# AR-7148

## M. Sc. IV Examination, 2013

## Specialization-Inorganic Chemistry

## (Inorganic Rings, Chains, Clusters)

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### Section A

### (Short Answer Type Questions)

10x2 = 20

**1.**

**(i)**

Heteropoly acids are the polyacids containing more than a single type of anhydride. Heteropoly acids are those acids obtained by the union of varying number of acid anhydride molecule, generally $WO_3$, $MoO_3$ and $V_2O_5$ with some other acids which could furnish of the central atom of central ion of the whole complex anion. The ability to act as the central atom in heteropoly acids is found amongst the acid forming elements as well as among the metals of the transition series.

The heteropoly acids are generally extracted from aqueous solutions by ethers and esters. Purification of these materials is usually done by crystallisation from water or organic solvents.
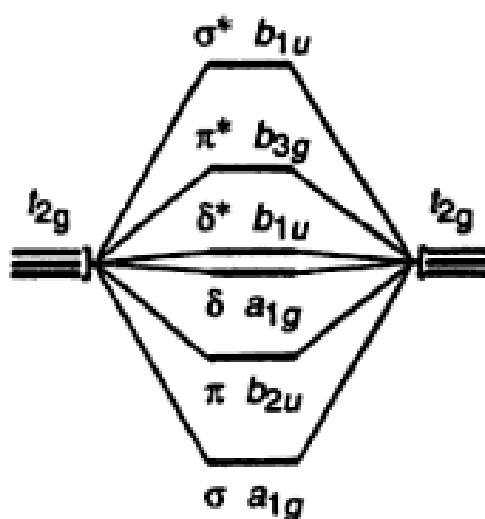
**(ii)** Isopolyacids are the poly acids containing only one type of acid anhydride.

The polychromic acids $H_2O$ $yCrO_3$ $(y > 1)$ is the example of this class.



(b) Octamolybdate ion, $[Mo_8O_{26}]^{4-}$
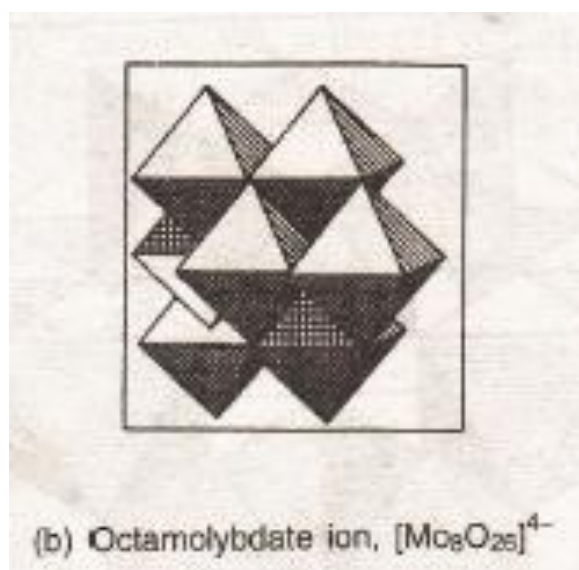
**(iii)**

*Pattern of energy level when only the d-d direct overlaps are considered in bioctahedral structure of a metal cluster.*



Orbital energy level diagram

**(iv)** Structure of tri (*Fig. 1*) and tetranuclear (*Fig 2*) carbonyl metal cluster
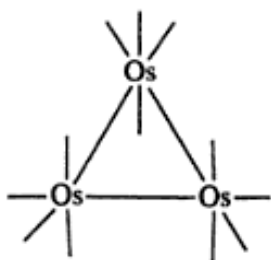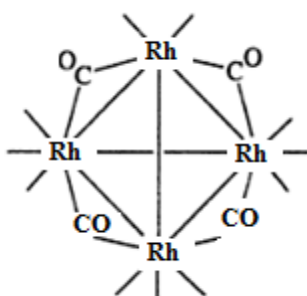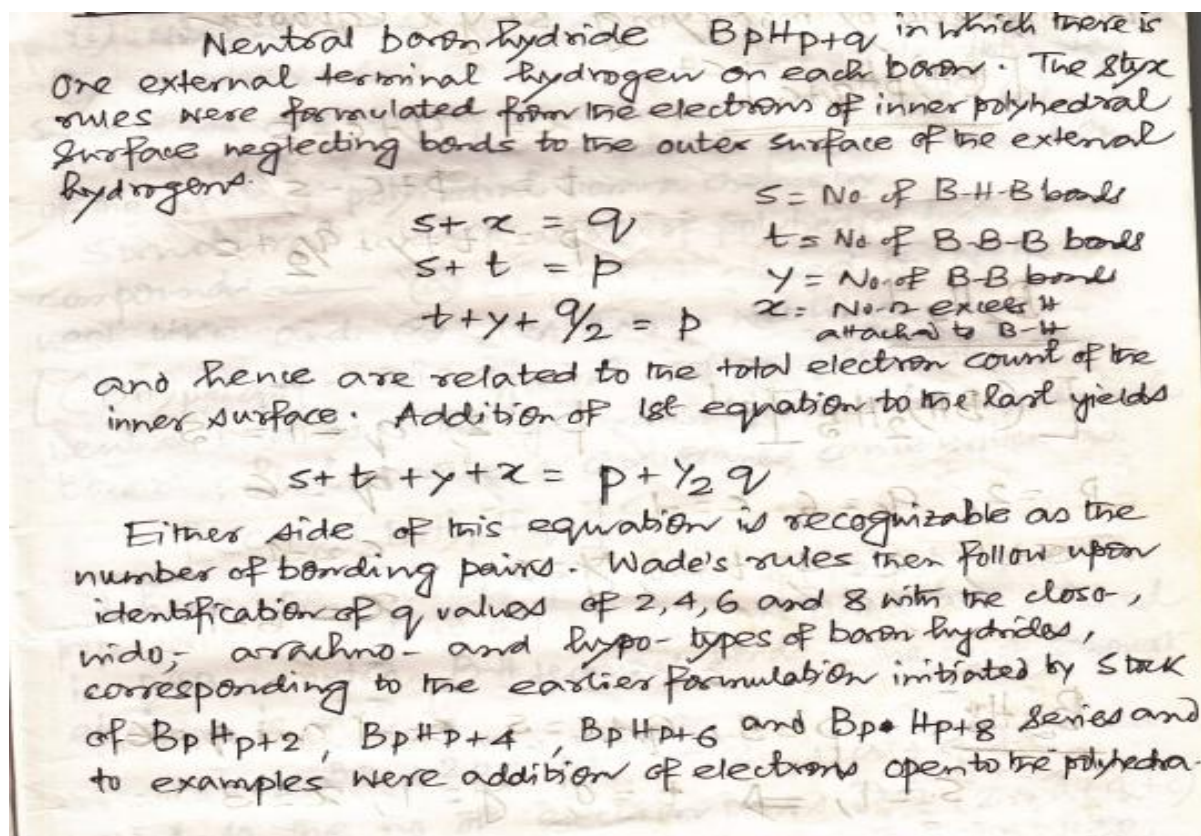


*Fig. 1 Os$_3$(CO)$_{12}$*



*Fig. 2 Rh$_4$(CO)$_{12}$ ; M$_4$(CO)$_{12}$ (M= Co, Rh, Ir)*

**(V)**



Neutral boron hydride $B_pH_{p+q}$ in which there is one external terminal hydrogen on each boron. The styx rules were formulated from the electrons of inner polyhedral surface neglecting bonds to the outer surface of the external hydrogens.

$$s + x = q$$
$$s + t = p$$
$$t + y + \frac{x}{2} = p$$

$s$ = No. of B-H-B bonds
$t$ = No. of B-B-B bonds
$y$ = No. of B-B bond
$x$ = No. o excess H attached to B-H

and hence are related to the total electron count of the inner surface. Addition of 1st equation to the last yields

$$s + t + y + x = p + \frac{1}{2}q$$

Either side of this equation is recognizable as the number of bonding pairs. Wade's rules then follow upon identification of $q$ values of 2, 4, 6 and 8 with the closo-, nido-, arachno- and hypo- types of boron hydrides, corresponding to the earlier formulation initiated by Stock of $B_pH_{p+2}$, $B_pH_{p+4}$, $B_pH_{p+6}$ and $B_pH_{p+8}$ series and to examples were addition of electrons open to the polyhedra.

