

Unit-II Magnetochemistry: Spin-orbit Coupling & Term Symbol.

L-S/Russel Saunders/Spin-orbit Coupling?

In spectroscopy, Russel-Saunders (L-S) Coupling specifies a coupling scheme of electronic spin and orbital angular momentum. It is useful mainly for the higher atoms roughly for atoms with atomic number less than 57. For light atoms, the spin-orbit interaction or coupling is small so that the total/resultant orbital angular momentum (L) and total/resultant spin angular momentum (S) are good quantum numbers. The interaction between L & S is known as L-S Coupling or Russel-Saunders Coupling. The main points of L-S Coupling scheme are:

1. The S term is one with maximum spin multiplicity (2S+1) or, maximum number of unpaired electrons.
2. If there are more than one term with same multiplicity ground state term will be one with lowest L value.
3. The lowest energy term (ground state) will be one with highest spin multiplicity.
4. For half filled/more than half filled, ground state term symbol will be of high J value (i.e., |L+S|). For less than half filled, the ground state term symbol will be of low J value (i.e., |L-S|).

Russel-Saunders Symbol or Term?

It is an abbreviated description of the total angular momentum quantum numbers in a multi-electronic system. However, even a single electron can be described by a term symbol. The Russel-Saunders Symbol or Term of a given system is represented as  $(2S+1)L_J$ , where S = Total/Resultant spin angular momentum quantum no. ( $\sum m_s, m_s = \text{spin} \times n$ );  $2S+1$  = Spin multiplicity; L = Total/Resultant orbital angular momentum quantum no. =  $\sum m_l$  ( $m_l = \text{magnetic quantum no.}$ ); J = Total/Resultant angular momentum = |L+S| to |L-S|.

- \* Ground state term symbol for less than half filled orbital =  $2S+1 L_{J_{min}}$  (e.g.,  $1G_4$ )
- \* Ground state term symbol for half/more than half filled orbital =  $2S+1 L_{J_{max}}$  (e.g.,  $1G_2$ )

Determination of Russel-Saunders Terms/Symbols:

The determination of Russel-Saunders terms for a given system involves following steps:

1. First of all electronic configuration (outer) of given system is shown in box representation according to Hund's rule. e.g.,  $d^3$  Conf. as  $\begin{array}{|c|c|c|} \hline \uparrow & \uparrow & \uparrow \\ \hline \end{array}$
2. The total/resultant spin angular momentum quantum no. (S) is known by  $\sum m_s$  (where  $m_s$  = spin quantum no., generally unpaired electrons are taken consideration). S arises due to  $s-s$  coupling (i.e., spinning motion of electron in orbital).  $m_s = +\frac{1}{2}$  for clockwise spins ( $\uparrow$ ) and  $m_s = -\frac{1}{2}$  for anticlockwise spins ( $\downarrow$ ).
3. Then spin multiplicity is known by  $(2S+1)$ . e.g., for  $d^3$  system,  $S = 3 \times (\frac{1}{2}) = \frac{3}{2}$   
 Spin multiplicity =  $2S+1 = 2 \times (\frac{3}{2}) + 1 = 4$ .
4. The total/resultant orbital angular momentum quantum no. (L) is known by  $\sum m_l$  (where  $m_l$  = magnetic quantum no.). L arises due to  $l-l$  coupling (i.e., angular motion of electron in orbital). The value of L ranges from  $(l_1+l_2)$  to  $(|l_1-l_2|)$ . L value will decide spectroscopic symbol.

(2)

The values of  $m_l$  for s, p, d & f orbitals are as follows:

$m_l$	0	+1 0 -1	+2 +1 0 -1 -2	+3 +2 +1 0 -1 -2 -3		
	$\square$	$\square \square \square$	$\square \square \square \square \square$	$\square \square \square \square \square \square \square$		
	s (l=0)	p (l=1)	d (l=2)	f (l=3)		
L-value:	0	1	2	3	4	5
Spectroscopic Symbol:	S	P	D	F	G	H

e.g. for  $d^5$  Conf.,  $L = +2+1+0-1+2 = 0$ , So spectroscopic symbol is S.

