M.Sc. Semester-II, CC-6 (Inorganic Chemistry)

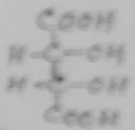
Unit-2 Symmetry in Chemistry (By Dr. Birendra Kumar, Maharaja College.)

Elements of Symmetry?

Elements of Symmetry offer a simple device to decide whether a molecule is chiral(unsymmetrical) or Achiral(~~un~~symmetrical). A element of Symmetry is a geometrical entity such as a line or axis, a plane or a point or Centre, with respect to which one or more symmetry operations may be carried out. When a molecule has a plane/~~line/axis~~ Centre/n fold alternating axis of symmetry, it is superimposable on its mirror image, and is achiral (unsymmetrical).

Symmetry elements and symmetry operations are so closely interrelated because the operation can be defined only with respect to the element.

The existance of a symmetry element can be demonstrated only by showing that the appropriate symmetry operation exist. There are four types of Symmetry elements in molecular chemistry. These are—

Symmetry element	Symmetry operation(s)
1. Centre of Symmetry or Inversion Centre (C_i)	Inversion of all atoms through the Centre e.g. $O=C=O$
2. Plane of Symmetry (σ)	Reflection in the plane. e.g. 
3. Proper Axis of Symmetry (C_n)	One or more rotations about the axis. e.g. 
4. Improper Axis of Symmetry (S_n)	Reflection in a plane perpendicular to the rotation axis. e.g. BF_3  has $3\sigma_v, 1\sigma_h$

Symmetry operations?

A symmetry operation is a movement of a molecule such that, after the movement has been carried out, every point(element) of the molecule is coincident with an equivalent or same point (element) of the molecule in its original Orientation. It can be defined as—"The geometrical operation such as reflection, rotation, inversion etc. which leads to a configuration/structure indistinguishable from the original configuration/structure."

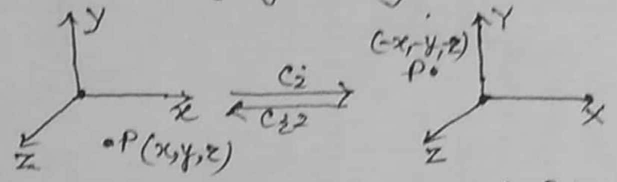
It must be emphasised that the two configurations/structures are not exactly identical, but they look like in all respects.

Different types of Symmetry elements/operations:

1. Identity(E): It is the operation of doing nothing. When we donot do anything and leave the molecule unchanged and identical to the original molecule in all respects, the operation is called Identity. It is denoted by 'E'. All systems

and extended an equal distance on the other side meet the same atoms/groups. In other words, this is an imaginary point in the centre of the molecule, through which the reflection of each atom can be carried out, to result in its coincidence with an equivalent atom.

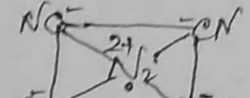
If a molecule can be brought into an equivalent configuration by changing the coordinates (x, y, z) of every atom and origin lie at a point within the molecule into $(-x, -y, -z)$, then the point at which the origin lie is, said to be a centre of symmetry. It is denoted by 'C_i' or 'i'.



* Repeat of inversion operation (C_i^2) gives identical/same configuration.
* If n is even, $C_i^n = E$ (Identity); If n is odd, $C_i^n = C_i$

<u>Examples</u>: (i) Carbon dioxide: $\underbrace{O=}_{-x}\underbrace{C=O}_{x}$ It has centre of symmetry (C_i) with respect to C, two O-atoms lie at equal distance, but opposite sides.

(ii) $[Ni(CN)_4]^{2-}$:



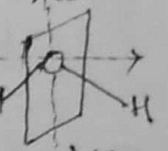
~~Here~~ Ni^{2+} is at inversion centre (i) two $\bar{C}N$ (ligands) lie at equal distance, but opposite sides of square plane.

3. <u>Plane of Symmetry</u>:

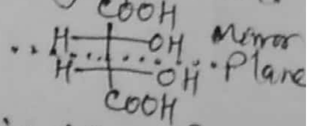
The plane which divides a molecule into two equal halves which are related as object and mirror image is known as plane of symmetry. It is denoted by σ (Sigma, comes from German word <u>Svegel</u>, meaning <u>mirror</u>).

The molecules having a plane of symmetry are achiral (symmetrical). A plane of symmetry is equivalent to a one fold alternating axis of symmetry.

<u>Examples</u>: (i) H_2O molecule, has a plane passing through the C_2-axis perpendicular to the molecular plane (i.e; through O-atom & between two H-atoms) If a reflection is carried out over the plane of symmetry and the new positions of the atoms are noted, the new orientation will be equivalent to the original orientation. Therefore, σ is a symmetry operation.



(ii) Meso-tartaric acid molecule has a plane of symmetry since one half is mirror image of other.



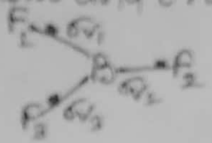
* Repeat reflection (σ^2) operation gives identical configuration, i.e., $\sigma_v^2 = E$.
* If n is even, $\sigma^n = E$ (Identity); If n is odd, $\sigma^n = \sigma$.

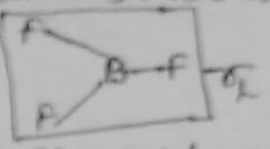
In a molecule following planes may exist:

(a) Vertical Plane (σ_v): The plane containing principal (vertical) axis
(b) Horizontal plane (σ_h): The plane perpendicular to principal axis.
(c) Dihedral Plane (σ_d): The plane bisecting the dihedral angle between two planes.

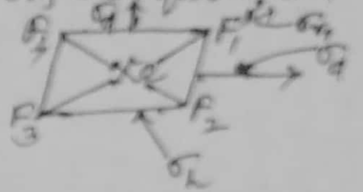
* All planar molecules have at least one plane of symmetry, identical with the molecular plane. Linear molecules have an infinite no. of σ planes which intersect along C_∞.

Other examples: (i) BF_3 molecule: It is a trigonal molecule. It consists of three σ_v each passing through the B-atom and one F-atom. It also consists of one σ_h lying in the plane of the molecule





(ii) XeF_4 molecule: It is square planar molecule. It consists of one σ_h, lying in the plane of the molecule, two σ_v lying in the diagonal of the square and two σ_d passing through the intersection of σ_v planes.
Here, two σ_v through XeF_1F_3 & XeF_2F_4; two σ_d between two F-atoms (F_1, F_2 or F_3, F_4 & F_1, F_4 or F_2, F_3).



4. Axis of Symmetry (C_n): A molecule is said to have a simple or proper axis of symmetry multiplicity n or n-fold axis of symmetry if a rotation of $360°/n$ around this axis leads to an arrangement which is indistinguishable from the original. Multiplicity $(n) = \frac{360°}{\theta}$ (where θ = numbers of degree of rotation required for superimposition on original. It is represented by C_n.

The general conventions for specifying coordinates are as follows:

(i) The rotational axis with the highest order is the principal axis & it is z-axis.

(ii) If the rotational axes (x, y, z) are of the same order, the axis passing through the largest number of atoms must be taken as the z-axis. If one does not find such an axis z is the one passing through a large number of bonds.

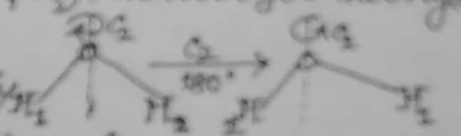
(iii) In a planar molecule, the rotational axis perpendicular to the plane of the molecule is taken as z-axis.

* All linear molecules have C_∞ axis of symmetry as in O=C=O, an equivalent arrangement is always obtained whatever be the angle of rotation.

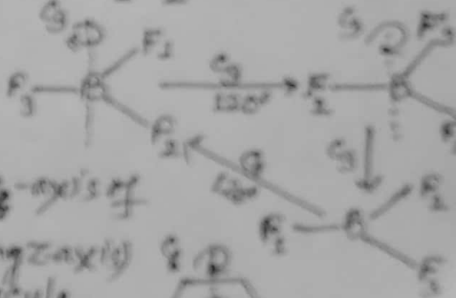
* All molecules have an infinite number of C_1-axis, hence, the C_1-axis is never considered.

* If C_2 operation perform twice for a linear molecule (A_1-A_2), we will get the original i.e., $C_2^2 = E$ (Identity)

Examples: (i) H_2O molecule: It has C_2 axis of symmetry passes through oxygen atom in the plane of the paper.

