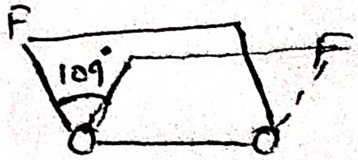
OF_2 is a strong oxidising agent and is used as a rocket ~~flo~~ fuel.

Structure: The central oxygen atom is sp^3 hybridised. Two of the sp^3 hybrid orbitals are occupied by lone pairs of electrons and the other two are involved in sigma bonding with the two fluorine atoms. The FOF angle is 103°



Dioxygen difluoride [O_2F_2] :

This compound is prepared by passing an electric discharge through a mixture of fluorine and oxygen at a very low temperature. It is an unstable yellowish ~~or~~ orange solid. It is a very good fluorinating and oxidising agent.



Structure : It has structure similar to H_2O_2. The two planes, each containing the O–O bond and one of the two O–F bonds, are at an angle of 109° to each other, as shown.

Halogen oxides:

Oxides of chlorine:

Chlorine forms a number of oxides such as cl_2o, clo_2, cl_2o_6 and cl_2o_7. All these oxides are unstable and highly reactive.

Dichlorine oxide [cl_2o]: It is obtained by passing chlorine over freshly precipitated mercuric oxide,

$$2cl_2 + 2HgO \longrightarrow HgO \cdot HgCl_2 + cl_2O$$

It is an ~~dry~~ orange liquid below 2°c. It boils at 2°c to give yellowish brown gas. At higher temperatures, the gas explodes.

It undergoes photochemical decomposition giving oxygen and chlorine

$$2cl_2O + h\nu \longrightarrow 2cl_2 + O_2$$

It dissolves in water to form hypochlorous acid with which it exists in equilibrium in aqueous solution

$$cl_2O + H_2O \rightleftharpoons 2HOcl.$$

cl_2O is regarded as the anhydride of hypochlorous acid.

~~Its~~ gaseous mixture with ammonia explodes violently. The overall reaction may be represented as

$$3cl_2O + 10NH_3 \longrightarrow 2N_2 + 6NH_4cl + 3H_2O,$$

Structure: The oxygen atom undergoes sp^3 hybridisation. Two of the four sp^3 hybrid orbitals are occupied by lone pairs of electrons and the remaining two are used in forming sigma bonds with the two chlorine atoms. Hence cl_2O has angular structure with cl-o-cl bond angle ~~110°~~ 110.9°

Chlorine dioxide: It is prepared by treating silver chlorate with dry chlorine at 90°c

$$2Agclo_3 + cl_2 \xrightarrow{90°} 2Agcl + 2clo_2 + O_2$$

It can also be prepared by the action of chlorine on sodium chlorite

$$2Naclo_2 + cl_2 \longrightarrow 2clo_2 + 2Nacl$$

ClO_2 is evolved as a paramagnetic yellowish-green gas which is condensed by cooling to give a coloured liquid (b.p. 11°C). It is a powerful oxidising and chlorinating agent. It dissolves in water exothermically.

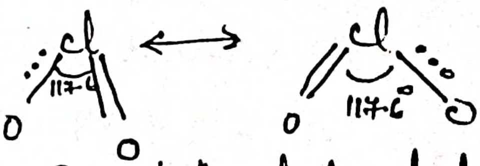
It reacts with alkalies to form chlorites and chlorates.

$$2ClO_2 + 2NaOH \dashrightarrow NaClO_2 + NaClO_3 + H_2O$$

The aqueous solution of ClO_2 undergoes photochemical decomposition to give a mixture of chloric acid and hydrochloric acid.

$$ClO_2 + H_2O \xrightarrow{h\nu} HCl + HClO_3 \rightarrow \left[\begin{array}{l} ClO_2 \rightarrow ClO + O \\ 2ClO + H_2O \rightarrow HCl + HClO_3 \end{array}\right]$$

Structure: It has an angular structure with O–Cl–O bond angle of 117.6° and Cl–O bond length of 1.47Å. Since it contains odd number of electrons, the molecule may be considered ~~to~~ be having a Three-electron bond in addition to a normal electron pair bond. Since both ClO bond distances are equal, its structure is ~~believed~~ believed to be a resonance hybrid of the two structures. The three electron bond accounts for the shorter bond length and its paramagnetic character.



Dichlorine Hexoxide [Cl_2O_6]:- It is obtained by mixing chlorine dioxide with ozonised air at 0°C

$$2ClO_2 + 2O_3 \longrightarrow Cl_2O_6 + 2O_2$$

It is a dark red liquid which freezes at 6°C. It is a strong oxidising agent. It reacts with alkalies to give chlorates and perchlorates.

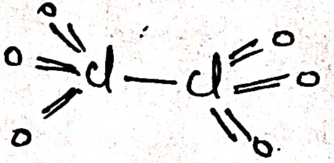
$$Cl_2O_6 + 2NaOH \longrightarrow NaClO_3 + NaClO_4 + H_2O$$

Hydrolysis of Cl_2O_6 yields a mixture of chloric and Perchloric acids.

$$Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4$$

Liquid Cl_2O_6 is diamagnetic and gives diamagnetic solution in CCl_4. However, its vapours are paramagnetic due to its partial dissociation to chlorine trioxide having an unpaired electron.

$$Cl_2O_6 \rightleftharpoons 2ClO_3$$



Structure: The structure of Cl_2O_6 has not been known with certainity. However, its dissociation to ClO_3 supports the structure as shown containing Cl–Cl linkage. Each Cl in Cl_2O_6 molecule appears to be sp^3 hybridised.