**(vi)**

**Jemmis rules (*mno*)** represent a unified rules for predicting and systematizing structures of compounds, usually clusters. The rules involve electron counting. They were formulated by <u>Eluvathingal Devassy Jemmis</u>. These rules are addition and extensions to <u>polyhedral skeletal electron pair theory</u>.

The following parameters are presented for Jemmis *mno* rules.

Where:

*m* is the number of condensed polyhedra

*n* is the number of vertices (corner points)

*o* is the number of single-vertex-sharing interactions (single-atom bridges between two polyhedra)

Extra electron pairs are added for open <u>polyhedra</u> that have $p$ number of vertices missing. When two <u>polyhedra</u> are condensed or share an edge or face $o$ is zero. As a result the $o$ parameter was not recognized for a long time, as examples of stability and electron count for many complexes were justified in Wade's original rules as a special case of Jemmis rules when $o$ is equal to zero.

**(vii)**

**Isolobal with examples**

Two molecular fragments are isolobal if the **number**, **symmetry properties**, **shapes**, and **approximate energies** of their frontier orbitals the same. They may or may not also be isolelectronic. For example HB and HC fragments are isolobal but not isoelectronic, whereas the $H_2C^-$ and $H_2N$ moieties are both isolobal and isolelectronic.
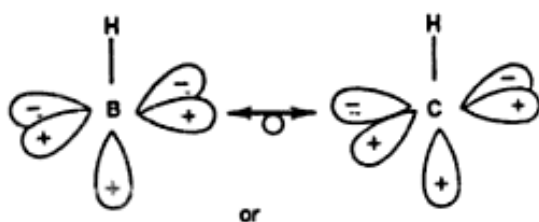
**(viii)**



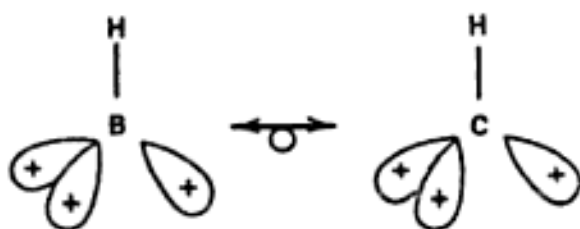**Fig. 1** *B-H and C-H with least hybridization.*

**Fig. 2** *B-H and C-H with least hybridization.*

*(ix)* Polymeric metal-ligand frameworks are called coordination polymers. A coordination polymer is an entity constructed by a supramolecular approach through metal coordination and consisting of a backbone, which is held together by metal-ligand interactions. Similar supramolecular architectures are also called Metal-organic frameworks (MOFs). Coordination polymers are inorganic structures containing metal cation centers linked by ligands, extending in an array (***Fig. 1***). They can also be described as polymers whose repeat units are coordination complexes, and coordination networks.
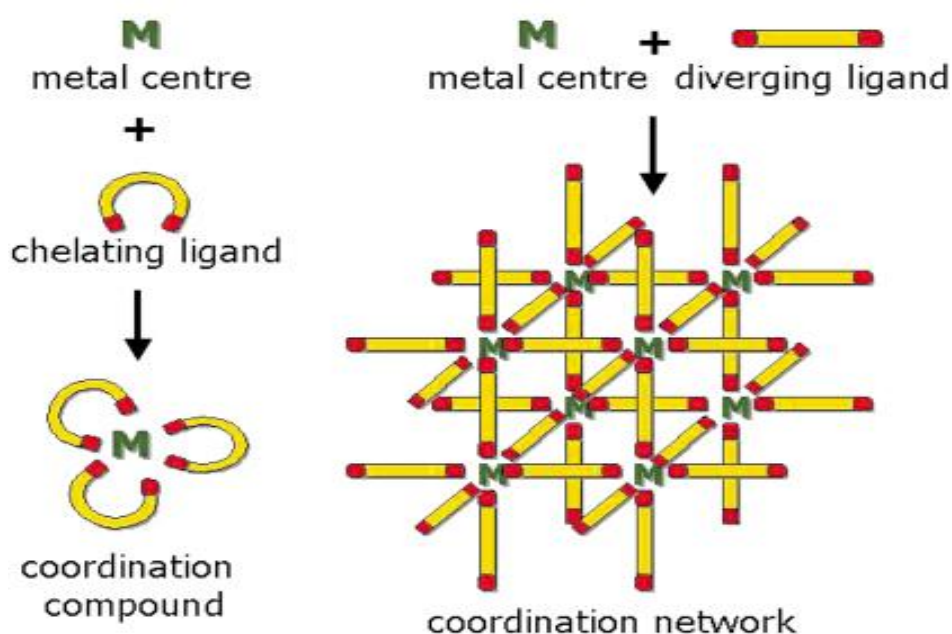


***Fig. 1***

*(x)* High molecular weight polymers with inorganic elements in their backbone are attractive and challenging, because of their physical and chemical differences with their organic counterparts. These polymers offer a unique combination of high temperature stability and excellent low temperature elastomeric properties

Aluminosilicate inorganic polymers have been proposed as low-energy cements since, unlike Portlandcement, their production does not require high temperatures or generate large quantities of greenhouse gases. Other environmental protection applications for inorganic polymers are to encapsulate hazardous mining or radioactive wastes for safe long-term storage and as fireproof components for buildings and vehicles. However, newly developed methods for synthesising these materials have opened up the possibility of other novel environmental protection applications. These include porous cladding material for passive cooling of buildings, cost-effective exchange materials for removing heavy metals from wastewater, bacteriocidal materials for purifying polluted drinking water and materials for photodegrading hazardous organic environmental pollutants. The nature and synthesis of inorganic polymers for these environmental applications will be discussed here.

**2.**

## Heteropoly Acids of Molybdenum

If a molybdate like sodium molybdate is made to react with an acid in the presence of phosphate, silicate and metal ions, heteropoly anions are produced.

**(1) 12–molybdo heteropoly acids (Series A)–** The phosphomolybdate test for the phosphate anion in qualitative analysis is an example of heteropoly anion formation. In this test a solution containing phosphate is treated with an excess of ammonium molybdate solution and the resulting mixture is strongly acidified with concentrated nitric acid and warmed when a canary yellow ammonium phosphomolydate is precipitated.

$$H_3PO_4 + 21HNO_3 + 12(NH_4)_2 MoO_4 \longrightarrow (NH_4)_3 [PMo_{12}O_{40}] + 21 NH_4NO_3 + 12H_2O$$

Similarly, a yellow precipitate of ammonium molybdo-arsenate, $(NH_4)_3[AsMo_{12}O_{40}]$ is obtained. These anions $(PMo_{12}O_{40})^{3-}$ and $[AsMo_{12}O_{40}]^{3-}$ are known as 12-molybdoheteropoly anions and they have the general formula, $[X^{n+} Mo_{12}O_{40}]^{-(8-n)}$.

**Structure–** The structure of such anions is shown in Fig. 34.6. The cavity which is the centre of the anion is surrounded by a tetrahedron of four oxygen atoms. This cavity is sufficiently big to contain a relatively small atom such as $P^{5+}$(0.52 A), $As^{5+}$(0.60), $Si^{4+}$(0.54 A), $Ge^{4+}$ (0.67A), $Ti^{4+}$(0.74 A) or $Zr^{4+}$ (0.86 A). Nearly 35 − 40 atoms form heteropoly acids. In Fig. 34.6 (a), the structure of 12–molybdophosphate and 12–tungstophosphate is given.



4.6 (a). Structure of 12–molybdophosphate or 12–tungstophosphate. (b) and (c) show structure (a) severed in such a way to show the tetrahedral cavity attached apically to three octahedra.

The $MoO_6$ octahedra share their apices with neighbouring octahedra. This gives a tetrahedral cavity in the centre which accommodates a small atom like phosphorus or arsenic.

**(2) 12–molybdoheteropoly acids (Series B)–** In this type the heteroatom is larger in size, e.g $Ce^{4+}$ (1.28A) and $Th^{4+}$ (1.35 A). The structure of $(NH_4)_2H_6 CeMo_{12}O_{42}$ is shown in Fig. 34.7. In this structure there is a distinctive feature which is unique. This feature is, that there are pairs of $MoO_6$ octahedra that share faces to form $MoO_9$ groups. These $MoO_9$ groups coordinate around the cerium atom. We have said earlier that in the polyacid structures, octahedra share generally edges or apices and rarely faces.
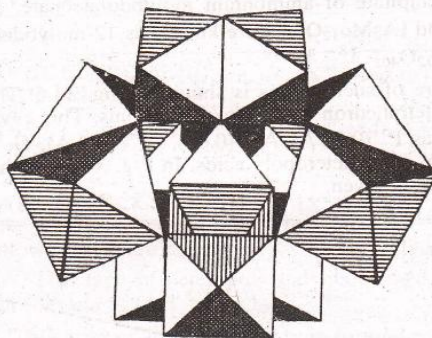


Fig. 34.7. Structure of $(CeMo_{12}O_{42})^{8-}$ anion.