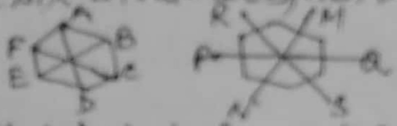


(ii) BF_3 molecule: It has C_3 axis passes through boron atom and is perpendicular to the plane of trigonal BF_3 molecule.



(iii) Benzene (C_6H_6): It has two main axis of rotation (a) C_6-axis of rotation perpendicular the plane of benzene molecule (along z-axis)

(b) C_2-axis of rotation lie in the plane of the benzene molecule, and these are six in numbers, viz AD, BE, CF, PQ, RS & MN.

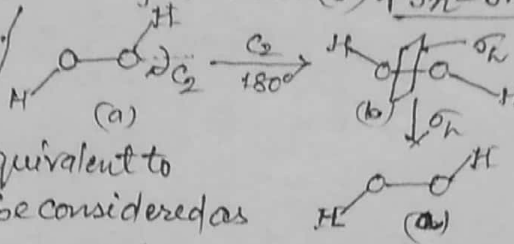


It can be noted that principal axis is C_6 axis (By conventions). C_6 axis of rotation performed twice to [redacted] give identical configuration of C_3-axis of rotation, i.e., $C_6^2 = C_3$

5. **Improper axis of Symmetry or Rotation-Reflection (S_n):** It is an imaginary axis, passing through the molecule, on which the molecule has to be rotated by $360°/n$ angle and then reflected on a plane perpendicular to the rotation axis to attain any equivalent orientation. It is represented by S_n, where n is the order of the axis. In other words, it is a process of rotation (C_n) followed by reflection in a plane perpendicular to the axis of rotation (σ). $\boxed{S_n = \sigma . C_n}$

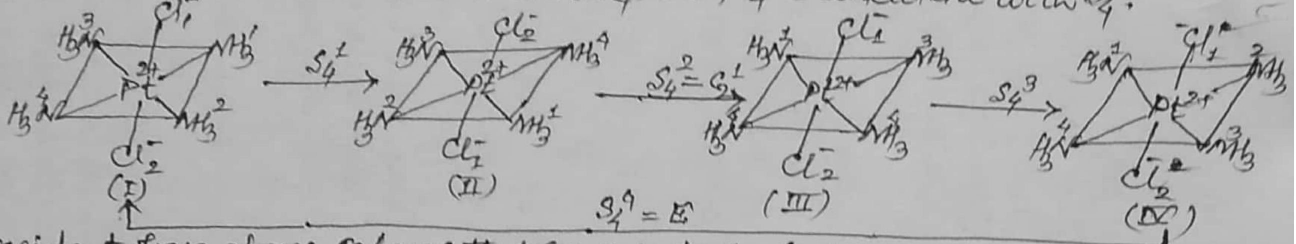
Examples: (i) H_2O_2: It has S_2 axis of rotation. $S_2 = C_2 + \sigma_h$

It is evident that S_2^2 on (a) gives the original orientation (a) and also S_2^1 operation on (a) is equivalent to inversion, i.e., $S_2^1 = i$. Hence, S_2^1 cannot be considered as a new operation.



In a molecule, an axis of improper rotation (S_n) may be concident with an axis of proper rotation (C_n). (a) $S_n^m = C_n^m \sigma_h$ (when m is odd) (b) $S_n^m = C_n^m \sigma_h^m$ (when m is even) $\sigma_h^m = E$ (identity) or, $S_n^m = C_n^m$. (c) $S_n^n = C_n^n \sigma^n = E . E = E$ (when $m = n$ = even)

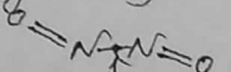
For example, a distorted octahedral trans complex, $[Pt(NH_3)_4Cl_2]$, the axis passing through Cl-Pt-Cl is C_n. The same axis is also S_4, i.e., C_4 is concident with S_4.



It is evident from above scheme that (a) Orientation (III) can be obtained by either performing S_4^2 on (I) or C_2^1 on (I). Hence, S_4^2 is not a new operation, i.e., $S_4^2 = C_2^1$ (b) on performing S_4^4 on (I) [four times S_4] we get (I) again. This is equivalent to identity (E), i.e., $S_4^4 = E$. (c) on S_4 axis, concident with C_4, new operations are S_4^1 and S_4^3 which give the equivalent orientations (II) & (IV) respectively.

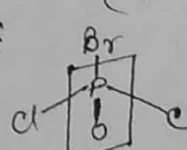
1.Q. Indicate symmetry elements in the following: (a) N_2O_2 (b) $POBrCl_2$ (c) PF_5 (d) NH_3

Ans. (a) N_2O_2: It has centre of symmetry (i)

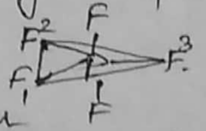


(inversion centre)

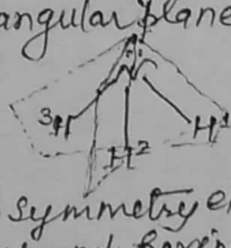
(b) $POBrCl_2$: It has plane of symmetry (σ_v). It consists of one σ_v passing through Br, P & O atoms and lying in zx plane.



(c) PF_5: It has improper axis of symmetry (S_3), since rotation by 120° ($= \frac{360°}{3}$) around axis perpendicular to triangular plane (PF_3) and reflection to it gives original configuration.



(d) NH_3: It is pyramidal molecule. It consists of three σ_v planes each passing through N-atom & one of the three H-atoms.



2.Q. How symmetry elements affect stereochemistry of compounds?

Ans. Compounds having centre of symmetry (i), plane of symmetry (σ) & improper axis of symmetry (S_n) do not show enantiomerism/optical activity as they are achiral. However, compounds having C_n axis of symmetry generally show enantiomerism/optical activity as they are chiral.

Unit-2 Symmetry in Chemisty

Groups / Point groups ?

Any Symmetry operation leaves a molecule physically unchanged and with the same orientation in space, its centre of mass must also remain fixed in space. Thus, all the axes and planes of symmetry of a molecule must intersect at least one common point. Such groups of symmetry elements are called point groups. Hence Point group is a collection of all symmetry operations that can be carried out on a molecule belonging to this group. e.g., H_2O belongs to C_{2v} group $[E, C_2, \sigma_{xz}, \sigma_{yz}]$.

Requirements / Conditions / Rules for Point groups / groups: Mathematically, a 'group' is a complete set of elements of symmetry, which must obey following rules/conditions:

1. The product of any two elements or square of an element should give the element which is also a member of the set (Group.) This is called closure property.
   i.e., $A \cdot B = C$ or $A \cdot C = B$; $A^2 = B$ or C [Here A, B, C are elements in the group,

Explanation: $A \cdot B$ (i.e, product of A&B) means that first operation A is carried (A, B, C) out on a molecule and then operation B is carried out on that molecule, and the product (Combination) of these two operations is equal to the operation C.

2. There must be one element in the group which commutes (i.e., $A \cdot B = B \cdot A$) with everyone of the other element and leaves it unchanged. The element is called identity (E), i.e., $A \cdot E = E \cdot A = A$

Explanation: If we perform identity (E) operation on a body and then A or viceversa, the result would be such that, only A operation were performed on the body.

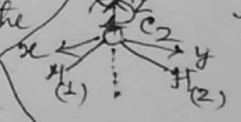
3. The combination/product of two or more elements of a group should satisfy the associative law; i.e; $A(BC) = (AB)C$.

Explanation: Result is the same, whether we perform A operation on a combination of B and C operations or a combination of A & B operations on C operation.

4. Every element of a group should have a reciprocal (inverse) and that reciprocal is also an element of the group. $A - A^{-1} = E$ (Identity)

Explanation: Inverse means performing operation in opposite direction, e.g. axis of rotation is performed in clockwise direction, hence its inverse will be performing it in anti-clockwise direction, must be equal to any other operation in the group.