Dichlorine Heptoxide [Cl_2O_7]: It is obtained by dehydrating perchloric acid with phosphorus pentoxide

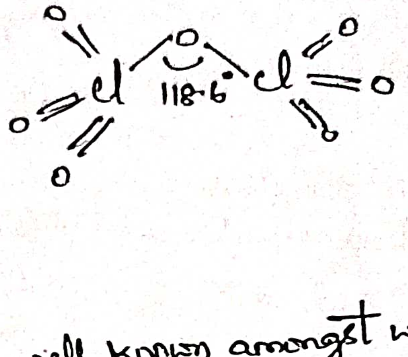
$$2HClO_4 \xrightarrow{P_2O_5} Cl_2O_7 + H_2O$$

It is a ~~cool~~ colourless oily liquid and dissolves in water giving perchloric acid.

$$Cl_2O_7 + H_2O \longrightarrow 2HClO_4.$$

∴ It is an anhydride of perchloric acid. It is not so strong as an oxidising agent as the other oxides of chlorine.

Structure: Chlorine heptoxide has the structure as shown in figure and Cl-O-Cl angle is 118.6°



Oxides of Bromine

Bromine forms a number of oxides, the most well known amongst which are Br_2O, BrO_2 and BrO_3.

Dibromine oxide [Br_2O]: It can be prepared by dropping bromine over dry HgO at 50-70°C

$$2Br_2 + 2HgO \longrightarrow HgBr_2 \cdot HgO + Br_2O.$$

It is a dark brown liquid which freezes at -17.5°c. It is the anhydride of hypobromous acid, HBrO. Its structure is similar to that of Cl_2O.

Bromine dioxide [BrO_2]:- It is obtained by passing an electric ~~dud~~ discharge through an ~~oxygen~~ ozone bromine mixture, at low pressure, at a temperature below -100°C

It can also be prepared by low temperature ozonolysis of bromine

$$Br_2 + 4O_3 \xrightarrow[CF_3Cl]{-78°C} 2BrO_2 + 4O_2$$

It is stable below -40°c when it exists as a yellow solid. It dissolves in alkalies giving bromides and bromates.

$$6BrO_2 + 6NaOH \longrightarrow NaBr + 5NaBrO_3 + 3H_2O.$$

Bromine trioxide [BrO_3]: It is prepared by the action of slow electric ~~dud~~ discharge on a mixture of bromine and oxygen between -10°c and 20°c

BrO_3 is a white crystalline solid which is stable only below -70°C. It is a strong oxidising agent. It gives acidic solution in water.

Oxides of Iodine:

Iodine forms oxides such as I_2O_4, I_4O_9 and I_2O_5. Among these, I_2O_5 is the most stable one.

Iodine Pentoxide [I_2O_5]: It is prepared by heating iodic acid to about 240°C.

$$2HIO_3 \xrightarrow{240^\circ C} I_2O_5 + H_2O.$$

It can also be prepared by heating iodine with concentrated HNO_3

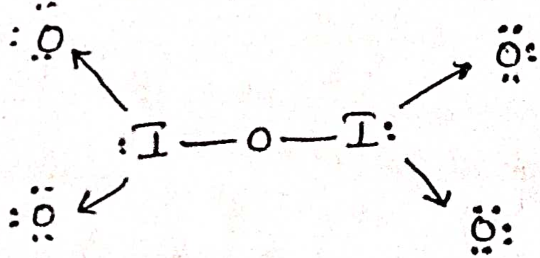
$$I_2 + 10HNO_3 \longrightarrow I_2O_5 + 10NO_2 + 5H_2O$$

It is a white solid which decomposes to iodine and oxygen above 300°C. ~~Its~~ It is a strong oxidising agent. It oxidises CO to CO_2 and Iodine is liberated quantitatively which can be titrated against sodium thiosulphate

$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$$

Hence, I_2O_5 is used for the detection and estimation of carbon monoxide. This forms the basis of analytical method for determining CO in atmosphere & in other gaseous mixtures.

Structure: The structure of I_2O_5 has been determined with a fair degree of ~~Relia~~ reliability from IR spectra data. It has two pyramidal IO_3 units joined through a common oxygen atom. Each I atom in I_2O_5 has a lone pair of electrons as well.



Nitrogen Compounds of Boron:

Benzene ring is the most important ring system in Organic chemistry. Such a ring can exist as a separate unit (entity) or in polynuclear hydrocarbon such as naphthalene, anthracene, Phenanthracene. The group BN is isoelectronic with C_2 and boron nitrogen compounds possess interesting similarities to carbon compounds. Inorganic chemistry has two analogues of benzene; borazene $B_3N_3R_6$ and ~~[illegible]~~ trimeric cyclophosphazene compounds $P_3N_3X_6$.

Stock synthesised Borazene by heating the adduct of diborane and ammonia.

$$3B_2H_6 + 6NH_3 \longrightarrow 3(BH_3\cdot NH_3)_2 \xrightarrow{200^\circ c} 2B_3N_3H_6 + 12H_2$$

More easily Borazine can be synthesised by the reaction between BCl_3 and NH_4Cl.

$$3NH_4Cl + 3BCl_3 \xrightarrow{\Delta} Cl_3B_3N_3H_3 + 9HCl.$$

$$Cl_3B_3N_3H_3 \xrightarrow{NaBH_4} B_3N_3H_6$$

Borazine can also be prepared by heating diborane with ammonia at high temperature.

$$3B_2H_6 + 6NH_3 \xrightarrow{473K} 2B_3N_3H_6 + 12H_2$$

Borazene is also prepared by heating a mixture of lithium borohydride or sodium borohydride and ammonium chloride in vaccum at 230°c

$$3NH_4Cl + 3LiBH_4 \xrightarrow{230^\circ c} B_3N_3H_6 + 3LiCl + 9H_2$$

The reaction between diborane and ammonia in presence of excess of ammonia and high temperature results in boron nitride.