**(3) 6–molybdoheteropoly acids–** These acids are produced with heteroatoms $Te^{6+}$ (0.70 A), $I^{7+}$ (0.67A) and $Rh^{3+}$ (0.80 A). In these structures the heteroatom is coordinated in an octahedral cavity which is formed by a ring of six $MoO_6$ octahedra which are joined at the edges. Fig. 34.8 gives the structure of the 6–molybdotellurate anion, $[TeMo_6O_{24}]^{6-}$.

If the position of the heteroatom in Fig 34.8 is taken up by a $MoO_6$ octahedron, we get another type of polyanion which is the heptamolybdate. In this anion a $MoO_6$ octahedron is surrounded by six
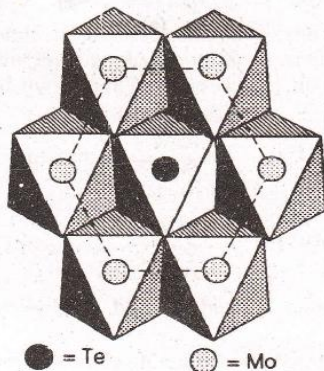


● = Te  ◎ = Mo

Fig. 34.8. Structure of 6-molybdotellurate anion.

9

$MoO_6$ octahedra. However, the structure of the heptamolybdate is not isomorphous with the 6–molybdo species.

In the 6–heteropoly acids (Fig. 34.8), the heteroatom is surrounded by a *planar* ring as shown in Fig. 34.9 (a), In the heptamolybdate the seventh $MoO_6$ octahedron-which is occupying the position of the hetero atom, is surrounded by a *puckered* ring of atoms Fig. 34.9 (b).



Fig. 34.9 (a). Planar ring of Mo atoms around heteroatom (6–heteropoly acids)
(b) Puckered ring of Mo atoms around the 7th Mo atom in $[Mo_7O_{24}]^{6-}$.

Just as complex isopoly acids are produced by changing the pH, it is possible to identify a sequence of a simple discrete heteropoly species giving rise to complex species on progressive acidification. The reverse situation is obtained when the pH is gradually raised. For example, if $Na_2SiO_3 - (NH_4)_2MoO_4$ solution is progressively acidified, we get 1–2–,6– and 12– silicomolybdate ions being formed in turn. If the pH is gradually decreased, the highly condensed heteropoly anions break down into smaller species. These changes can be followed by analytical techniques like paper chromatography and pH titration.

### Heteropoly Acids of Tungsten

In general the heteropoly acids of tungsten are similar to those of molybdenum.

**(1) 12–tungstoheteropoly acids (Series A)–** These acids have the general formula $[X^{n+} W_{12}O_{40}]^{-(8-n)}$. The heteropoly anions are formed if a tungstate solution is acidified in the presence of phosphate, silicate or metal ions. The second anion provides a centre around which the $WO_6$ octahedra condense by sharing oxygen atoms with other neighbouring octahedra and with phosphate, silicate or borate ions which are in the centre, It may be mentioned here that the first study of the structure of a heteropoly acid was made by Keggin on a crystalline hydrate of 12–phosphotungstic acid having the formula $P_2O_5. 24WO_3. 9H_2O$. Here twelve $WO_6$ octahedra surround a $PO_4^{3-}$ tetrahedron (Fig. 34.10). In the figure we can see a tetrahedron ($PO_4^{3-}$) which is surrounded by four groups of three octahedra ($WO_6$).
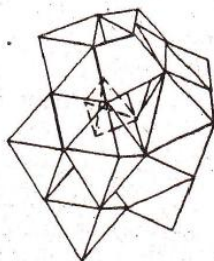


Fig. 34.10. Structure of 12-tungstoheteropoly acid, $H_3(PO_4W_{12}O_{36})$.

**(2) 6–tungstohereropoly acids–** These acids can accomodate larger central atoms inside their structure so that the coordination number is six. The structure of these acids is comparable to the 6–molybdo heteropoly acids (Fig. 34.8).

**(3) 9–tungsto heteropoly acids–** Very little is known about the structures of these acids. In Fig. 34.11 the structure of the $(P_{12}W_{18}O_{62})^{6-}$ anion is shown in which there are two $PO_4^{3-}$ tetrahedra enclosed with in $WO_6$ octahedra.

## 3. *Energy Level diagram of different metal clusters*

❖ The tetragonal prismatic structures provide a large and thoroughly investigated group of compounds with M-M bonds up to quadruple.

❖ The prototypal example examples are $[Re_2Cl_8]^{2-}$ and $[Mo_2Cl_8]^{4-}$ ions, whose general, idealized structure is shown in *Scheme 1*.
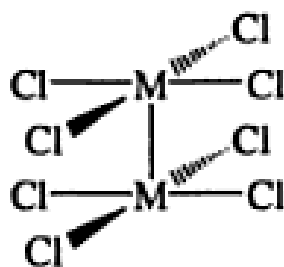


*Scheme 1*

❖ To understand the M-M bonding possibilities within this structural context we consider the five possible overlaps of the d orbitals on two metal atoms, as shown in *Fig. 1*.
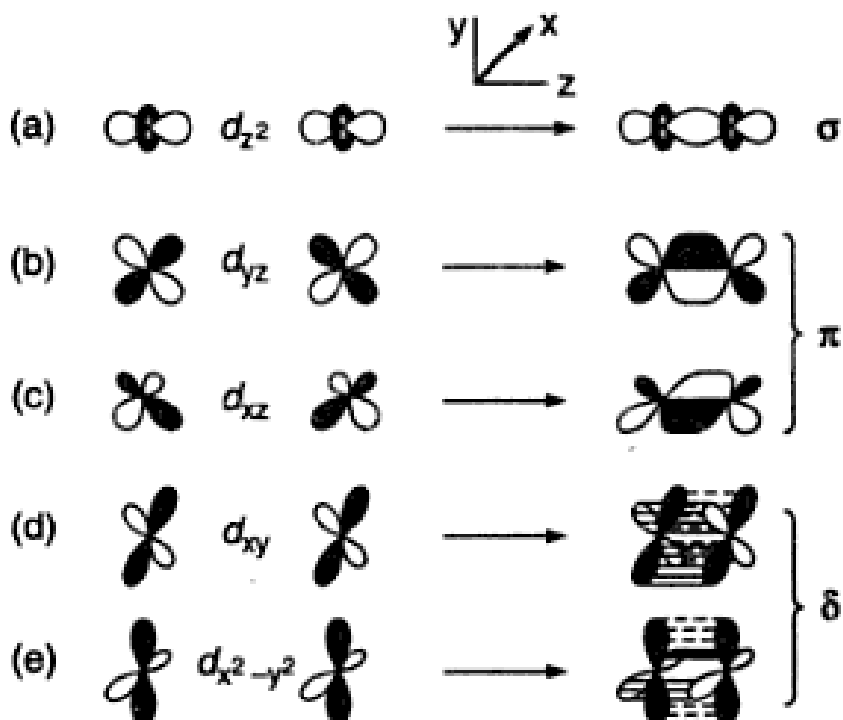
***Fig 1:*** *σ, π,* and *δ* overlaps between two sets of *d* orbitals on adjacent metal atoms with the internuclear axis as the *z* axis.