Let us consider the symmetry elements of H_2O molecule. The symmetry elements in H_2O molecule are E, C_2, σ_{xz} & σ_{yz}. We know that the combination of two symmetry elements C_2 & σ_{xz} results into σ_{yz}. While product of C_2 & σ_{yz} is σ_{xz} and multiplication product of σ_{xz} & σ_{yz} is E and $C_2 \times C_2 = E$. It's clearly visible that the combination of two symmetry operations results in another symmetry operation. Symmetry operations of H_2O molecule form an abelian group as all the symmetry operations are commutable, i.e., $\sigma_{xz} \cdot C_2 = \sigma_{yz}$; $C_2 \cdot \sigma_{xz} = \sigma_{yz}$.



Identity operation present in all the molecules is commutable with all other operations and leaves them unchanged, e.g. $C_2 \cdot E = E \cdot C_2 = C_2$

Thus, the importance of identity operation can be seen in considering the molecule as a group. $C_2(\sigma_{xz} \cdot \sigma_{yz}) = (C_2 \cdot \sigma_{xz})\sigma_{yz}$.

Each operation in H_2O molecule is its own reciprocal, i.e., $C_2 \cdot C_2 = E$; $\sigma_{xz} \cdot \sigma_{xz} = E$; $\sigma_{yz} \cdot \sigma_{yz} = E$. It is evident from above facts, symmetry operations E, C_2, σ_{xz} & σ_{yz} form a group, i.e. Point group of H_2O is $[E, C_2, \sigma_{xz}, \sigma_{yz}]$.

Subgroup?

The number of elements of symmetry in a group is called the order of group (h). Subgroups are the smaller groups within a bigger group. The subgroup must satisfy all the rules/conditions to be called a group. The order of a subgroup must be sub-multiples of the order of the bigger group. If 'h' is the order of bigger group and 'k' is the order of subgroup, then h/k = an integer.

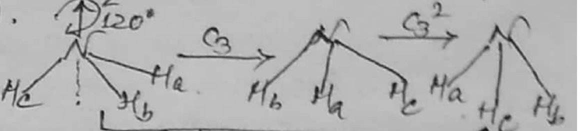
for example, In C_{2v} point group of H_2O, the symmetry elements are $E, C_2, \sigma_{xz}, \sigma_{yz}$. Hence, its order ($h$) = 4 (no. of elements in the group). Now, let us consider E & C_2 as the elements of a subgroup. Now applying conditions (1-4) for a group- (1) Closure property: $E \cdot C_2 = C_2$ & $C_2 \cdot C_2 = E$. (2) Identity: $E \cdot C_2 = C_2 \cdot E = C_2$ $\therefore$ E is the identity (3) Associative law: $(E \cdot C_2) C_2 = C_2 \cdot C_2 = E$ & $E \cdot (C_2 \cdot C_2) = E \cdot E = E$. Hence, $(E C_2) \cdot C_2 = E \cdot (C_2 \cdot C_2)$ holds. (4) Inverse: $C_2^{-1} = C_2$ & $E^{1} = E$.

$\therefore$ (E, C_2) form a group. This group (E, C_2) is called a subgroup of C_{2v} of order $(g) = 2$

Conjugate?

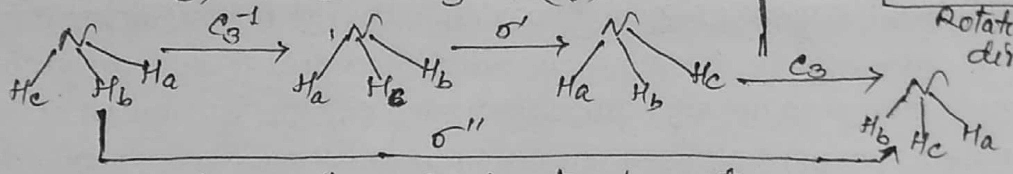
The symmetry elements of a group can be classified into smaller sets of classes. This is based on the similarity transformation given as: $B = [X^{-1}][A][X]$, where A, B & X are the elements of a group, and $[X^{-1}]$ is the reciprocal of $[X]$. If A & B are related by a similarity transformation, they are called '<u>conjugate</u>' elements.

for example, In NH_3 molecule, the z-axis is C_3 axis, and there are three reflection planes (σ' w.r.to N-H_a ; σ'' w.r.to N-H_b ; σ''' w.r.to N-H_c).



Rotation ~~by~~ anticlockwise direction by 120°c

Now let us find the similarity transform of σ' w.r.to C_3, i.e; $(C_3)^{-1} \cdot \sigma' \cdot C_3 = \sigma''$ (?)



Thus, σ' and σ'' are conjugate elements.

The following rules are important for <u>Conjugate</u> elements:-

1. Every element is conjugate to itself because every element is similarity transform of itself w.r.to identity (E). i.e., $E = E^{-1}$; $A = E^{-1} \cdot A \cdot E$.
2. If A is the conjugate of B, then B is the conjugate of A. This means that if A is the similarity transform of B by X, B is the similarity transform of A by X^{-1}.
3. If A is the conjugate of B and B is the conjugate of C, then A, B & C are mutually conjugate.

<u>class?</u> Mutually conjugate operations form a set called a '<u>class</u>'.

for example, NH_3 molecule: $C_3^3 = C_3^2 \cdot C_3 = E = (C_3)^{-1} \cdot C_3$. Hence, $C_3^2 = C_3^{-1}$

Now get similarity transform of σ' by C_3.

$$C_3^{-1} \cdot \sigma' C_3 = C_3^2 \cdot \sigma' C_3 = \sigma''$$

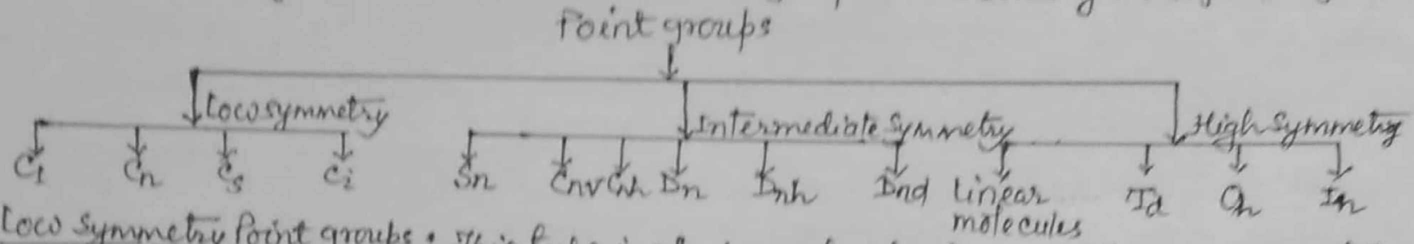
Thus, σ' & σ'' are conjugate. Similarly, we can show that σ', σ'' & σ''' are mutually conjugate. Therefore $\sigma', \sigma'', \sigma'''$ form a class.

It is to be noted that order of a group is an integral multiple of the member of element in a class of the group. In an abelian group, $A^{-1}XA = A^{-1}AX = X$. Each element is in a class of its own and the number of classes is the same as the order of the group.

The simplest way of arranging the operations of a symmetry group into classes is to arrange them into sets of equivalent operations. These sets will be classes

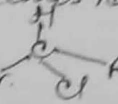
Classification of Point groups:

All the symmetry elements, necessary for a molecule to examine its geometry form a point group. Two molecules having a common set of symmetry elements/operations should belong to the same point group. Point groups can be broadly classified as follows:

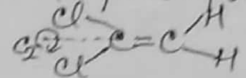


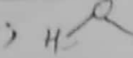
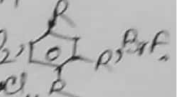
1. Low symmetry Point groups: This type includes molecules having either no symmetry element (except E) or only one characteristic element (C_n, i or σ).

(i) Group C_1: This group has only identity (E) or C_1. This group includes all molecules having one asymmetric atom (C, N, P, Si etc) e.g., Bromochlorofluoromethane.

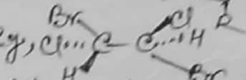


(ii) Group C_n: This point group has only one axis of symmetry (C_n) of order $n (n>1)$ and identity (E). The molecules belonging to this group possess a non-superimposable mirror image, called dissymmetric. e.g., 1,1-Dichloroethane.



(iii) Group C_s: This point group has symmetry elements σ (plane of sym.) and E. e.g.,  has molecular plane as the symmetry element. Other examples: SO_2, 

(iv) Group C_i: This group has only two elements E & i (Centre of symmetry). e.g.,



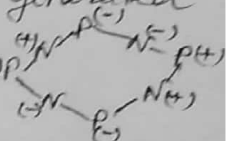
(Trans staggered)

C_1, C_s & C_i are Non-axial groups while C_n is axial group.