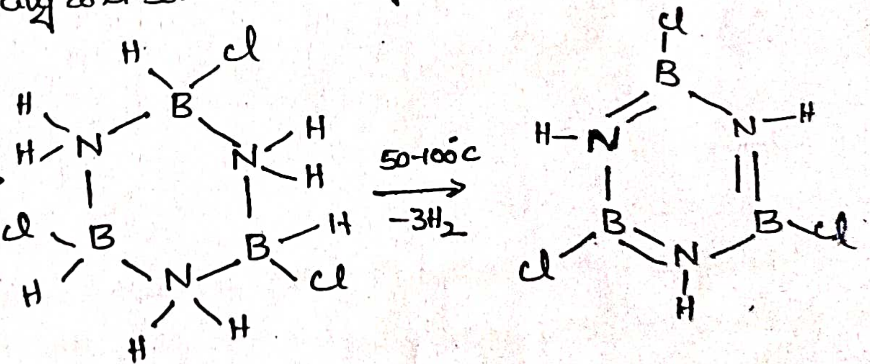
$$B_2H_6 + NH_3 \xrightarrow[\text{high temperature}]{\text{excess } NH_3} (BN)_x$$ boron nitride.

Properties:

Borazine is isoelectronic with benzene, as B=N is with C=C. In physical properties, borazine is indeed a close analogue of Benzene. The close similarity in physical properties is much predominantly observed for borazine and benzenee. Because of such close similarity in properties between benzene and borazine; Borazine is called as inorganic benzene. However, the chemical properties of borazine and benzene are quite different. Both compounds possess aromatic π electron clouds, but the π-electron density in borazine is due to the overlap of empty p orbital of boron with filled p orbital of nitrogen

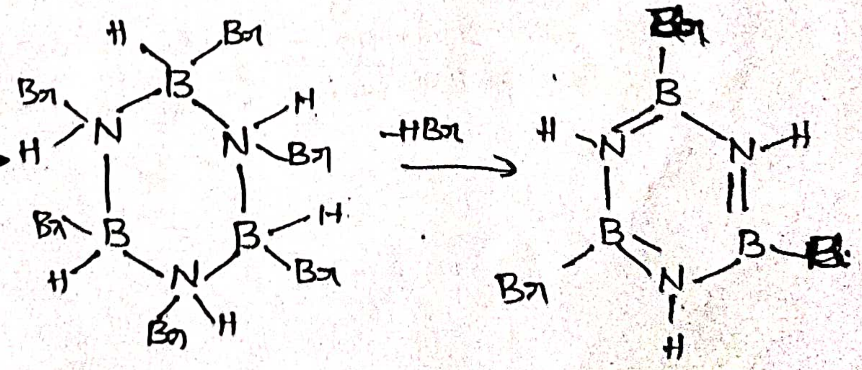
The electronegativities of boron and nitrogen are different. Due to the difference in electronegativity between boron and nitrogen, the electron cloud in borazine is 'lumpy'; because more electron density is localised on the nitrogen atom. This partial localization weakens the π-bonding in the ring. Each nitrogen receives more a electron density from neighbouring boron than it gives away as a π-donor. As a result of this, the charge density on nitrogen increases. In addition nitrogen retains its basicity and boron its acidity. Hence, borazine readily undergoes addition reactions.

1. $B_3N_3H_6 + 3HCl \longrightarrow$



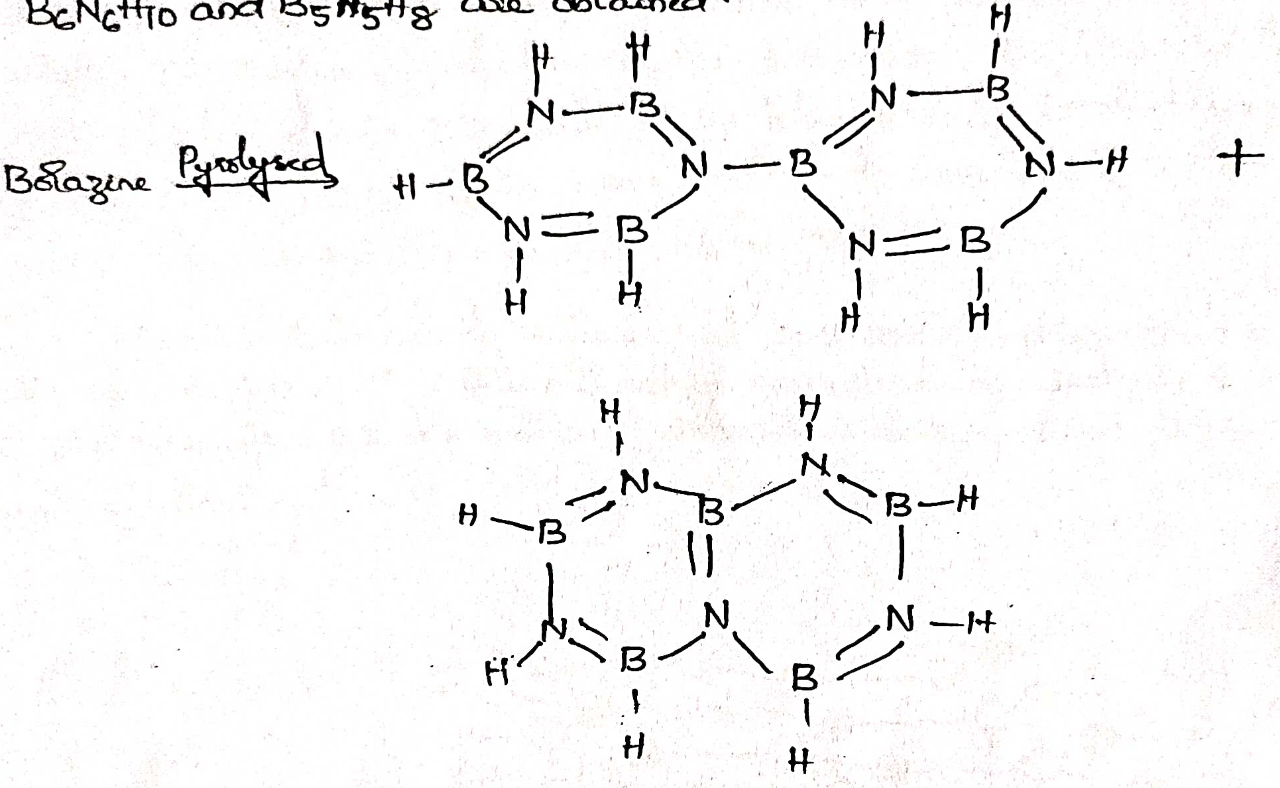

+ HCl ⟶ no reaction.