$\square \square \square \square \square$

5. Now, total/resultant angular momentum quantum no. (J) is known. J arises due to L-S coupling in multi electronic system. J can have the values ranging from  $(L+S)$  to  $(L-S)$  or  $S-L$  whichever is positive. For half filled or more than half filled, high J-value, i.e.,  $|L+S|$ , and for less than half filled low J-value, i.e.,  $|L-S|$  is used in writing Russel-Saunders ground state term symbol.
6. Finally, spin multiplicity  $(2S+1)$  is written as superscript on LHS and total resultant angular momentum (J) as subscript on RHS of spectroscopic symbol corresponding to L-value as follows:  $(2S+1)_L J$ .

Q. Determine ground state term symbol of following: (a)  $Mg^+$  (b)  $P^{3+}$  (c)  $V^{3+}$  (d)  $Ni^{2+}$

Ans. (a)  $Mg^+$ : It has  $2s^1$  Conf. or  $\square$  ;  $S = \sum m_s = +\frac{1}{2}$ ;  $2S+1 = 2 \times (\frac{1}{2}) + 1 = 2$ .

$L = 0 (S)$ ;  $J = |0 + \frac{1}{2}|$  to  $|0 - \frac{1}{2}| = \frac{1}{2}$

Spectroscopic term:  $2S$ ; Term symbol/G.S. Term symbol:  $2S_{\frac{1}{2}}$ .

(b)  $P^{3+}$ : It has  $2p^2$  Conf. or  $\square \square$  ;  $S = \sum m_s = +\frac{1}{2} + \frac{1}{2} = 1$ ;  $2S+1 = 2 \times 1 + 1 = 3$

$L = +1+0 = 1 (P)$ ;  $J = |1+1|$  to  $|1-1|$  or 2 to 0 = 2, 1, 0

Spectroscopic term:  $3P$

Term symbol:  $3P_2, 3P_1, 3P_0$ ; G.S. Term symbol:  $3P_0$ .

(c)  $V^{3+}$ : It has  $3d^2$  Conf. or  $\square \square$  ;  $S = \sum m_s = +\frac{1}{2} + \frac{1}{2} = 1$ ;  $2S+1 = 2 \times 1 + 1 = 3$

$L = +2+1 = 3 (F)$ ;  $J = |3+1|$  to  $|3-1|$  or 4 to 2 = 4, 3, 2

Spectroscopic term:  $3F$ ; Term symbol:  $3F_4, 3F_3, 3F_2$ .

Ground state term symbol:  $3F_2$

(d)  $Ni^{2+}$ : It has  $d^8$  Conf. or  $\square \square \square \square \square \square$  ;  $S = \sum m_s = +\frac{1}{2} + \frac{1}{2} = 1$ ;  $2S+1 = 2 \times 1 + 1 = 3$

$L = +2+1+0-1+2 = 0$ ;  $J = |1+0|$  to  $|0-1|$  or 1

Spectroscopic Symbol:  $3S$

Term symbol/Ground state term symbol:  $3S_1$

In complexes, ligands surrounding central metal ion suppress the orbital motion of the electrons, thus the contribution due to orbital magnetic moment is quenched. The magnetic moment is due to only spin magnetic moment and the values of magnetic moment are called spin only values.

The concept of quenching can be explained with the help of crystal field theory (CFT). In the presence of ligands, the degeneracy of d-orbitals of central metal atom/ion is removed. Due to removal of degeneracy of the d-orbitals of metal, the motion of the electrons is much hindered so that the quenching of orbital contribution to magnetic moment takes place.

Value of  $L=0$  for ions like  $Mn^{2+}$ ,  $Fe^{3+}$  etc. indicates there is no contribution of orbital magnetic moment. Thus, magnetic moment can be calculated as:

$$\mu_{eff} = \sqrt{4S(S+1)} = \sqrt{n(n+2)} \text{ BM} \quad (\text{where } n = \text{number of unpaired electrons})$$

The magnetic moments for the ions containing electrons 1, 2, 3, 4 & 5 will be 1.73, 2.83, 3.87, 4.90 & 5.92 BM respectively by above formula.