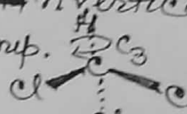
2. Intermediate Symmetry Point groups:

The presence of a C_n (n-fold axis of symmetry) associated with other symmetry elements (σ, C_2, i) is characteristic of this. The lowest symmetry groups are S_n (n = even) and the highest ones are D_{nh}. All are axial groups.

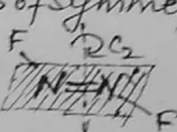
(i) Group S_n: This includes molecules having a S_n axis (rotation-reflection). Total number of operations generated by S_n = 2 (for n = even) / 2n (for n = odd). Operations generated by S_4 are S_4, C_2, S_4^3, E while S_3 are $S_3, C_3^2, \sigma, C_3, S_3^{-1}, E$. for example $(PNCl_2)_4$ has point group S_4. Here (+) sign indicates atom above the plane while (−) sign indicates atom below the plane of the paper.



(ii) Group C_{nv}: This group has molecules with an axis of symmetry (C_n), ~~and~~ n vertical planes and E as symmetry elements. e.g. Chloroform ($CHCl_3$) has C_{3v} point group. Symmetry elements of C_{3v} group are $E, C_3, C_3^2 = C_3^{-1}, \sigma_v, \sigma_v', \sigma_v''$ (2n elements i.e., 6)

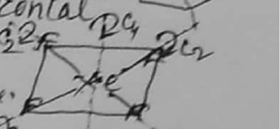


(iii) Group C_{nh}: This point group includes molecules having rotation axis of symmetry (C_n), one horizontal symmetry plane and identity (E). e.g. N_2F_2 (trans) has C_{2h} point group. When n is odd, the C_{nh} group is identical with the S_n group. So, the S_n groups are included only for molecules with 'n' even.

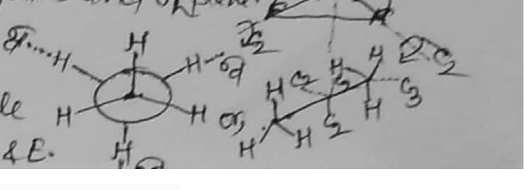


(iv) Group D_n: This point group includes molecules with a C_n rotation axis and n C_2 axis perpendicular to the C_n rotation axis. usually D_n elements are associated either with σ_h or σ_d mirror planes. e.g., $Cr(C_6H_{11})_2$ has D_6 point group.

(v) Group D_{nh}: This point group includes molecules with rotation axis of symmetry (C_n) along with n C_2 axis perpendicular to the C_n axis and a horizontal symmetry plane. e.g; Xenon tetrafluoride (XeF_4) has D_{4h} point group. Symmetry elements are C_4 axis, 4 C_2 axes perpendicular to C_4 axis and σ_h plane.



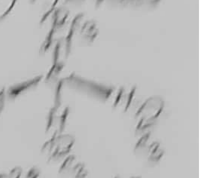
(vi) Group D_{nd}: This point group includes molecules with rotation axis C_n, n C_2 axes perpendicular to the C_n axis and n dihedral symmetry planes. e.g., staggered ethane molecule has D_{3d} point group, Symmetry operations: $2C_3, 3C_2, 3\sigma_d, i, 2S_6$ & E.



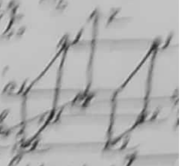
3: High Symmetry Points groups: This includes linear molecules or molecules related through their geometry to regular geometric bodies, such as the tetrahedron (T_d), the octahedron (O_h) or the icosahedron (I_h).

(i) Linear molecules: A linear molecule contains C_∞ rotation axis, as a small rotation about this axis will bring the molecule into coincidence with itself, hence $n = \frac{360°}{0°} = \infty$. There are two cases: (a) Linear molecules with a symmetry centre (A-A or A-B-A type) belong to $D_{\infty h}$ group. e.g. Cl-Cl, O=C=O etc. (b) Linear molecules devoid of a symmetry centre (A-B, X-Y-Z type), belong to $C_{\infty v}$ group. e.g., H-Cl, D-C≡C-H etc.

(ii) Group T_d: A system of four C_3 is characteristic of tetrahedron group (T_d). It has 24 elements [E, $8C_3$ (C_3 & C_3^2), $3C_2$, $6S_4$ (S_4, S_4^2) and $6\sigma_d$. for example, CH_4



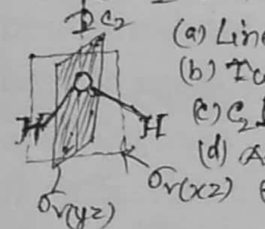
(iii) Group O_h: It is a characteristic system of three C_4 axis. This includes octahedral complexes & Cubane. The total number of symmetry operations involved is E, $8C_3$ (C_3 & C_3^2), $6C_4$ (C_4, C_4^2 & C_4^3), $6C_2$, $3C_2$ ($=C_4^2$); i, $6S_4$ {S_4, $S_4^2 = C_2$ & S_4^3}, $8S_6$ {S_6, S_6^2 (C_3), S_6^3 (i) ($S_6^4 \in C_3^2$) & S_6^5}, $3\sigma_h$ and $6\sigma_d$. eg. $[Fe(CN)_6]^{2-}$, CsCl crystal etc.



(iv) Group I_h: Characteristic to this group is the presence of $12C_5$ rotation axes. This includes icosahedron, dodecahedron structures. The total number of symmetry operations involved = 120 [E, $24C_5$ ($12C_5$, $12C_5^2$), $24S_{10}$ ($12S_{10}$, $12S_{10}^3$), $20C_3$ ($10C_3$, $10C_3^2$), $20S_6$, $15C_2$, 15σ & i. In icosahedron (I_h), a C_5 rotation axis passes through each of the 12 vertices.

Q. Check or Identify the point groups in the following: (i) H_2O (ii) NH_3 (iii) PCl_5 (iv) $[Co(NH_3)_4ClBr]$

Ans. (i) H_2O (water)

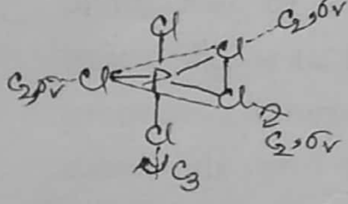


(a) Linear → No
(b) Two or more C_n → No.
(c) $C_2 \perp C_n(C_2)$ → No
(d) As principal axis is C_2 → $2\sigma_v$ Yes
(e) Point group - C_{2v}.

(ii) NH_3 (Ammonia)
(a) Linear → No
(b) 2 or more C_n → No (only one C_3)
(c) Any $C_2 \perp C_3$ → No
(d) $3\sigma_v$ → Yes
(e) Point group → C_{3v}

(one C_3 & $3\sigma_v$ each containing one N-H bond)

(iii) PCl_5 (Phosphorus pentachloride)



(a) Linear → No
(b) 2 or more C_n → No (only one C_3)
(c) $3C_2 \perp C_3$ → Yes
(d) σ_h → Yes
(e) D_{3h} - point group

(iv) $[Co(NH_3)_4ClBr]$
(a) Linear → No
(b) 2 or more C_n → No (only one C_4)
(c) Any $C_2 \perp C_4$ → No
(d) $4\sigma_v$ → Yes
(e) Point group - C_{4v}.

(All σ_v containing C_4)

Multiplication Table for Point groups C_{2v} & C_{3v}:

The combinations of symmetry elements can be represented in the form of table called multiplication table. In the multiplication table, all combinations of symmetry elements possible are shown by writting the one symmetry operation at the left of each row and at the head of each column.

M. Table of C_{2v}: → Let us consider water (H_2O) molecule, which has C_{2v} point group. The point group C_{2v} has the following operations: E, C_2, $\sigma_{v(xz)}$ and $\sigma_{v(yz)}$. The multiplication table for C_{2v} point group is shown below:

This multiplication table has four rows and four columns involving a total number of 16 combinations.