2. $B_3N_3H_6 + Br_2 \longrightarrow$



$B_3N_3H_6 + 9H_2O \longrightarrow 3B(OH)_3 + 3NH_3 + 3H_2$

4. When Borazine is pyrolysed at temperature above 340°C then the products $B_6N_6H_{10}$ and $B_5N_5H_8$ are obtained.



Structure:

Borazine: The structure of borazine is similar to that of benzene. It is a planar molecule in which B and N atoms are sp^2 hybridised. In benzene the π-bond is formed by the overlap of half-filled p-orbitals of carbon, whereas in that of borazole the π-bonding is dative and it arises from overlap of empty p-orbitals of boron with filled p-orbitals of nitrogen. Thus the six electrons in the π-orbitals of borazole are derived from three nitrogen atoms and not from each of the six atoms of the ring as in case of benzene.

Phosphorus - Nitrogen Compounds:

The catenating tendency of nitrogen and phosphorus is limited. The maximum chain length for nitrogen is three in the azide ion N_3^- and two for phosphorus in a few compounds such as P_2H_4 etc. Though the individual catenating capabilities of nitrogen and phosphorus is limited, the nitrogen and Phosphorus may bond together forming a large number of phosphazenes & phosphonitrilic compounds. The general formula for the phosphonitrilic compounds is $(PNX_2)_n$ where $X = F, Cl, Br, SCN, CH_3, C_2H_5$ etc.

When Phosphorus pentachloride is heated with ammonium chloride in tetrachloroethane & chlorobenzene, phosphonitrilic chlorides are obtained.

$$nPCl_5 + nNH_4Cl \longrightarrow (NPCl_2)_n + 4nHCl.$$

If the product is a monomer then its structure could be drawn as $Cl_2P \equiv N$, which is analogous to organic nitriles, $R-C \equiv N$. Hence these compounds were named as phosphonitriles. However monomer $(PNCl_2)$ and dimer $(PNCl_2)_2$ are not known.

The above reaction produces a mixture of colourless solids of formula $(NPCl_2)_n$, with n mostly 3 & 4. The trimeric and tetrameric compounds are easily separated by distillation under reduced pressure. The actual mechanism of the above reaction is complicated. The higher polymers or oligomers upto $n=8$ have been characterised. Analogous bromo compounds may be prepared in the same manner.

$$PBr_5 \rightleftharpoons PBr_3 + Br_2$$

$$PBr_5 + NH_4Br \xrightarrow[\text{Excess of } Br_2]{} [NPBr_2]_3$$

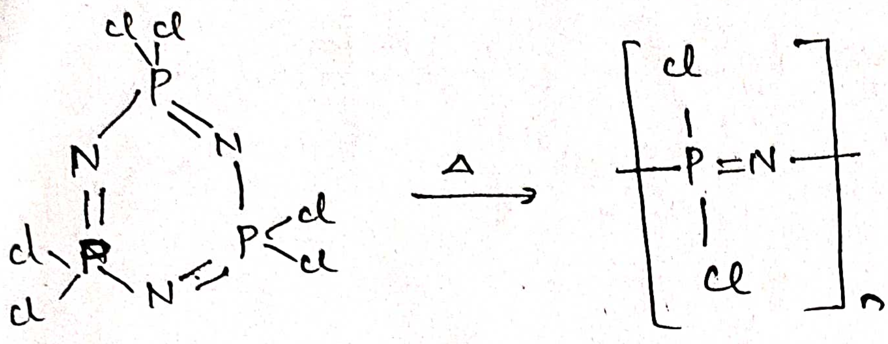
The only exception, in this reaction is that bromine must be added to supress the decomposition of the phosphorus pentabromide.

The analogous fluoride trimer can be prepared by fluorination of the chloride.

$$(NPCl_2)_3 + 6NaF \longrightarrow (NPF_2)_3 + 6NaCl.$$

phosphazenes can be polymerised and in many ways these polymers are much advantageous than polyolefins and Polyesters.

Trimeric chlorophosphazene can be polymerised thermally.



The temperature which is usually employed in these polymerisation reactions is 250–300°C. Extensive cross-linking can be avoided by carrying out reaction under required conditions.

Properties:

I The chlorine atoms are reactive and most reactions of chlorophosphazenes involve replacement of chlorine by groups such as alkyl, aryl, OH, OR, NCR & NR_2.

Alkyl & aryl groups may be introduced using lithium & grignard reagent.

$$[NPCl_2]_3 + 6\,CH_3MgI \longrightarrow [NP(CH_3)_2]_3 + 3MgCl_2 + 3MgI_2$$

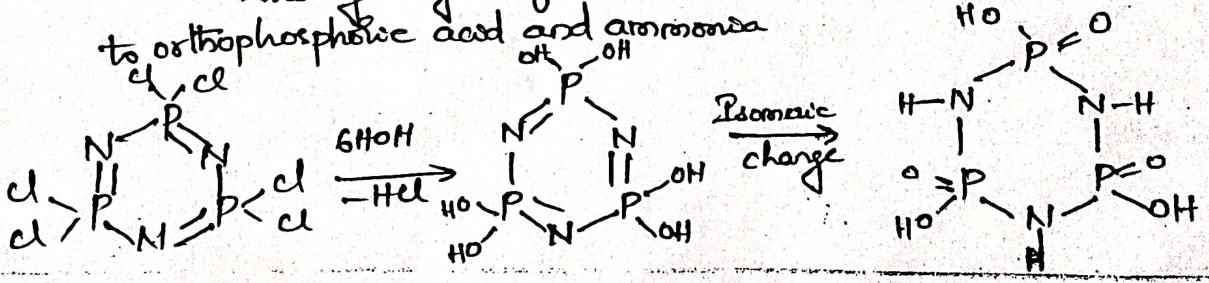
$$[NPCl_2]_3 + 6\,C_6H_5Li \longrightarrow [NP(C_6H_5)_2]_3 + 6LiCl$$