- ❖ The relative values of the three types of overlap sgown, σ, π, and δ decrease in that orderand thus the ordering of bonding and antibonding orbitals might be expected to appear as in the column labelled $M_2$ of *Fig 2*
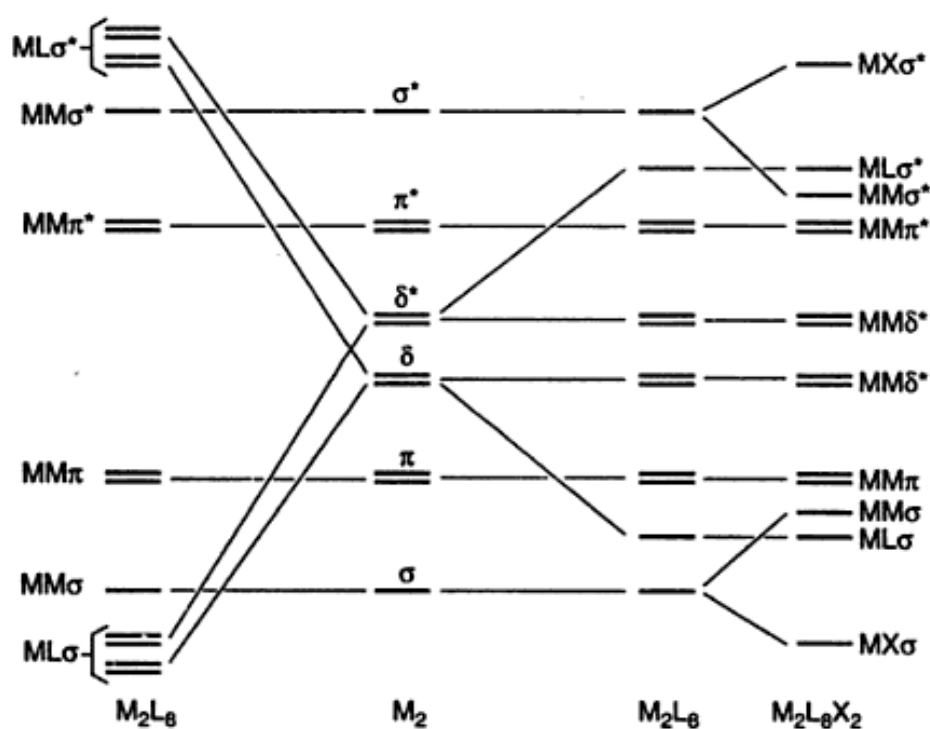


***Fig 2:*** ***Energy level diagrams showing schematically how d-orbital overlaps between two metal atoms ($M_2$) can be modified by bonding ligands to give triple bonds in $M_2L_6$, strong quadruple bonds in $M_2L_8$ and weaker quadruple bonds in $M_2L_8X_2$.***

❖ When the four ligand atoms are brought up to each metal atom to give the arrangement shown in *Scheme I.* the order of the MO's is modified.

❖ If we consider the M-M axis as the *z* direction and the M-L bond axes as $\pm x$ and $\pm y$, the eight lobes of the two $d_{x^2-y^2}$ orbitals will become engaged in the formation of metal-to-ligand σ bonds.

❖ Therefore one member of the δ set of $M_2$ drops to lower energy and becomes an MLσ orbital-at the same time one member of the δ' pair rises in energy and becomes an ML σ* orbital.

❖ The exact extent to which these MLσ and MLσ* orbitals move relative to the other M-M bonding and antibonding orbitals will vary from case to case, and arrangement shown in the $M_2$ coulmns of *Figure 2* is only one possibility. In any case, however the MLσ orbital will befilled by electrons that contribute to M-L bonding and will play no further role in M-M bonding.

❖ The remaining orbitals that result primarily from M-M overlaps are MMσ, MMπ a degenerate pair, and δ MM orbitals.

 ❖ In case where the metal atoms each have four d electrons to contribute, these four orbitals are filled to give a metal-metal quadruple bond, the electron configuration of which is $\sigma^2\,\pi^4\,\delta^2$

 ❖ Such a bond has two characteristics properties:

 ❖ (1) It is very strong, therefore very short and (2) because of the angular properties of the $d_{xy}$ that overlap to form the σ bond, it has an inherent dependence on the angle of internal rotation.

 ❖ The σ bond is strongest ($d_{xy}$– $d_{xy}$ overlap maximizes) when the two $ML_4$ halves have an eclispsed relationship.

- ❖ However, L……L nonbonded repulsions are also maximized in this conformation. Therefore, the rotational conformation about a quadruple bond might in some cases be expected to be twisted somewhat away from the exactly eclipsed one.

- ❖ Indeed, the $d_{xy}$– $d_{xy}$ overlap decreases only slightly through the first few degrees of rotation, so that little $\delta$-bond energy is lost by small rotations.

- ❖ Examples of rotations up to $20^{o}$ have been observed but the majority of quadruple bonds are essentially eclipsed.

**4.** (a) (i) $\mathbf{B_6H_6^{2-}}$

1. Total number of valence electrons = (6 x 3) + ( 6 x 1) + 2  =  26
2. Number of electrons for each B-H unit = (6 x 2) = 12
3. Number of skeletal electrons = 26 – 12 = 14
4. Number SEP = 14/2 = 7
5. If $n$+1 = 7 and $n$ = 6
6. Structure of $n$ = 6 is octahedral, therefore $B_6H_6^{2-}$ is a *closo* structure based upon an octahedral structure with no apex missing.
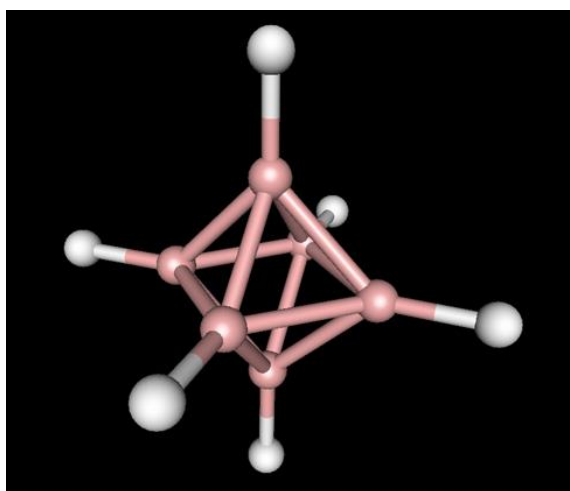
(ii) **B$_5$H$_9$**

1. Total number of valence electrons = (5 x B) + (9 x H) = (5 x 3) + (9 x 1) = 24

2. Number of electrons for each B-H unit = (5 x 2) = 10

3. Number of skeletal electrons = 24 – 10 = 14

4. Number SEP = 14/2 = 7

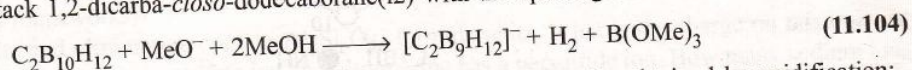5. If $n$+1 = 7 and $n$-1 = 5 boron atoms, then $n$ = 6

Structure of $n$ = 6 is octahedral, therefore B$_5$H$_9$ is a *nido* structure based upon an octahedral structure with one apex missing
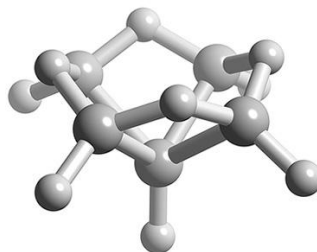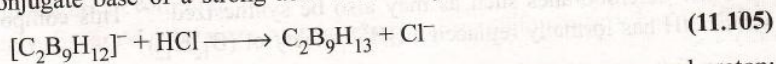
(b)

## Metallacarboranes[106]

Strong bases attack 1,2-dicarba-*closo*-dodecaborane(12) with the splitting out of a boron atom:

$$C_2B_{10}H_{12} + MeO^- + 2MeOH \longrightarrow [C_2B_9H_{12}]^- + H_2 + B(OMe)_3 \qquad (11.104)$$

The resulting anion is the conjugate base of a strong acid which may be obtained by acidification:

$$[C_2B_9H_{12}]^- + HCl \longrightarrow C_2B_9H_{13} + Cl^- \qquad (11.105)$$

Conversely, treatment of the anion with the very strong base sodium hydride abstracts a second proton:

$$[C_2B_9H_{12}]^- + NaH \xrightarrow{\text{thf}} [C_2B_9H_{11}]^{2-} + H_2 + Na^+ \qquad (11.106)$$

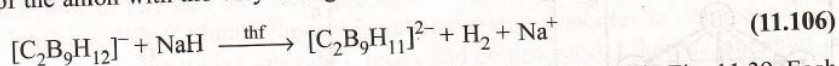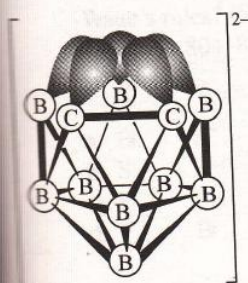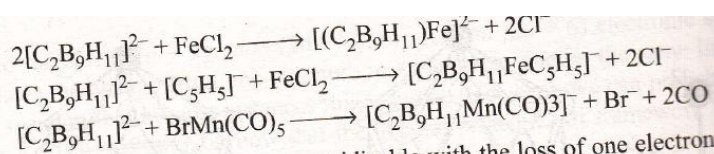**Fig.11.39** Structure of the $[C_2B_9H_{11}]^{2-}$ anion. The five orbitals directed toward the missing apical boron are included. [From Adler, R. G.; Hawthorne, *M. F. J. Am. Chem. Soc.* **1970**, *92*, 6174. Reproduced with permission.]