For any molecule, two symmetry operations are performed one after other

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
E	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$
C_2	C_2	E	$\sigma_v(yz)$	$\sigma_v(xz)$
$\sigma_v(xz)$	$\sigma_v(xz)$	$\sigma_v(yz)$	E	C_2
$\sigma_v(yz)$	$\sigma_v(yz)$	$\sigma_v(xz)$	C_2	E

the result will be the same as that obtained on performing one single operation, which means that two symmetry operations may be combined/multiplied to give a third symmetry operation. for example, in H_2O molecule, the symmetry operation C_2 is followed by symmetry operation $\sigma_v(xz)$, the result is the same as that of the single operation $\sigma_v(yz)$. The combination of symmetry operation $C_2 \cdot \sigma_v(xz) \cdot \sigma_v(yz)$ indicates $\sigma_v(yz)$ operation followed by $\sigma_v(xz)$ followed by C_2 means the sequence of symmetry operations is right to left.

<u>Multiplication table for C_{3v}</u>: Let us consider, ammonia (NH_3) molecule, which has C_{3v} point group. The point group C_{3v} has the following symmetry ~~operations~~/elements: E, C_3, σ_v, σ_v', σ_v'', and the symmetry operations involved are E, C_3, C_3^2, σ_v, σ_v', σ_v''. In this case, larger multiplication table obtained since more symmetry operations (6) are there (i.e, NH_3 molecule). There are altogether 36 combinations from 6 rows & 6 columns in the multiplication table of C_{3v} as shown below:

C_{3v}	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
E	E	C_3	C_3^2	σ_v	σ_v'	σ_v''
C_3	C_3	C_3^2	E	σ_v''	σ_v	σ_v'
C_3^2	C_3^2	E	C_3	σ_v'	σ_v''	σ_v
σ_v	σ_v	σ_v'	σ_v''	E	C_3	C_3^2
σ_v'	σ_v'	σ_v''	σ_v'	C_3^2	E	C_3
σ_v''	σ_v''	σ_v	σ_v	C_3	C_3^2	E

Here E = Identity, C_2 = axis of symmetry/rotation passing through O atom, $\sigma_v(xz)$, $\sigma_v(yz)$ = reflection planes containing one O-H bond each, C_3 = axis of symmetry/rotational axis passing through N atom, σ_v', σ'', σ = reflection planes containing one N-H bond each, $C_3^2 = C_3$-operation duplicated (twice again repeated).

M.Sc Semester-II; CC-6 (Inorganic Chem)

Unit-5: Metal Carbonyls

(By Dr. Birendra Kumar, Deptt. of Chem., Maharaja College, Ara.)

Coordination compounds in which carbonmonoxide (CO) molecules (Carbonyl), a π-acceptor ligand are bonded directly or substantially (bridged) with transition metals in lower oxidation states (mainly ~~0~~ (zero), but sometimes low positive or negative) are called metal carbonyls. Metal carbonyls agree to the effective atomic no. rule, except $[V(CO)_6]$. e.g. $[Fe(CO)_5]$, $[Rh(CO)_8]$, $[Os_3(CO)_{12}]$ etc.

Classification of metal Carbonyl Compounds: Metal carbonyls, $[M_y(CO)_x]$ are classified into three types, depending on the number of metal atom(s) per molecule.

1. **Mononuclear Carbonyls:** Metal carbonyls, $[M(CO)_x]$ containing only one metal atom per molecule are called mononuclear carbonyls. Transition metals which have an even atomic number and zero oxidation state form such carbonyls. e.g. $[Os(CO)_5]$, $[Fe(CO)_5]$, $[Cr(CO)_6]$, $[Mo(CO)_6]$, $[Ni(CO)_4]$ etc $[W(CO)_6]$ or $[Ru(CO)_5]$
2. **Dinuclear Carbonyls:** Metal carbonyls, containing two metal atoms per molecule directly linked and CO (carbonyl) groups bonded to terminal metal atoms with coordinate bonds are called dinuclear carbonyls. They may be homotype, e.g. $[Fe_2(CO)_9]$, $[Co_2(CO)_8]$, $[Rh_2(CO)_8]$ etc or heterotype, e.g. $[MnCo(CO)_9]$, $[MnRe(CO)_{10}]$ etc.
3. **Polynuclear Carbonyls:** Metal carbonyls, $[M_y(CO)_x]$ containing more than two metal atoms per molecule are called polynuclear carbonyls. Here CO (carbonyl) groups linked with metal in terminal as well as bridge positions. e.g. $[Os_3(CO)_{12}]$, $[Os_4(CO)_{12}]$, $[Co_4(CO)_{12}]$, $[Fe_3(CO)_{12}]$

Methods of Preparation: A number of methods used for preparation of metal carbonyls.

1. Mono or dinuclear metal carbonyls are generally prepared by direct interaction of finely divided metal and CO(g) at suitable temperature.

e.g., $Ni + 4CO(g) \xrightarrow[(1\,Atm)]{Room\ Temp.} [Ni(CO)_4]$, $Fe + 5CO \xrightarrow[100\,Atm]{200^\circ C} [Fe(CO)_5]$

$2Co + 8CO(g) \xrightarrow[(100\,Atm)]{200^\circ C} [Co_2(CO)_8]$,

2. Polynuclear metal carbonyls are prepared by photo or thermal decomposition of mono or dinuclear metal carbonyls.

e.g., $2[Os(CO)_5] \xrightarrow{h\nu} [Os_2(CO)_9] + CO$

$2[Fe(CO)_5] \xrightarrow[CH_3COOH/\Delta]{Glacial} [Fe_2(CO)_9] \longrightarrow [Fe_3(CO)_{12}]$

3. Heteronuclear metal carbonyls are prepared by interaction of two different carbonyl complexes e.g. $Na[Mn(CO)_5] + [Re(CO)_5]Cl \longrightarrow [(OC)_5Mn\text{-}Re(CO)_5] + NaCl$.

Structure & Bonding of Metal Carbonyls: The structure of monocarbonyls, e.g. $[Ni(CO)_4]$, $[Fe(CO)_5]$ etc have been studied by X-ray diffraction, Infrared spectroscopy, Electron diffraction methods. All the monocarbonyls, $[M(CO)_x]$ have linear M-CO bonds. Hexacarbonyl, $[M(CO)_6]$ have octahedral shape (d^2sp^3 hybridised), $[M(CO)_5]$ trigonal bipyramid (dsp^3 hybridised), $[M(CO)_4]$ tetrahedral shape (sp^3 hybridised).

$C\equiv O$ (Carbonyl gr.) → Vacant π antibonding orbital $\xleftarrow{\pi\text{-acceptor}}$ Filled metal d-orbital.

$C\equiv O$ (Carbonyl gr.) → Filled bonding orbital $\xrightarrow{\sigma\text{-donating}}$ Empty metal d-orbital

Here $C\equiv O$ (Carbonyl) behaves as π-acceptor ligand. The carbonyls are highly stable at low oxidation state. Molecular orbital electronic configuration of CO:

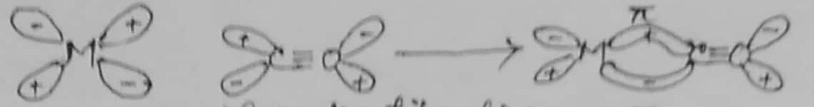
$(\sigma sp)^2, (\sigma^*_{sp})^2, (\pi^b_y)^2 = (\pi^b_z)^2, (\sigma sp)^2, (\pi^*_y)^0 = (\pi^*_z)^0, (\sigma^*_{sp})^0$

Formation of Metal-Ligand σ-bond:

(Vacant d-orbital) Filled bonding orbital (M $\xleftarrow{\sigma}$ CO bond)

In the formation of M $\xleftarrow{\sigma}$ CO bond, empty hybrid orbital of metal atom overlap with the filled (sp) hybrid orbital on C-atom of CO molecule. In the formation of this bond, metal atom acts as an electron pair acceptor while CO acts as an electron pair donor.

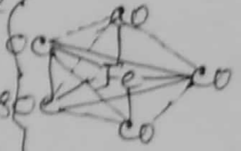
Formation of metal-ligand π-bond:



Filled metal d-orbital
Vacant antibonding (π^*) Orbital (lower energy)
M $\xrightarrow{\pi}$ C≡O

In the formation of M $\xrightarrow{\pi}$ C bond, filled d-orbital of metal overlap with empty π-antibonding orbitals (π_x^* or π_y^*) on C-atom of carbonyl (CO) ligand. This bonding mechanism is synergic, since the transfe of metal electrons into -C≡O gr. (ligand) will tend to make, as a whole, negative and hence to enhance its basicity via the σ-orbital of C-atom. At the same time the transfer of electrons to the metal in the σ-bond tends to make, ~~as a whole, negative~~ the carbonyl ligand positive, thus increasing the acceptor strength of the π-orbital of ligand. The effect of σ-bond formation strengthens the π-bonding and vice-versa i.e., electroneutrality in the molecule.