$$[NPCl_2]_3 + 6\,NaOR \longrightarrow [NP(OR)_2]_3 + 6NaCl$$

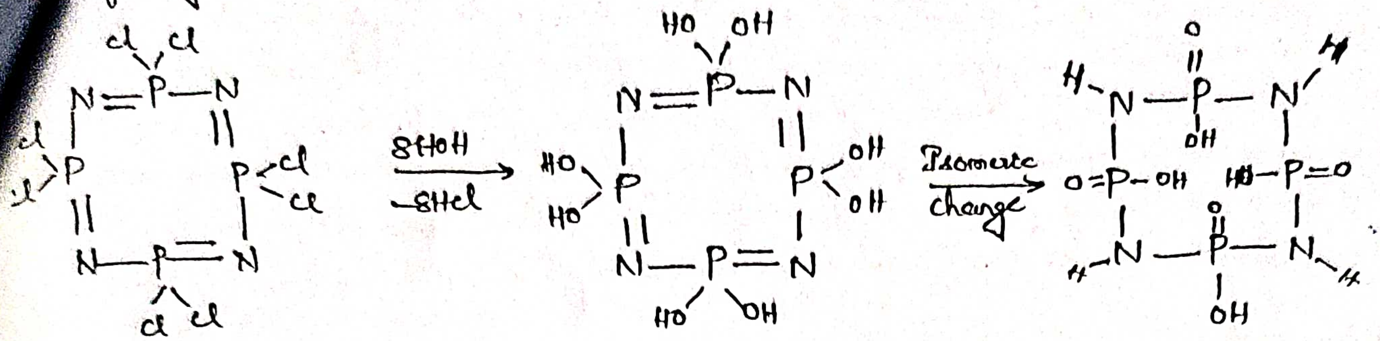
$$[NPCl_2]_3 + 6\,NaSCN \longrightarrow [NP(SCN)_2]_3 + 6NaCl.$$

II Hydrolysis:

The hydrolysis of trimer is slow. Trimer in acid solution is hydrolysed to orthophosphoric acid and ammonia

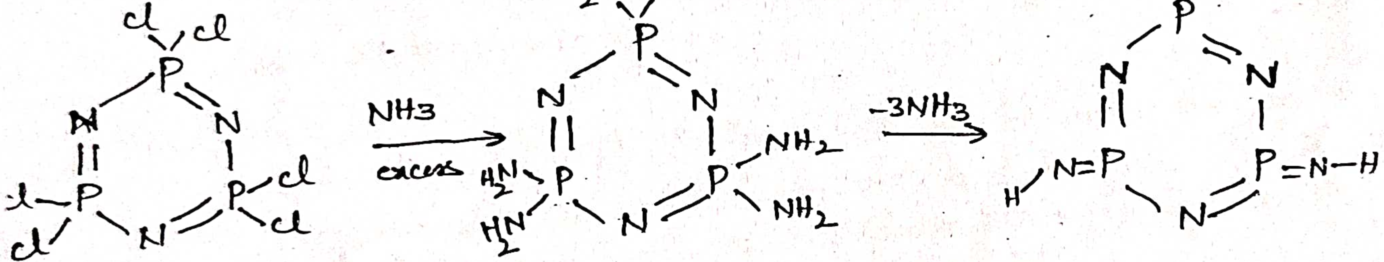


Hydrolysis of tetramer by boiling water is rapid and the product obtained is fairly stable.



III Reaction with Ammonia:

Trimer reacts with ammonia to give products such as $P_3N_3Cl_3(NH_2)_3$. If the reaction is allowed to continue, all the chlorine atoms are replaced by amino groups $P_3N_3(NH_2)_6$



Phospham

Tetramer undergoes the same reaction with ammonia.

IV Basic Properties:

Lewis acids can attack phosphonitrilic compounds as a lone pair of electrons are present on the nitrogen. The basic properties of phosphonitrilic halides are however weak. Trimeric chlorides form 1:1 and 1:2 adducts with $HClO_4$

$$N_3P_3Cl_6 + HClO_4 \longrightarrow N_3P_3Cl_6 \cdot HClO_4$$

$$N_3P_3Cl_6 + 2HClO_4 \longrightarrow N_3P_3Cl_6 \cdot 2HClO_4$$

$$N_3P_3Cl_6 + 2AlCl_3 \longrightarrow N_3P_3Cl_6 \cdot 2AlCl_3$$

Structure of Trimer:

In the phosphonitrilic polymers, the trimer and tetramer have been studied in detail. The cyclic structures of trimer and tetramer with alternative nitrogen and phosphorus atoms was confirmed by x-ray analysis. The trimer consists of planar six membered ring similar to that of benzene. The bond angles in trimer are consistent with sp^2 hybrid of the nitrogen & sp^3 hybrids of the phosphorus. Two of the sp^2 hybrid orbitals of nitrogen (which are half filled) are used for σ bonding and the third sp^2 hybrid contains a lone pair. The unhybridised p-orbital is left with one electron.

The four sp^3 hybrid orbitals of phosphorus are used in σ bonding and the fifth unpaired electron occupy a d-orbital. The planarity of the phosphonitrilic compound and the equal P-N distance and short P-N distances and stability of the compound are indicative of delocalisation of electron cloud. The π-bonding in cyclophosphazenes involve d and p-orbitals, whereas the π-bonding in benzene involve p-orbitals. The pπ-dπ orbitals combine to give delocalised electron density. The presence of two chlorines on phosphorus was chemically proved by the reaction of phosphazenes with benzene in $AlCl_3$.

Structure of tetramer:

The structure of $(NPF_2)_4$ is planar, but other tetramers are found in a variety of conformations (tub, boat, chair, crown and structures in between). The two ~~forms~~ forms in which the tetrameric chloride has been isolated are the more stable chair conformation and the other form in tub conformation.