The structure of the $[C_2B_9H_{11}]^{2-}$ anion is shown in Fig. 11.39. Each of the three boron atoms and the two carbon atoms on the open face of the cage directs an orbital (taken as $sp^3$ for convenience) toward the apical position occupied formerly by the twelfth boron atom. Furthermore, these orbitals contain a total of six electrons. They thus bear a striking resemblance to the $p$ orbitals in the $\pi$ system of cyclopentadienide anion. Noting this resemblance, Hawthorne suggested that the $(C_2B_9H_{11})^{2-}$ anion could be considered isoelectronic with $C_5H_5^-$ and should therefore be capable of acting as a $\pi$ ligand in metallocene compounds. He and his coworkers then succeeded in synthesizing metallacarboranes, launching a new area of chemistry which is still being actively investigated:[107]

[106] *Metal Interactions with Boron Clusters*; Grimes, R. N., Ed.; Plenum: New York, 1982. Grimes R. N. In *Comprehensive Organometallic* Chemistry, Wilkinson, G.; Stone, F. G. A.; Abel, E., Eds.; Pergamon: Oxford, **1982**. See also Kennedy, J. D. *Prog. Inorg. Chem.* **1986**, *34*, 211–434.
[107] Baker, R. T.; Delaney, M. S.; King, R. E., III; Knobler, C. B.; Long, J. A.; Marder, T. B.; Paxson, T. E.; Teller, R. G.; Hawthorne, M. F. J, *Am. Chem. Soc.* **1984**, *106*, 2965–2978. Long, J. A.; Marder, T. B.; Behnken, P. E.; Hawthorne, M. F. Ibid. 2979–2989. Knobler, C. B.; Marder, T. B.; Mizusawa, E. A.; Teller, R. G.; Long, J. A.; Behnken, P. E.; Hawthorne, M. F. Ibid.2990–3004. Long, J. A.; Marder, T. B.; Hawthorne, M. F. Ibid. 3004–3010.

$$2[C_2B_9H_{11}]^{2-} + FeCl_2 \longrightarrow [(C_2B_9H_{11})Fe]^{2-} + 2Cl^-$$

$$[C_2B_9H_{11}]^{2-} + [C_5H_5]^- + FeCl_2 \longrightarrow [C_2B_9H_{11}FeC_5H_5]^- + 2Cl^-$$

$$[C_2B_9H_{11}]^{2-} + BrMn(CO)_5 \longrightarrow [C_2B_9H_{11}Mn(CO)3]^- + Br^- + 2CO$$

The ferrocene analogues, like ferrocene, are oxidizable with the loss of one electron. In cases for which structures have been determined, they have been found to correspond to that expected on the basis of metallocene chemistry (Fig. 11.40).



○ BH  ● NH
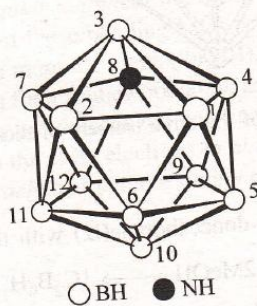
Other heteroboranes such as may also be synthesized.[108] This compound may be regarded as one in which NH has formally replaced a $BH_2^{2-}$ moiety of $(B_{12}H_{12})^{2-}$.



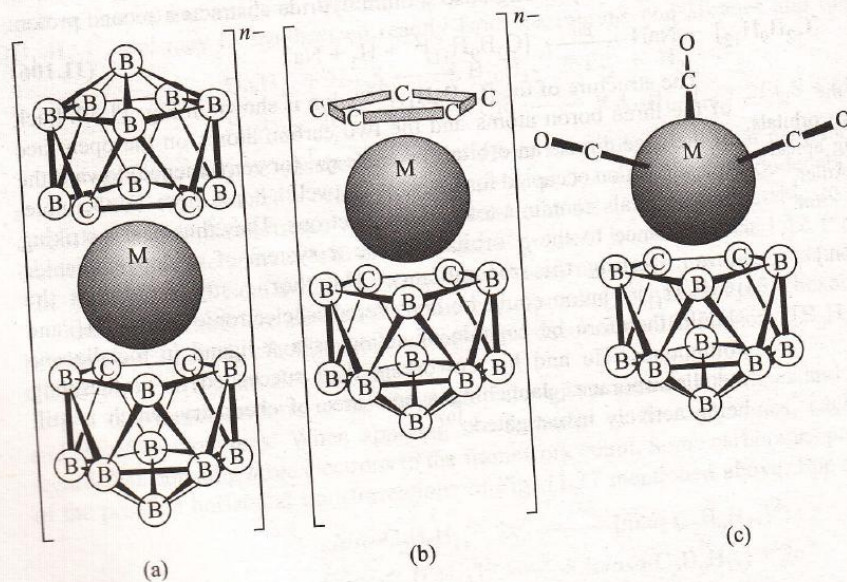**Fig.11.40** Structures of some carbollyl metallocene compounds. (a) Dicarbollyl species; M = Fe, n = 2 and M = Co, n = 1 are isoelectronic with ferrocene and cobaltocenium ion; M = Fe, n = 1 is isoelectronic with ferrocenium ion; (b) mixed carbollyl–cyclopentadianyl analogue of ferrocere, n = 1; (c) mixed carbollyl–carbonyl compound, M = Mn, Re. [(a) and (b) fromg Hawthorne, M. F.; Andrews, T. D. *J. Am. Chem. Soc.* **1965**, 87, 2496; (c) from Adler, R.G.; Hawthorne, M.F. J. *Am. Chem. Soc.* **1970**, 92, 6174. Reproduced with permission.]

[108] Müller, J.; Runsink, J; Paetsold, P. *Angew. Chem. Int. Ed. Engl.* **1991**, 30, 175.

## 5.    *Capping Principle*                                    *4+4*

 A large number of structures is known in chich triangular cluster faces are capped. An example in $[Rh_7(CO)_{16}]^{3-}$ **Fig.1a** , where an $[Rh(CO)_3]^{3+}$ group caps an octahedral face on $[Rh_6(CO)_{13}]^{3-}$. Mingos has showed that such structure can be explained and rationalized, which states that the *skeletal electron count for a capped structure is the same as that for the parent.*

- In the present example, the parent $[Rh_6(CO)_{13}]^{6-}$ has a count of 86 as expected for a closo octahedron.

- The $[Rh(CO)_3]^{3+}$ fragment has 12 electrond occupying non-bonding and Rh-Co bonding and thus contributes to skeletal bonding only its three empty orbitals of A and E symmetry, which is referred to be the three fold axis of the caped triangular face.