18-e rule: Total number of electrons in outermost orbital of metal atom and electrons donated by ligand (CO molecule) is always 18 in metal carbonyls. Such carbonyls are more stable. This is called 18-electron rule.



e.g., $[Fe(CO)_5]$: It is triangular bipyramid structure, and Fe-atom is dsp^3 hybridised. No. of electrons in outermost orbit of Fe = 8

No. of electrons donated by 5CO (ligand molecules) = 5×2 = 10.

Total number of electrons on Fe in metal carbonyl formation = 8+10 = 18.

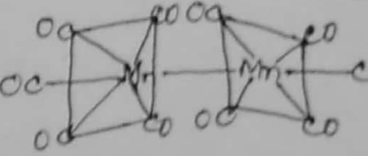
Thus, the metal carbonyl $[Fe(CO)_5]$ follows 18-e rule, and hence stable.

Structure of Polynuclear metal Carbonyls: In polynuclear carbonyls, there are M-M bonds, but in many metal carbonyls bridging carbonyl groups of several types are found.

Case-I When there is direct M-M bond and each metal is bonded to terminal CO groups by coordinate bond (M ← C≡O). e.g., $[Mn_2(CO)_{10}]$, $[Fe_2(CO)_{10}]$, $[Tc_2(CO)_{10}]$ e

Let us consider $[Mn_2(CO)_{10}]$, it has D_{4d} Symmetry.

Two Mn-atoms are directly bonded by σ bond and five CO (ligand) bonded (terminal) to each metal atom.



$[Mn_2(CO)_{10}]$
(D_{4h} Symmetry)

Here, valence electrons of Mn(0), $3d^5 4s^2$ = 7

No. of electrons donated by 5CO (ligand) = 5×2 = 10

Electron from M-M bond = 1.

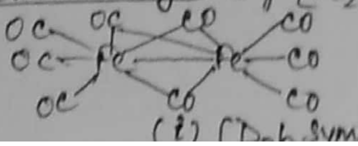
Total numbers of electrons on each Mn = 7+10+1 = 18 (stable)

It is diamagnetic nature.

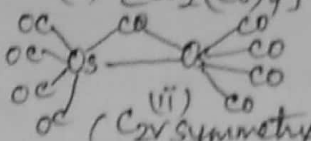
Case-II When both terminal and bridging carbonyl groups are present. The bridging Carbonyl attached to metal by $\overset{M}{\underset{M}{|}}$ C=O. Terminal carbonyl group by M ← C≡O.

e.g. $[Fe_2(CO)_9]$, $[Os(CO)_9]$, $[Co_2(CO)_8]$, $[M_3(CO)_{12}]$, $[M_4(CO)_{12}]$, $[M_5(CO)_{16}]$ etc.

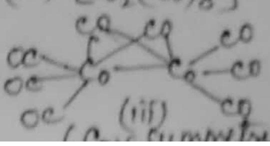
Binuclear Carbonyls: e.g. (i) $[Fe_2(CO)_9]$ (ii) $[Os_2(CO)_9]$ (iii) $[Co_2(CO)_8]$



(i) (D_{3h} Symmetry)

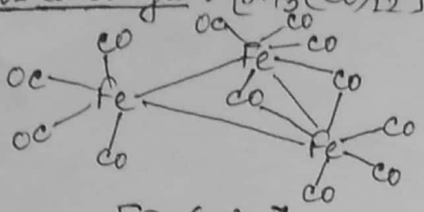


(ii) (C_{2v} Symmetry)

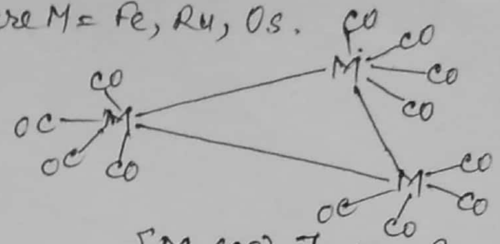


(iii) ([illegible] Symmetry)

Trinuclear Carbonyls: $[M_3(CO)_{12}]$ type, where M = Fe, Ru, Os.

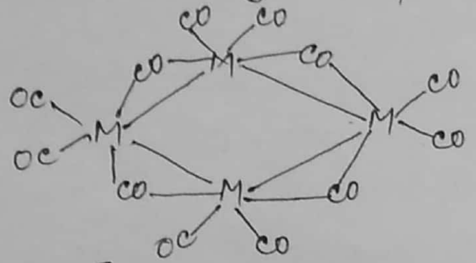


$[Fe_3(CO)_{12}]$
(C2v Symmetry)

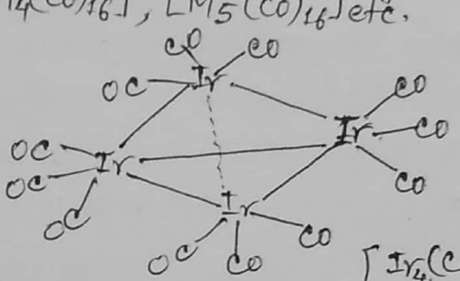


$[M_3(CO)_{12}]$; M = Ru or Os.
No bridging carbonyls.
(D_2h symmetry)

Polynuclear Carbonyls: (i) $[M_4(CO)_{12}]$ (ii) $[M_4(CO)_{16}]$, $[M_5(CO)_{16}]$ etc.

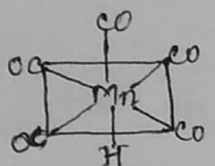


$[M_4(CO)_{12}]$; M = Co or Rh
(C3v Symmetry)

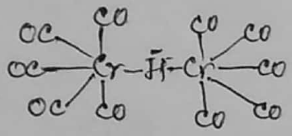


$[Ir_4(CO)_{12}]$
No bridging carbonyl gr.
(Td Symmetry)

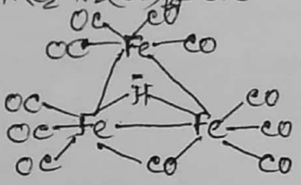
Heteronuclear Carbonyls: A number of heteronuclear carbonyl are also known e.g. $[HMn(CO)_5]$, $[HFe(CO)_4]$, $[HCr_2(CO)_{10}]^-$, $[HFe_2(CO)_8]^-$, $[HFe_3(CO)_{11}]^-$, $[HRe_2Mn(CO)_{14}]$ etc.



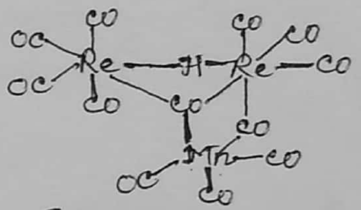
$[HMn(CO)_5]$



$[HCr_2(CO)_{10}]^-$



$[HFe_3(CO)_{11}]^-$



$[HRe_2Mn(CO)_{14}]$

Vibrational spectra of carbonyl compounds: The vibrational spectra of metal carbonyls is a convenient and effective technique for explaining their structure and bonding.

The carbonyl stretching frequency appears as sharp and intense band at a region 1700–2200 cm⁻¹. This technique used in the study of carbonyl compounds in three ways:

1. The range of frequencies for absorption. 2 The number of vibrational bands
3. The relative intensities of the bands.

In the mononuclear carbonyls, all the $[M(CO)_x]$ have linear M-CO bonds. Hexa carbonyls, e.g $[Cr(CO)_6]$ have octahedral shapes, pentacarbonyls, e.g $[Fe(CO)_5]$ - trigonal bipyramidal/square pyramidal shape and tetracarbonyls, e.g. $[Ni(CO)_4]$ tetrahedral shape. For a tetrahedral carbonyl, $M(CO)_4$, group theory predicts only one Infrared active (F_2) and two Raman active CO stretching vibrations (A_1 & F_2)

Two types of vibrations are possible: (i) $C\equiv O$ stretching vibration (ii) M-C stretching vibration. In polynuclear carbonyls, bridging $C=O$ gr. present.