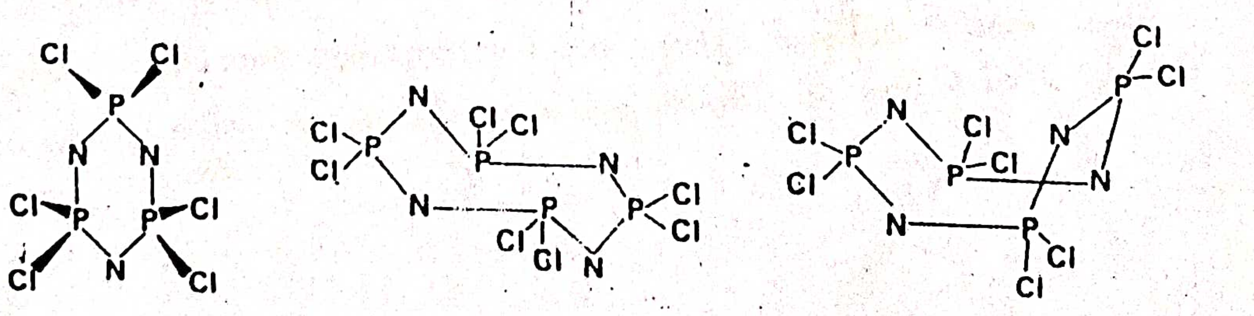
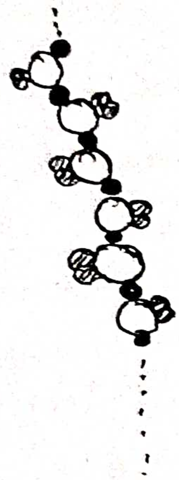


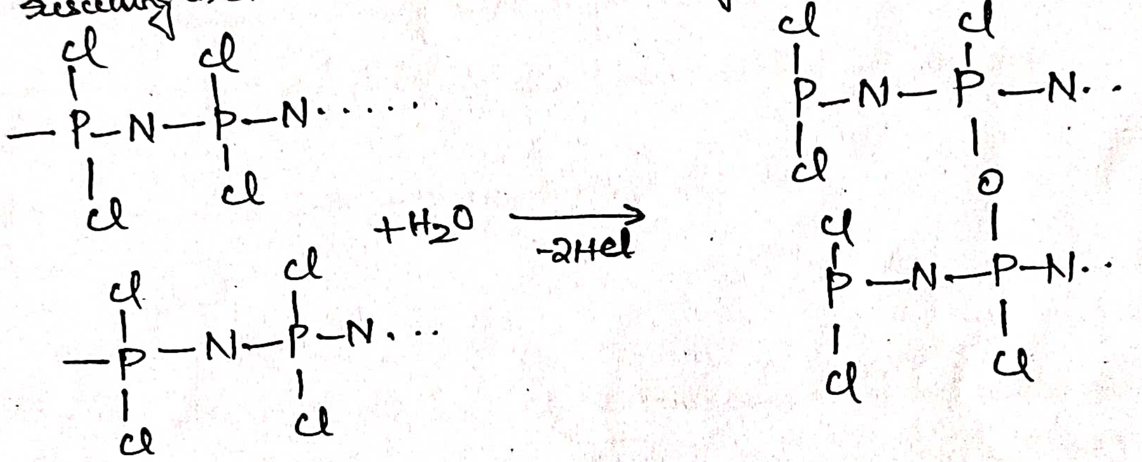
Figure 14.21 Some cyclophosphazene compounds.

Applications:

(1) The lower members of phosphonitrilic chlorides polymerize on heating to and produce rubber like material of high molecular weight. Hence the name inorganic rubber was given for these materials. These rubber-like materials contain long spiral chains.



One draw back of the inorganic rubber is its susceptibility to hydrolytic attack and on storage in air for several months the material becomes brittle presumably due to hydrolytic condensation resulting in chain to chain cross-linking through oxygen atoms.



(2) In the phosphonitrilic compounds like $[PN(OR)_2]_n$ & $[PN(NR_2)_2]_n$ by varying the nature of the side chain R, various elastomers, plastics, films, expanded foams and fibers have been prepared.

(3) Thin films of poly(amino phosphazene) are used in hospitals to cure severe burns and other extensive wounds since they prevent the loss of body fluids and keep germs out.

Sulphur-nitrogen compounds:

In the compounds of sulphur and nitrogen, sulphur is less electronegative than nitrogen and hence it is correct to call them as sulphur nitrides. Among the sulphur-nitrogen compounds, tetrasulphur tetranitride (S_4N_4) is best known. It is a diamagnetic orange solid.

Preparation:

1. S_4N_4 is prepared by the action of anhydrous ammonia on sulphur

$$10S + 4NH_3 \rightleftharpoons 6H_2S + N_4S_4$$

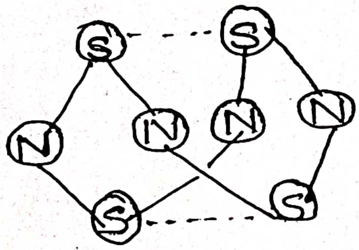
In the above reaction silver iodide is added to remove H_2S as insoluble Ag_2S and hence the reaction proceeds quantitatively to the right side.

2. By passing ammonia into a warm solution of disulphur dichloride in dry carbon tetrachloride.

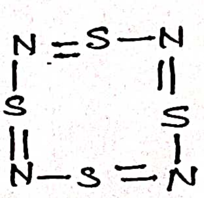
$$6S_2Cl_2 + 16NH_3 \longrightarrow S_4N_4 + 12NH_4Cl + S_8$$

Structure of S_4N_4:

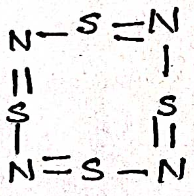
The structure of S_4N_4 is cradle like eight membered ring. In this all S-N bonds are of same length 1.62Å, a value in between that of single (S-N) and double bonds (S=N)