- The result of interaction of this anti-orbitals with filled cluster orbitals of suitable symmetry i.e. 1.a. and a pair of e bonding orbitals along with their anti-bonding counter parts is shown in **fig. 1b**.
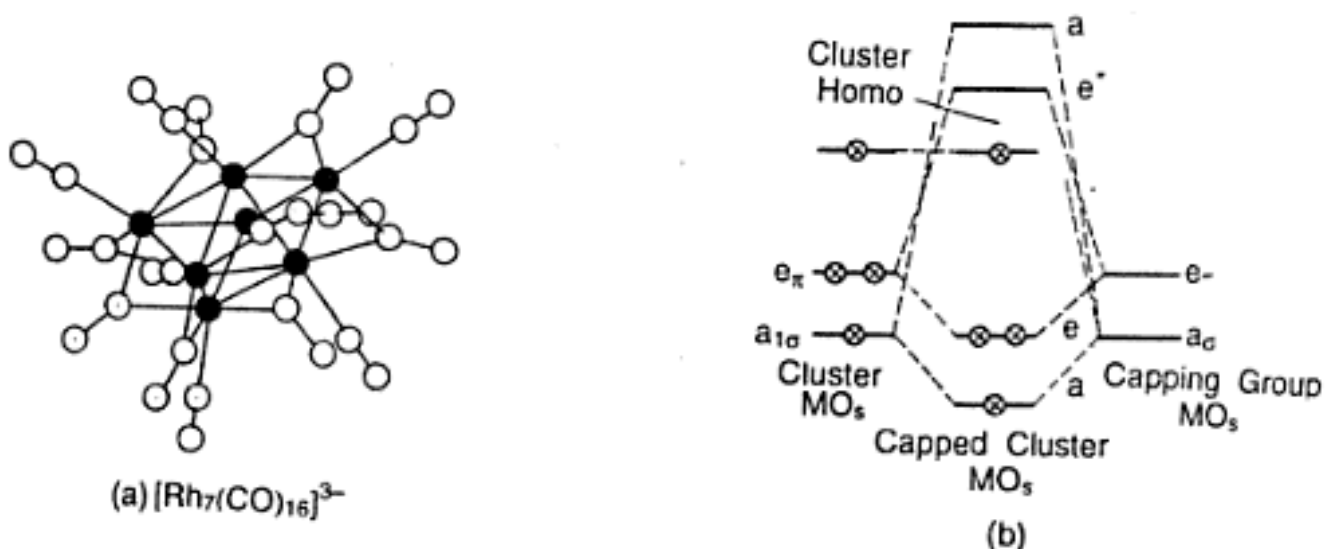
**Fig. 1** *(a) The structure of $[Rh_7(CO)_{16}]^{3-}$ (b) Schematic diagram showing the result of capping a triangular cluster face. Symmetry labels refer to the pseudo-threefold axis passing through the face center.*

- In his interaction only the bonding orbitals are occupied which are more stable than those in the original cluster due to interaction with the anti-capping group orbitals.

- Thus for capped *closo* structure the total electron count is expected to be 14n+2+12m, where m is the number of capping groups. The various examples of the different geometry and electron counts for capped $\pi$-acid clusters are given in *Table -1.*

- *Fig. 1b* also provides insite into the possibility of vertices of octahedral clusters when the electrons are left behind and a structure may be converted from *closo* to *nido* to *archano .*

- As the three valence orbitals on the vertex are removed, a set of three bonding and a set of three anti-bonding MO's collapses to a single set of three.

| Gemetry | Electron count | Example |
|---|---|---|
| *closo* parent cluster | $(14n + 2 + 12m)$ | |
| Capped trigonal bipyramid | $72 + 12 = 84$ | $Os_6(CO)_{18}$ |
| Monocapped octahedron | $86 + 12 = 98$ | $Os_7(CO)_{21}$ |
| Bicapped octahedron | $86 + 24 = 110$ | $[Os_8(CO)_{22}]^{2-}$ |
| Tetracapped octahedron | $86 + 48 = 134$ | $[Os_{10}C(CO)_{24}]^{2-}$ |
| | | |
| *nido* parent cluster | $(14n + 4 + 12m)$ | |
| Bicapped tetrahedron = capped trigonal bipyramid | $60 + 24 = 84$ | $Os_6(CO)_{18}$ |
| Monocapped square pyramid | $74 + 12 = 86$ | $H_2Os_6(CO)_{18}$ |

+ Sufficient electrons remain to occupy this less bonding set. The skeletal electron count remain the same but the number of vertex group decreases by one.

+ In metal containing clusters this reduces the total electron count by 12.

A two dimensional capping principal can rationalize edge-bridged structure $M(CO)_4$ metal is isolobal with $CH_2$, which often forms bridge.

 + MO's interactions analogous those in Fig. 2 can be predicted leading to stabilization via edge-bridging.

 + Leaving vacant the radial and one tangential orbitals for interaction with cluster orbitals and filling the remaining $M(CO)_4$ metal orbitals with non-bonding or ligent bonding electrons leads to an electron count of 14 for the fragment.

- Thus as bridged structure to have a total electron count of *N+14* where N is the count for the parent.

- Thus, $[Os(CO)_4]^{2+}$ has 14 electrons and bridges one tetrahedral edge of $[H_2Os_4(CO)_{12}]^{2-}$ ;

- The electron count for $[H_2Os_5(CO)_{16}]$ is $60+14= 74$ .

- Likewise the 'bowite' structure of $H_2Os_4(CO)_{12}^{2-}$ the "bowtie" structure of $Os_5(CO)_{19}$ can be rationalized as resulting of capping linear $[Os_3(CO)_{11}]^{4-}$ (50e) with two $Os_5(CO)_4^{2+}$ fragments for a total count 78.

6. A **siloxane** is a functional group in organosilicon chemistry with the Si–O–Si linkage. The parent siloxanes include the oligomeric and polymeric hydrides with the formulae $H(OSiH_2)_nOH$ and $(OSiH_2)_n$. Siloxanes also include branched compounds, the defining feature being that each pair of silicon centres is separated by one oxygen atom. The siloxane functional group forms the backbone of silicones, the premier example of which is polydimethylsiloxane.
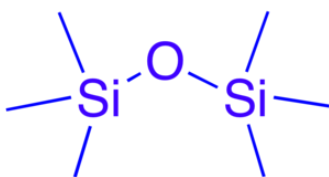


**Silicone rubber** is an elastomer (rubber-like material) composed of silicone—itself a polymer—containing silicon together with carbon, hydrogen, and oxygen. Silicone rubbers are widely used in industry, and there are multiple formulations. Silicone rubbers are often one- or two-part polymers, and may contain fillers to improve properties or reduce cost. Silicone rubber is generally non-reactive, stable, and resistant to extreme environments and temperatures from −55 °C to +300 °C while

still maintaining its useful properties. Due to these properties and its ease of manufacturing and shaping, silicone rubber can be found in a wide variety of products, including: automotive applications; cooking, baking, and food storage products; apparel such as undergarments, sportswear, and footwear; electronics; medical devices and implants; and in home repair and hardware with products such as silicone sealants.

During manufacture, heat may be required to vulcanize (set or cure) the silicone into its rubber-like form. This is normally carried out in a two stage process at the point of manufacture into the desired shape, and then in a prolonged post-cure process. It can also be injection molded.

**Silicone resins** are a type of silicone material which is formed by branched, cage-like oligosiloxanes with the general formula of $R_nSiX_mO_y$, where R is a non reactive substituent, usually Me or Ph, and X is a functional group H, OH, Cl or OR. These groups are further condensed in many applications, to give highly crosslinked, insoluble polysiloxane networks.

When R is methyl, the four possible functional siloxane monomeric units are described as follows:

- "M" stands for $Me_3SiO$,
- "D" for $Me_2SiO_2$,
- "T" for $MeSiO_3$ and
- "Q" for $SiO_4$.

Note that a network of only Q groups becomes fused quartz.

The most abundant silicone resins are built of D and T units (DT resins) or from M and Q units (MQ resins), however many other combinations (MDT, MTQ, QDT) are also used in industry.

Silicone resins represent a broad range of products. Materials of molecular weight in the range of 1000-10 000 are very useful in pressure sensitive adhesives, silicone rubbers, coatings and additives.

Silicone resins are prepared by hydrolytic condensation of various silicone precursors. In early processes of preparation of silicone resins sodium silicate and various chlorosilanes were used as starting materials. Although the starting materials were the least expensive ones (something typical for industry), structural control of the product was very difficult. More recently, a less reactivetetraethoxysilane - (TEOS) or ethyl polysilicate and various disiloxanes are used as starting materials.
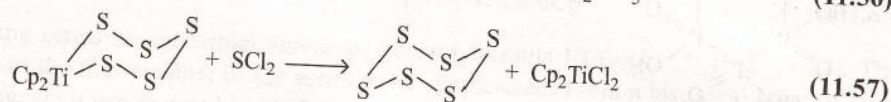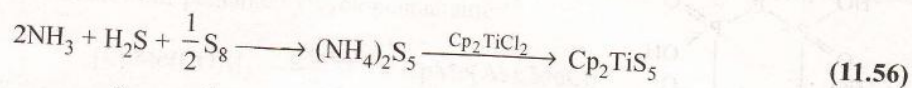
**7.**

Several elements form homocyclic rings. Rhombic sulfur, the thermodynamically stable form at room temperature, consists of $S_8$ rings in the crown conformation. Unstable modifications, $S_n$, are known which
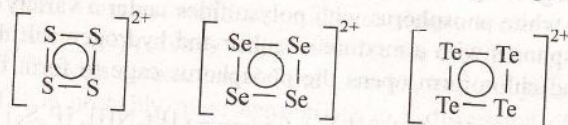
include $n = 6$ through $n = 36$. In fact, sulfur has more allotropes than any other element.[64] Selenium also forms five-, six-, seven-, and eight-membered rings, but they are unstable with respect to the chain form.