(i) <u>$C\equiv O$ stretching vibration</u>: Terminal and bridging carbonyl groups can be identified by the range of frequencies observed. In terminal carbonyl (CO) groups, absorption occur in the range of 1850-2125 cm^{-1} while in bridging carbonyl (CO) groups in the region 1700-1860 cm^{-1}. Free carbonyl ($-C\equiv O$) absorbs at 2143 cm^{-1}, and the carbonyl group ($-\overset{O}{C}-$) present in ketones (R_2CO) absorbs in the range 1715 ± 10 cm^{-1}. When some of the carbonyl groups in a ~~metal~~ carbonyl compds are replaced by ~~atom~~ donor ligands with low or negligible π-acceptor/in the presence of a negative charge on the metal atom, the back donation from metal to carbon would be enhanced, therefore, a lowering in C-O bond order. The position of the carbonyl absorption (ν_{CO}) indicates bond order between C & O. Upon donation of the CO: lone pair to a metal atom, there should be an increase in the ν_{CO} as the lone pair on C-atom in CO ligand is present in slightly anti-bonding orbital. $\overset{\delta-}{M} \leftarrow \overset{\delta+}{C}\equiv O \rightleftharpoons M=C=O$

ν_{CO} of some of the metal carbonyls are as follows:-

$[Cr(CO)_6]$: 2100, 2000, 1985 cm^{-1}; $[V(CO)_6]^-$: 1800 cm^{-1}; $[M(CO)_6]^+$: 2090 cm^{-1}; $[Ti(CO)_6]^{2-}$: 1748 cm^{-1}; $[Ni(CO)_4]$: 2060 cm^{-1}; $[Co(CO)_4]^-$: 1890 cm^{-1}; $[Fe(CO)_4]^{2-}$: 1790 cm^{-1}

The decrease in ν_{CO} (stretching frequency of CO) of hexacarbonyls is in the order- $[Mn(CO)_6]^+ > [Cr(CO)_6] > [V(CO)_6]^- > [Ti(CO)_6]^{2-}$, and tetracarbonyls is in the order: $[Ni(CO)_4] > [Co(CO)_4]^- > [Fe(CO)_4]^{2-}$.

A decrease in the C-O bond order will cause a decrease in the C-O stretching vibration (ν_{CO}) frequency, hence the stretching vibration frequency of C-O bond gives a qualitative measure of bond strength, with the stronger bonds gives vibrational absorptions at higher frequencies. With the increase in extent of M-C back bonding, the C-O stretching frequencies shifts to lower frequency values. In the presence of a negative charge on the metal atom the back donation of π-electrons from metal to carbon of CO ligand would be increa and hence a decrease in the C-O bond order is found. The greater, the positive cha on metal atom, the less readily the metal can transfer electron density into π-antibonding orbital of the carbonyl ligands to weaken the C-O bond stretchi

(ii) <u>M-C stretching vibration</u>: metal-carbon (M-C) stretching vibration frequency ($\tilde{\nu}_{M-C}$) fall in the range 600-300 cm^{-1}. With the increase in the back donation of π-electrons from the metal to the CO (carbonyl) groups, the M-C stretching vibration frequency ($\tilde{\nu}_{M-C}$) increases. The order of M-C stretching force constant is in the order: $[W(CO)_6] > [Cr(CO)_6] > [Mo(CO)_6]$.

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Unit-4 Transition metal nitrosyls:

Compounds containing NO (nitrosyl gr.) as ligand, i.e; M–NO linkage are usually called metal nitrosyl complexes. They are metal-π complexes, and generally formed by transition metals. In most nitrosyl complexes, NO^+ (Nitrosonium ion) present, which forms an $M \xleftarrow{\pi} N$ bond by transferring 3 electrons to transition metal (M). A few complexes containing only nitrosyl (NO) as ligands, e.g; $[Co(NO)_3]$ $[Fe(NO)_4]$ etc. But many mixed carbonyl/halide/thio/cyano-nitrosyl complexes are known e.g. [Mn(CO), $[Mo(NO^+)_2Cl_2]$, $Na[Fe(NO^+)_2S]$, $[Co(NO^+)(NH_3)_5]^{2+}$, $[Fe(NO^+)(CN)_5]$, $[Ru(NO^+)Cl_5]^{2-}$ etc.

Preparation: Metal nitrosyl complexes are prepared by a number of methods:

1. From metal carbonyl: (i) When metal carbonyl is treated with NO (nitric oxide) gas at lower temp. ≃ 90°C, carbonyl nitrosyl complexes are formed.

e.g; $[Fe(CO)_5] + NO \xrightarrow{95^\circ C} [Fe(CO)_2(NO)_2] + 3CO$; $[Fe_3(CO)_{12}] + 6NO \xrightarrow{95^\circ C} 3[Fe(CO)_2(NO)_2] + 6CO\uparrow$

$$[Co_2(CO)_8] + 2NO \longrightarrow 2[Co(CO)_3NO] + 2CO\uparrow$$

(ii) Recently, carbonyl-nitrosyl complexes prepared from metal carbonyl by treatment with nitrosonium salts (e.g; NO^+Cl^-) or nitrites.

e.g. $[Mn(CO)_5]^- + NO^+Cl \longrightarrow [Mn(CO)_4NO] + Cl^- + CO\uparrow$

$[Co(CO)_4]^- +$ [illegible] $NO_2^- + 2CO_2 + H_2O \longrightarrow [Co(NO)(CO)_3] + 2$ [illegible] $HCO_3 + CO\uparrow$

2. From metal halides: When metal halides is treated with nitric oxide (NO) in the presence of a suitable metal (as halogen acceptor), e.g. Zn, Co, Fe etc, metal nitrosyl halides are formed. $2NiI_2 +$ [illegible] $Zn + 8NO \longrightarrow 2[Ni(NO)_3I] +$ [illegible] ZnI_2.

3. Specific method: Sodium nitroprusside is prepared by treating sodium hexacyanoferrate(II) with conc. nitric acid or sodium nitrite.

$$Na_2[Fe(CN)_6] + 4H^+ + NO_3^- \longrightarrow [Fe(CN)_5NO] + CO_2 + NH_4^+$$

Important Reactions: Nitrosyl complexes show following reactions:

1- Substitution reactions: Metal carbonyl-nitrosyl complexes, NO^+ (ligand) are more firmly bonded than carbonyl (CO) ligands. When such complexes treated with ligands like phenthroline, PR_3, CNR etc, only CO ligands are substituted giving substituted complexes.

e.g., $[Fe(CO)_2(NO)_2] + Phen \longrightarrow [Fe(phen)(NO)_2] + 2CO\uparrow$

2 Formation of Roussin's salts: metal nitrosyl halide reacts with potassium sulphide (K_2S) and chloromethane (CH_3Cl), a dark red colour compound, $K_2[Fe(NO)_2S]_2$ & $[Fe(NO)_2(SCH_3)]_2$ called Roussin's salt, formed.

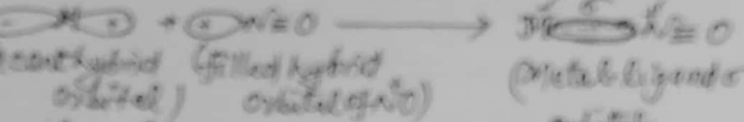
e.g. $[Fe(NO)_2I]_2 + K_2S + CH_3Cl \longrightarrow K_2[Fe(NO)_2S]_2 + [Fe(NO)_2(SCH_3)]_2$

Structure & Bonding: Most nitrosyl ligands appear to be linear (N≡O), consistent with the sp hybridisation of N-atom. A few cases of bridging & bent NO ligand (NO^-) are known. A bent nitrosyl is an analogue of an organic nitroso (NO) group in CH_3–N=O, where the N atom can be sp^2 hybridised with a lone pair. Due to presence of lone pair, nitrosyl group is bent. A linear nitrosyl ligand ($M-\overset{+}{N}\equiv O$) is regarded as a three-electron donor and a bent nitrosyl (NO^-) as a one electron donor. Linear nitrosyl includes the non-bonding electron pair on N atom and the unpaired antibonding electron in NO molecule.