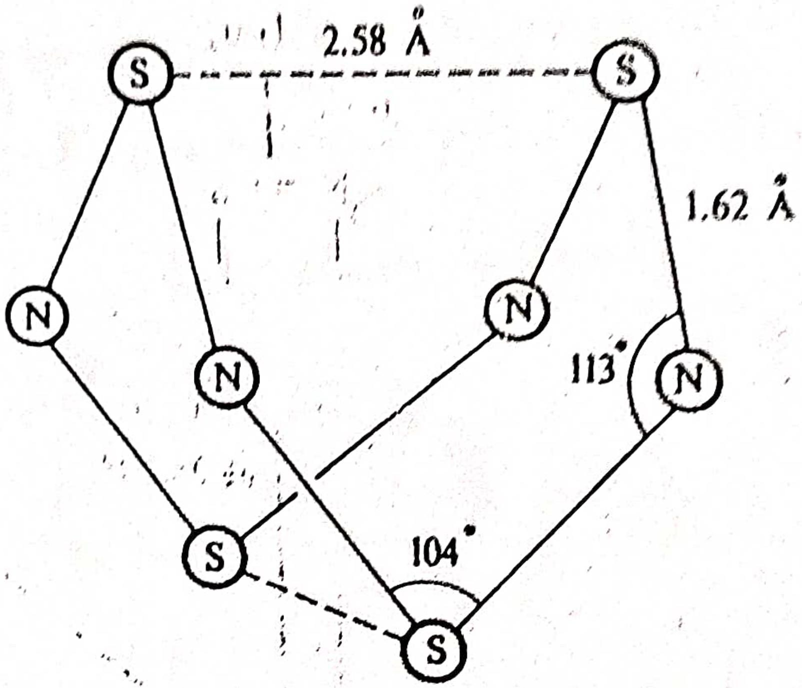


The structure of S_4N_4 may be written as a hybrid of



and





're [illegible]
structure of S_4N_4.

The S-N bond ~~[illegible]~~ order in S_4N_4 is 1.5. The two pairs of sulphur atoms at the top and bottom of the cradle are near enough (2.58Å) to have a weak interaction between them. Therefore S_4N_4 is supposed to be cage compound though the bonds closing the cage are very weak.

Properties:

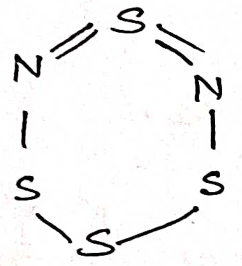
1. Tetrasulphur tetranitride is hydrolysed by water slowly, whereas S_4N_4 is hydrolysed rapidly by warm alkali

$$S_4N_4 + 6OH^- + 3H_2O \longrightarrow S_2O_3^{-2} + 2SO_3^{-2} + 4NH_3$$

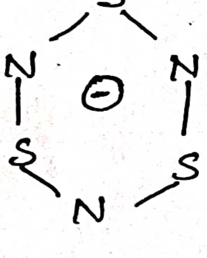
2. Number of other sulphur nitrides can be prepared starting from S_4N_4

(a) on heating S_4N_4 under pressure in a solution of CS_2 containing sulphur yields S_4N_2

This S_4N_2 has a half-chair conformation.



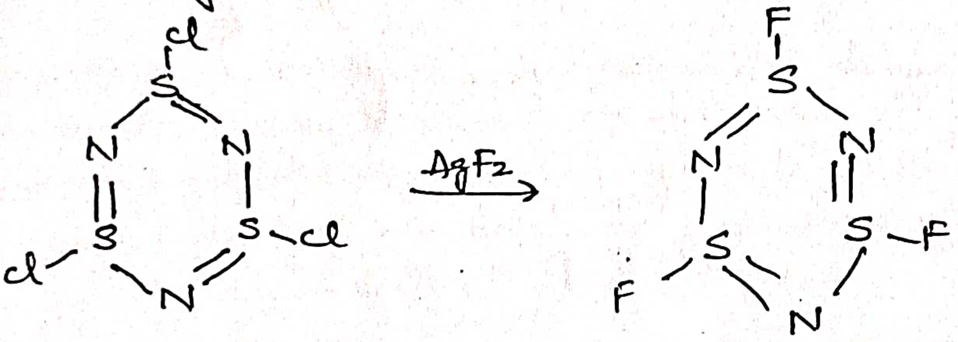
(b) Reduction of S_4N_4 with metallic sodium or potassium azide yields the planar sixmembered ring $S_3N_3^-$. The number of π electrons in $S_3N_3^-$ are different from that of benzene



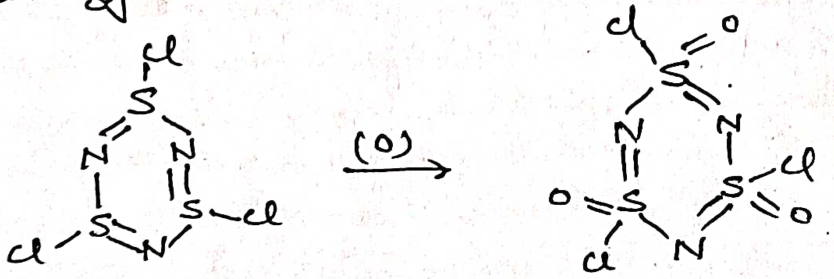
(3) S_4N_4 on treatment with chlorine yields trithiazyl trichloride

$$3S_4N_4 + 6Cl_2 \longrightarrow 4N_3S_3Cl_3$$

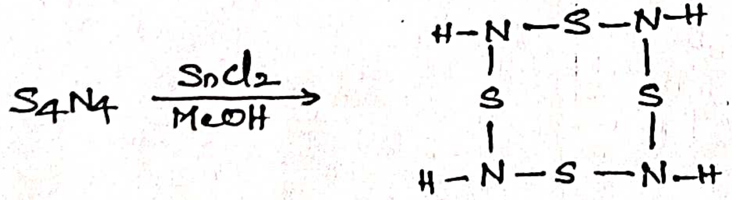
Trithiazyl trichloride on treatment with AgF_2 gives $N_3S_3F_3$