Organometallic chemistry has become an important player in the rings of sulfur.[65] The existence of an isolobal relationship between S and $Cp_2Ti$ leads to the prediction that it should be possible to substitute the latter for the former in sulfur rings. The formal replacement of one sulfur atom in $S_6$ by $Cp_2Ti$ gives $Cp_2TiS_5$ [or replacing two sulfur atoms in $S_8$ by two $Cp_2Ti$ units gives 1, 5-$(Cp_2Ti)_2S_6$]. In practice one takes these reactions in the reverse direction. For example, $S_6$, which is unstable with respect to $S_8$, may be prepared from the readily available $Cp_2TiS_5$ complex.
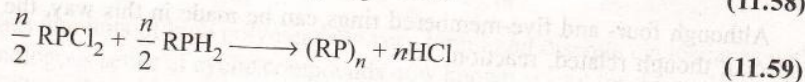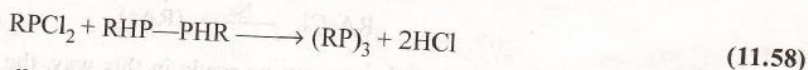
$$2NH_3 + H_2S + \frac{1}{2}S_8 \longrightarrow (NH_4)_2S_5 \xrightarrow{Cp_2TiCl_2} Cp_2TiS_5 \qquad (11.56)$$

$$Cp_2Ti \underset{S-S}{\overset{S-S}{\diagup S \diagdown}} + SCl_2 \longrightarrow \underset{S-S}{\overset{S-S}{\diagup S \diagdown}} + Cp_2TiCl_2 \qquad (11.57)$$

The $S_5^{2-}$ anion that forms in the first step is one of several polysulfides ($S_2^{2-}$, $S_3^{2-}$, $S_4^{2-}$, $S_6^{2-}$), all of which have open chain structures.

Oxidation of several nonmetals in strongly acidic systems produces polyatomic cationic species of the general type $Y_n^{m+}$.[66] Among those characterized are $S_4^{2+}$, $Se_4^{2+}$, $Te_4^{2+}$, $S_8^{2+}$, $Se_8^{2+}$, $Se_{10}^{2+}$, $S_{16}^{2+}$, $S_{19}^{2+}$ and $Te_2Se_{10}^{2+}$. The structures of $S_4^{2+}$ $Se_4^{2+}$, and $Te_4^{2+}$ ions have been shown to be square planar.

$$\left[\begin{array}{c} S-S \\ |\ O\ | \\ S-S \end{array}\right]^{2+} \quad \left[\begin{array}{c} Se-Se \\ |\ O\ | \\ Se-Se \end{array}\right]^{2+} \quad \left[\begin{array}{c} Te-Te \\ |\ O\ | \\ Te-Te \end{array}\right]^{2+}$$

Note that these are isoelectronic with the previously mentioned $S_2N_2$. All three are thought to be stabilized to a certain extent by a Hückel sextet of $n$ electrons.

Many cyclopolyphosphines are known.[67] The simpler ones, $(RP)_n$ ($n = 3-6$) (Fig. 11.21), are prepared by pyrolysis or elimination reactions.

$$RPCl_2 + RHP-PHR \longrightarrow (RP)_3 + 2HCl \qquad (11.58)$$

$$\frac{n}{2} RPCl_2 + \frac{n}{2} RPH_2 \longrightarrow (RP)_n + nHCl \qquad (11.59)$$

In addition to the +3 oxidation state seen in the homocyclic rings discussed above, phosphorus rings exist in which the +5 oxidation state is exhibited:
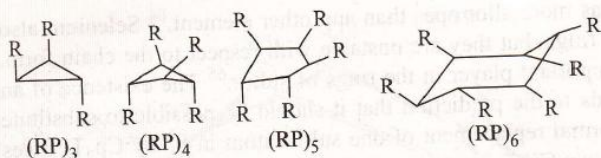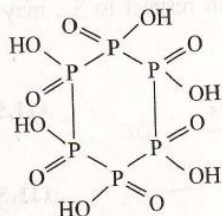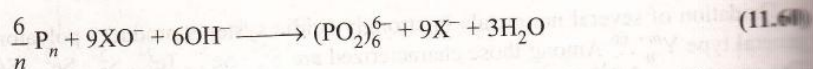
**Fig. 11.21** Structures of $(RP)_n$ ($n = 3 - 6$) molecules.

(RP)$_3$     (RP)$_4$     (RP)$_5$     (RP)$_6$



The anion of this acid results from the oxidation of red phosphorus with hypohalites in alkaline solution:

$$\frac{6}{n} P_n + 9XO^- + 6OH^- \longrightarrow (PO_2)_6^{6-} + 9X^- + 3H_2O \tag{11.60}$$

There is a series of analogous cyclic thiophosphoric acids with the formula $(HS_2P)_n$ that may be prepared by the oxidation of red or white phosphorus with polysulfides under a variety of conditions. For example, the reaction of white phosphorus with a mixture of sulfur and hydrogen sulfide dissolved in triethylamine (which acts as a base) and chloroform opens the phosphorus cage to form the tetrameric cyclic anion:

$$P_4 + 4Et_3N + 2H_2S + 6S \longrightarrow [Et_3NH]_4 [P_4S_8] \tag{11.61}$$
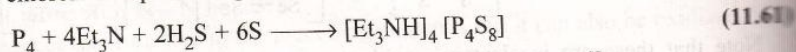
The square structure of the anion has been confirmed by X-ray crystallography.[68]

A series of cyclopolyarsines is known. They may be prepared by a generally useful reaction that is reminiscent of the Wurtz reaction of organometallic chemistry:

$$RAsCl_2 \xrightarrow{Na} (RAs)_{4,\ 5} \tag{11.62}$$
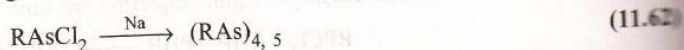
Although four- and five-membered rings can be made in this way, the three-membered ring requires a special, though related, reaction:



$$(t\text{-Bu})As - As (t\text{-Bu}) + (t\text{-Bu})AsCl_2 \longrightarrow \tag{11.63}$$
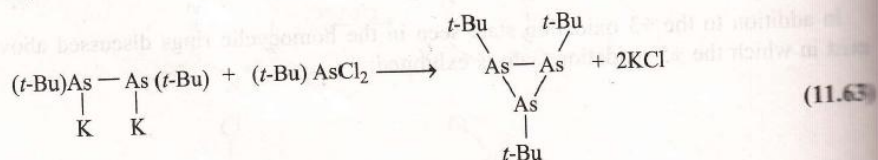
This compound is stable only at −30°C in the dark and in the absence of air. It spontaneously ignites on exposure to air.[69]

Alkali metal pentaphosphacyclopentadienides (Li and Na) have been obtained in solution from reactions of red phosphorus and dihydrogenphosphide in dimethyl formamide:[70]

68  Falius, H.; Krause, W.; Sheldrick, W. S. *Angew. Chem, Int. Ed. Engl.* **1981**, *20*, 103–104.

69  Baudler, M.; Etzbach. T. *Chem. Ber.* **1991**, *124*, 1159–1160.

70  Baudler, M.; Akpapoglou, S.; Ouzounis, D.; Wasgestian, F.; meinigke, B.; Budzikiewicz, H.; Münster. H. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 280–281, Hamilton, T. P.; Schaefer, H.F., III. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 485.

Fig. 6.12 Molecular structure

## 2. Tetrathiazyl Tetrafluoride, : (NSF)$_4$

It is prepared by fluorination of $S_4N_4$.

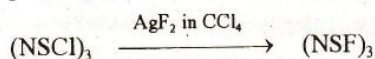$$S_4N_4 + 4AgF_2 \longrightarrow S_4N_4F_4 + 4AgF$$

It is a water-sensitive white solid. It dissociates at 200-250°C to NSF which polymerises to the (NSF)$_3$.

The $^{19}$F *n.m.r.* spectrum of tetrathiazyl tetrafluoride gives a single resonance peak thereby indicating that all of the fluorine atoms are equivalent. The molecule has a puckered ring structure with two alternating S—N distances of 1.66 and 1.54 Å in the ring (Fig. 6.12). This indicates that the presence of fluorine substituents appears to destroy the delocalisation of the electrons in the ring (atleast in part) because the bond lengths in the ring alternate in length. Further, the presence of fluorine substituents lead to a contraction of the sulphur *d* orbitals and consequently thereby a better overlap. As the sulphur electrons are more strongly held, it means that these are less available for delocalisation.