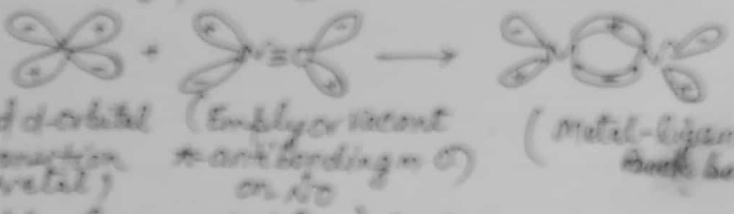
$$\underset{\text{(Transition metal)}}{M} + \underset{\text{(Nitrosyl)}}{:N\equiv O:} \longrightarrow M^- - \overset{+}{N}\equiv O: \longleftrightarrow M = \overset{+}{N} = \ddot{O}$$

In oxidation state method, the ligand is viewed as a coordinated nitrosyl (cation) when linear and a coordinated NO^- when bent, two electrons donor in both cases.

On the basis of MOT, the hybrid orbital on nitrogen containing a lone pair, i.e., [illegible] overlaps with the suitable vacant hybrid orbital on M^- ions to form $ON \rightarrow M$ σ-bond.



Now, the empty π_z^* or π_y^* (anti-bonding π orbitals [redacted]) molecular orbitals can overlap with the filled d-orbitals to form $M \rightarrow NO$ π-bond, i.e., back bonding transfers some electronic charge/cloud from M to NO ions.



The NO vibration frequencies ($\bar{\nu}_{NO}$) for linear M–NO groups verify the idea of extensive metal to nitrogen π-bonding leading to appreciable population of NO π* orbitals. The Infrared frequency bands in the range 1800–1900 cm⁻¹ characteristic of linear MNO groups in the metal nitrosyl complexes having zero/small charge.

In linear metal nitrosyls, there is short M–N bond (173.5 pm) indicating appreciable π-bonding as seen in metal carbonyls. In the bent metal nitrosyls, a relatively long, essentially σ-only M–N bond (185.9 pm) is present. It should be expected that the N–O bond of a bent nitrosyl would be longer than of a linear nitrosyl.

Cobalt nitrosyl [$Co(NO)_3$] shows two N–O stretching frequencies ($\bar{\nu}_{NO}$). It must be pyramidal rather than planar but the detailed structure not known. However, $[Co(NH_3)_5NO]X_2$ contains nitrosyl as NO^- (bent) shown by a very low N–O stretching frequency of 1170 cm⁻¹ and a long N–O bond

Dinitrogen complexes/Nitrogenyl Complexes

Molecular nitrogen (N_2) is isoelectronic with both CO & NO^+ (14e), however, the numerous complexes of CO & NO^+ as ligands are known but N_2 cannot form any complex easily. The difference in behaviour was usually attributed to the lack of polarity of N_2 ($\mu = 0$) and a resultant inability to behave as a π-acceptor.

Allen & Senoff (1965) first reported dinitrogen complex, $[Ru(NH_3)_5N_2]^{2+}$. We prepare

Preparation: the complex by following methods/reactions.

1. By reaction of $[Ru(NH_3)_5H_2O]^{3+}$ with sodium azide (NaN_3).

$$[Ru(NH_3)_5(H_2O)]^{3+} + NaN_3 \longrightarrow [Ru(NH_3)_5N_3]^{2+} \longrightarrow [Ru(NH_3)_5N_2]^{2+} + \tfrac{1}{2}N_2$$

Aquapentaammine ruthenium(III) — Azidopentaammine ruthenium(III) — Pentaammine dinitrogen ruthenium(II)

2. Reaction of aqueous ruthenium chloride with zinc in ammonia.

$$RuCl_3 + NH_3 + Zn \xrightarrow[ZnCl_2]{[redacted]} [Ru(NH_3)_5Cl]^{2+} \xrightarrow{H_2O} [Ru(NH_3)_5H_2O]^{2+} \xrightarrow{N_2} [Ru(NH_3)_5N_2]^{2+}$$

3. Direct method: Dinitrogen complexes are conveniently prepared by treating N₂ with metal complexes at atmospheric pressure. e.g., $[Co(acac)_3] + 3PPh_3 + N_2 \xrightarrow{Al(C_2H_5)_3} [Co(H)(N_2)(PPh_3)_3]$

$$[Co(H_3)(Ph_3P)_3] + N_2 \xrightarrow{C_6H_6} [Co(H)(N_2)(Ph_3P)_3]$$

4. Bridged dinitrogen complexes can be prepared by the displacement of water which shows donor properties of coordinated N_2.

e.g. $[Ru(NH_3)_5N_2]^{2+} + [Ru(NH_3)_5H_2O]^{2+} \longrightarrow [(NH_3)_5Ru{-}N_2{-}Ru(NH_3)_5]^{4+} + H_2O$.

Properties: 1. Dinitrogen complexes of heavier members/high atomic masses (gr. 8&9) are most stable. Some of them are unaffected by dry air (O_2) and can be heated to 100–200°C ~~before~~ without thermal decomposition. Most dinitrogen complexes are ~~readily~~ rapidly oxidised by air and decomposed when heated gently.

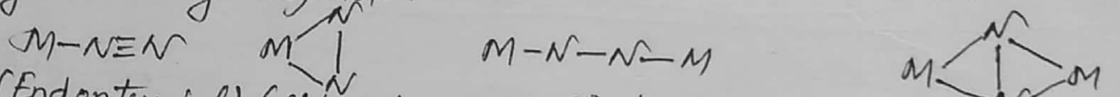
2. **Displacement/substitution reactions:** Coordinated N_2 of dinitrogen complexes can be easily displaced by other ligands. e.g. $[Ir(PPh_3)_2Cl N_2] + PPh_3 \longrightarrow [(Ph_3P)_3IrCl] + N_2\uparrow$

$[Ir(PPh_3)_2N_2Cl] + CO \longrightarrow [(PPh_3)_2Ir(CO)Cl] + N_2\uparrow$

$[Ir(PPh_3)_2Cl N_2] + HCl \longrightarrow [(PPh_3)_2IrHCl_2] + N_2\uparrow$

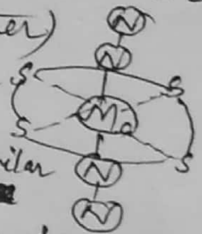
It is noted that displacement of N_2 by hydrogen (H_2), ethene (C_2H_4) or ammonia (NH_3) is reversible while that of by CO (stronger ligand) is irreversible.

Structure & bonding: There are two structural possibilities each for terminal and bridged dinitrogen ligands.



(End on terminal) (side on terminal) (End on bridging) (Side on bridging)

An X-ray study of Ru-N_2 complex revealed that the nature of Ru-N≡N linkage was end-on but disorder in crystal prevented accurate determination of bond lengths. Since then, structures of many other dinitrogen complexes have been determined. The results for the complex (bis dinitrogen crown thio ether) are typical and show that nitrogen resembles very much with CO in its bonding to metals. Back donation of electron density from the metal into antibonding π-orbitals of N_2 to form short Mo-N bond more similar [redacted] to Mo-CO bond than Mo-NH_3 bond. The mean N-N bond length (110.7 pm) is slightly greater than that found in N_2 (i.e. N≡N), suggested a weakening of the N≡N [redacted] bond because donation of electron density into the antibonding π-orbitals of N_2 takes place. The Raman stretching frequency of free N_2 gas is 2331 cm^{-1}. upon coordination, this vibration becomes IR active and shifts to lower frequency. for example, strong N-N stretching frequency bands appear at 2105 cm^{-1} for $[Ru(NH_3)_5N_2]Cl_2$ and 1953 & 1890 cm^{-1} for trans $[Mo(N_2)_2Me_8[16]aneS_4]$. The terminal type N_2 ligands have strong IR bands in the range 1930–2230 cm^{-1} (100–400 cm^{-1} below that of free nitrogen 2331 cm^{-1}). These bands may be used diagnostically.



When nitrogen function as a bridging ligand, it usually shows end-on coordination which is observed in diruthenium complex. The Raman spectrum of this complex, $[Ru(NH_3)_5(N_2)]$ has a strong line at 2100 cm^{-1} suggestive of a linear $Ru^{2+}-N\equiv N-Ru^{2+}$ rather than a bent $Ru^{3+}-N\equiv N-Ru^{3+}$ structure.

Bridging side-on complexes are also known recently. In the samarium complex obtained from the reaction of $[Sm(C_5Me_5)_2]$ & N_2, the two Sm-atoms & two N_2-atoms are in a planar arrangement. The Sm-N bond distance (108.8 pm) is even shorter than that found in free nitrogen (N≡N).