Trithiazyl trichloride on oxidation yields $N_3S_3Cl_3O_3$

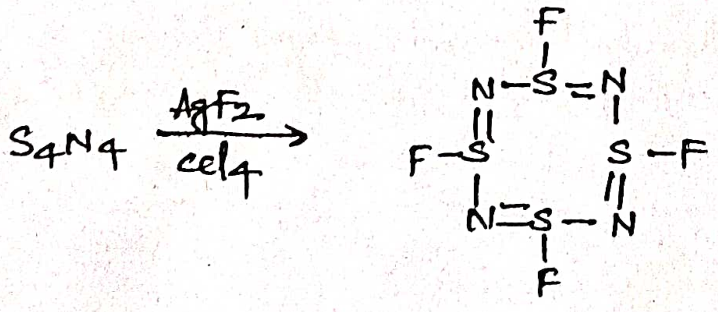


(4) Tetrasulphur tetranitride on reduction with $SnCl_2$ yields tetrasulphur tetraimide



this tetrasulphur tetraimide has crown structure similar to that of S_8

(5) Tetrasulphur tetranitride on treatment with AgF_2 in CCl_4 yields $N_4S_4F_4$.

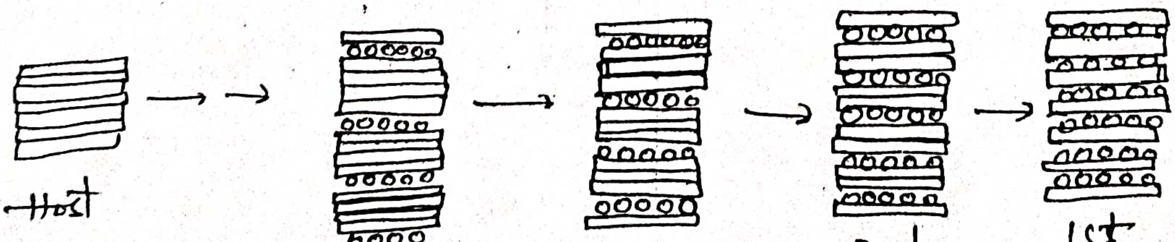


Intercalation Compounds:

Intercalation compounds consists of different chemical species arranged as layers. In the process of synthesis of certain compounds, some atoms, ions & molecules have been inserted between layers of the host material. Minerals of clay, have water molecules ~~intercalated~~ intercalated between the framework sheets. These compounds on heating lose water molecules and the water molecules leave faster than they can diffuse along the layer.

<u>Example</u>: The best known example is sodium beta alumina, where the sodium ions are free to move between the spinel layers. The sodium ions can be replaced by almost any +1 cation such as Li^+, K^+, Rb^+, Cs^+, NH_4^+, H_3O^+, Tl^+ etc. The conductivity of these materials ~~vary~~ varies with the size of the ions moving between the fixed-distance (Al–O–Al) layers.

Graphite has layered structure and the intralayer C–C distance (142pm) is twice the covalent radius of aromatic carbon (139 pm in benzene) and the interlayer C–C distance is 335pm, which is twice the vanderwaals radius of carbon. The layers of graphite are held together by week vanderwaals forces. In between the layers of graphite a number of substances can be intercalated. Among them, the well known is intercalation of potassium ions between layers of graphite. The intercalation occurs until a stage [limiting formula C_8K is reached] is reached i.e. C_8K. The intercalation of potassium occurs in several stages until it becomes C_8K.



The graphite layers move apart somewhat (205pm) which is less than expected basing on diametre of potassium ion (304 pm)

clathrate compounds of Noble gases:

clathrate compounds of the noble gases are well known. Normal chemical compounds have ionic or covalent bonds. However, in the clathrates atoms or molecules of appropriate size are trapped in cavities in the crystal lattice of other compounds. Though the gases are trapped, they do not form bonds.

If an aqueous solution of quinol (1,4-dihydroxybenzene) is crystallised under a pressure of 10-40 atmospheres of Ar, Kr or Xe, the gas becomes trapped in cavities of about 4Å diameter in the β-quinol structure. When the clathrate is dissolved, the hydrogen bonded arrangement of β-quinol breaks down and the noble gas escapes. Other small molecules such as O_2, SO_2, H_2S, MeCN and CH_3OH form clathrates as well as Ar, Kr and Xe. The smaller noble gases He and Ne do not form clathrate compounds because the gas atoms are small enough to escape from the cavities. The composition of these clathrates corresponds to 3 quinol : 1 trapped molecule, though normally all the cavities are not filled.

The gases Ar, Kr and Xe may be trapped in cavities in a similar way when water is frozen under a high pressure of the gas. These are clathrate compounds but are commonly called 'the noble gas hydrates'. They have formulae approximating to $6H_2O$: 1 gas atom. He and Ne are not trapped because they are too small. The havier noble gases can also be trapped in cavities in synthetic zeolites. Samples of these synthetic zeolites, containing upto 20% of Ar by weight are known. Clathrates provide a convenient means of storing radioactive isotopes of Kr and Xe produced in nuclear reactors.

Nitrogen dioxide formed in equation ⑤ can react with oxigen free radicals and prevent their possible recombination with molecular oxygen to regenerate ozone (equation 2)

$NO_2 + O^{\cdot\cdot} \longrightarrow NO + O_2$ ———— ⑥

The combination of ⑤ and ⑥ reactions, results in the net conversion of ozone to oxygen.

$O^{\cdot\cdot} + O_3 \longrightarrow 2O_2$ ———— ⑦

The chlorofluorocarbons, used as refrigerants, also deplete the ozone layer.

$F_3CCl + h\nu\ (190\text{-}220\ nm) \longrightarrow F_3C^{\cdot} + Cl^{\cdot}$ ———— ⑧

$Cl^{\cdot} + O_3 \longrightarrow ClO^{\cdot} + O_2$ ———— ⑨

$ClO^{\cdot} + O^{\cdot\cdot} \longrightarrow Cl^{\cdot} + O_2$ ———— ⑩

Combined reaction of ⑨ and ⑩

$O^{\cdot\cdot} + O_3 \longrightarrow 2O_2$ ———— ⑪