(NSF)$_4$ isoelectronic with (NPF$_2$)$_4$ in which delocalisation, at least to the extent that there are 3-centre N...P...N$\pi$ systems, is thought to occur.

Fig. 6.12 (a) Diagram structure of $S_4N_4F_4$ illustrating alternating bond lengths

## 3. Trithiazyl Trifluoride (NSF)$_3$

It is prepared by fluorinating trithiazyl trichloride (NSCl)$_3$.

$$(NSCl)_3 \xrightarrow{\text{AgF}_2 \text{ in CCl}_4} (NSF)_3$$

It is also prepared by heating (NSF)$_4$ at 200-250°C which dissociates to NSF, followed by polymerisation of (NSF)$_3$.

The structure of (NSF)$_3$ is unknown although its n.m.r. spectrum reveals that all the fluorine atoms are equivalent. However, it is likely to resemble that of (NSCl)$_3$.

## 4. Trithiazyl trichloride, (NSCl)$_3$

Whenever attempt is made to prepare (NSCl)$_4$ by treating tetrasulphur tetranitride with Cl$_2$, this compound is not obtained but instead trithiazyl trichloride is obtained.
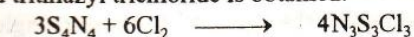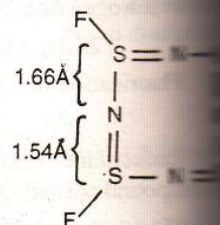
$$3S_4N_4 + 6Cl_2 \longrightarrow 4N_3S_3Cl_3$$
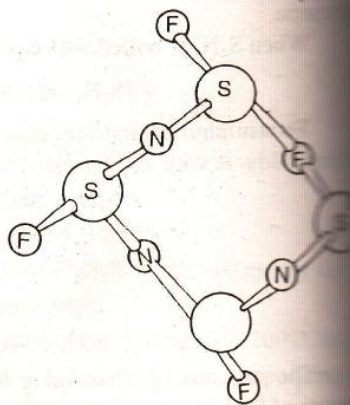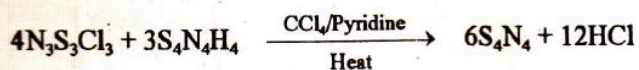
Fig. 6.12 (b) Perspective drawing of the molecule.

Reduction of the trithiazyl trichloride, (NSCl)$_3$ with tetrasulphur tetraimide results in the formation of products, containing eight numbered rings, i.e., S$_4$N$_4$.

$$4N_3S_3Cl_3 + 3S_4N_4H_4 \xrightarrow[\text{Heat}]{\text{CCl}_4/\text{Pyridine}} 6S_4N_4 + 12HCl$$

The above reaction takes place in the presence of pyridine which absorbs HCl. The nature of the product in this reaction suggests an initial depolymerisation to NSCl and NSH.

This compound may be converted into the corresponding fluoride or oxidised to sulphanuryl chloride.
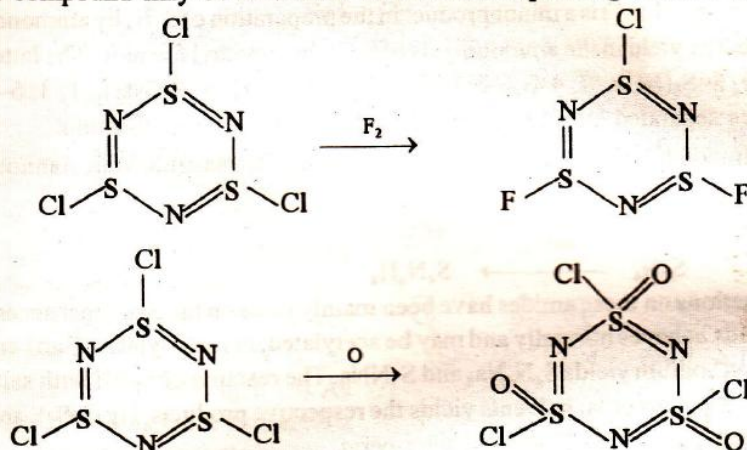


The structure of (NSCl)$_3$ is known. It is a six-membered ring which is almost planar with all of the chlorine atoms on one side of the ring in axial positions. All of its N—S distances are the same, i.e., 1.60 Å.
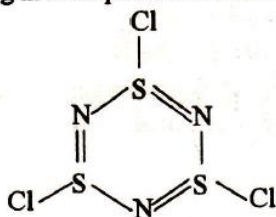
## 8. (a) Wade's rules:

British Chemist Kenneth Wade in the year 1970 proposed a set of rules for predicting the structures of cluster compounds based in the number of electrons in the framework counted in a particular way.

Wade's rules are used to rationalize the shape of borane clusters by calculating the total number of skeletal electron pairs (SEP) available for cluster bonding. In using Wade's rules it is key to understand structural relationship of various boranes.

The following general methodologies are followed in Wade's rules

1.  Determination the total number of valence electrons from the chemical formula, i.e., 3 electrons per B, and 1 electron per H.
2.  2 electrons for each B-H unit (or C-H in a carborane) are subtracted.
3.  The number of remaining electrons is divided by 2 to get the number of skeletal electron pairs (SEP).
4.  A cluster with $n$ vertices (i.e., $n$ boron atoms) and $n$+1 SEP for bonding has a *closo* structure.
5.  A cluster with $n$-1 vertices (i.e., $n$-1 boron atoms) and $n$+1 SEP for bonding has a *nido* structure.
6.  A cluster with $n$-2 vertices (i.e., $n$-2 boron atoms) and $n$+1 SEP for bonding has an *arachno* structure.
7.  A cluster with $n$-3 vertices (i.e., $n$-3 boron atoms) and $n$+1 SEP for bonding has an *hypho* structure.
8.  If the number of boron atoms (i.e., $n$) is larger than $n$+1 SEP then the extra boron occupies a capping position on a triangular phase.

**Example: Structure determination of $B_5H_{11}$**

1. Total number of valence electrons = (5 x B) + (11 x H) = (5 x 3) + (11 x 1) = 26

2. Number of electrons for each B-H unit = (5 x 2) = 10

3. Number of skeletal electrons = 26 – 10 = 16

4. Number SEP = 16/2 = 8

5. If $n$+1 = 8 and $n$-2 = 5 boron atoms, then $n$ = 7

6. Structure of $n$ = 7 is pentagonal bipyramd, therefore $B_5H_{11}$ is

   an *arachno* based upon a pentagonal bipyramid with two apexes missing

# CARBORANES :

In many known compounds, one or more framework BH groups are replaced by atoms of different elements. For example, $CH^+$, $P^+$ and $S^{2+}$ are all equivalent to BH (having two electrons for framework bonding plus two more in a bond to an exo-H or as a lone pair.). Hence a series of neutral closo compounds exists of formular $C_2B_pH_{p+2}$, derived by substitution of BH by $CH^+$. These are called carboranes. Although $B_5H_5^{2-}$ has not yet been prepared, isoelectronic $C_2B_3H_5$ having the antipated trigonal bipyramid structure is known.

Now from given molecular formula of carboranes we can achieve the structure. Let us assume the general formula of the carborane is $[(CH)_a (BH)_p H_{q+c}]^{+c}$. The number of electron pairs contributed by CH is $3/2$, then the total number of skeletal electron pair is,

$$\frac{3}{2}a + p + \frac{1}{2}(q+c) - \frac{1}{2}c$$

where the number of vertices of the polyhedron or polyhedral fragment is $a + p = n$, and q H's are involved in BHB or extra B-H terminal bonds.
The no. of framework electrons is given by

$$3a + 2p + q + c = 2n + a + q + c$$

and so the no. of electron pairs is $\frac{1}{2}(2n+a+q+c)$. It is assumed that a structure is adopted in which all of these electrons completely occupy only the available bonding molecular orbitals. (There are $3n+q$ valence atomic orbitals at hand, so at most $\frac{1}{2}(3n+q)$ bonding mo's can arise.) Thus

if $a+q+c = 2$, the compound assumes closo

$a+q+c = 4$, " " " nido st

$a+q+c = 6$, " " " arachn

$s$

Let us suppose, $C_2B_8H_{12} = [(CH)_2(BH)_8 H_2]$