The magnetic moments of 2nd & 3rd transition series metals cannot be calculated by  $\mu_{eff}$  formula due to spin-orbit coupling constant is high. Conditions for Orbital Contribution: Any system can have orbital moment, three conditions must be fulfilled: (i) The orbitals should be degenerate (i.e., equivalent energies) (ii) The orbitals should be similar shape & size, i.e., they should be transformable by rotation about some axis. All d orbitals (except  $d_{z^2}$ ) have orbital angular momentum. (iii) The orbitals must not contain electrons of similar spin.

Orbital Contribution to magnetic moment: The CFT introduces a concept of splitting of degenerate d-orbitals. In an octahedral & tetrahedral complexes, the five d-orbitals split into two sets of different energy ( $t_{2g}$  &  $e_g$ ). The moment of the electrons is restricted due to the setup of an energy barrier in the presence of ligands. Although  $d_{z^2}$  &  $d_{x^2-y^2}$  orbitals ( $e_g$ -set) are degenerate in octahedral field but their shapes are such that they are not transformable into one other by rotation. Thus, the  $e_g$  set in octahedral (or tetrahedral) geometry cannot produce any orbital moment. Hence, they are known as non-magnetic doublet - non magnetic in the sense of only orbital moment but the spin moment remains. The  $t_{2g}$  set ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$  orbitals) fulfill the conditions (i) & (ii). As  $d_{xz}$  orbital is transformed to the  $d_{yz}$  orbital on rotation through  $90^\circ$  about z-axis. So it will the condition (iii) that will decide whether or not, we will get orbital moment from the  $t_{2g}$  set. Thus  $d^1$  &  $d^2$  complexes will obey all the three conditions in octahedral geometry/complexes but  $d^3$  Conf. will not agree to the condition (iii). Hence,  $d^1$  &  $d^2$  Conf. complexes will

Casey Orbital moment but  $d^3$  conf. complex will not do so.

The  $d_{xy}$  &  $d_{x^2-y^2}$  are now separated by  $\Delta$  (crystal field splitting energy) and a  $d_z^2$  electron has no orbital angular momentum, and that orbital contribution of a  $d_{xy}$  or  $d_{x^2-y^2}$  orbital electron is now completely quenched or suppressed by the ligand field. In octahedral complexes, the total orbital angular momentum becomes zero if the central metal ion has the ground state configuration  $t_{2g}^3$  or  $t_{2g}^6$  and among high spin complexes only the conf.  $d^1, d^2, d^6, d^7$  ( $t_{2g}^1, t_{2g}^2, t_{2g}^4 e_g^2, t_{2g}^5 e_g^2$ , respectively) have any angular momentum. Similarly, the high spin configurations  $d^3, d^4, d^8$  &  $d^9$  ( $e_g^2 t_{2g}^1, e_g^2 t_{2g}^2, e_g^4 t_{2g}^1, e_g^4 t_{2g}^2$ , respectively) of tetrahedral complexes should have orbital moments. The orbital moment for  $d^7$  ( $e_g^1 t_{2g}^3$ ) complex should be quenched or suppressed in a high spin tetrahedral complex but not in a high spin octahedral complex.

A & E state arrangements have no orbital contributions but T state has orbital contribution to magnetic moment. Higher than spin only moments in tetrahedral  $Ni^{2+}$ , octahedral  $Co^{2+}$  and octahedral  $Fe^{2+}$  are thus elaborated. But we would expect only spin moments for octahedral  $Ni^{2+}$  & tetrahedral  $Co^{2+}$ . The magnetic moment values of these complexes are substantially higher than the spin only magnetic moment values. For example, complexes of  $Ni^{2+}$  ( $d^8$  conf.) with A & E ground terms show magnetic values significantly higher than the spin only magnetic moments. Whenever there exists a T term above an A & E ground state with the same spin multiplicity, then some orbital angular momentum is drawn from the excited T term into the A & E terms through spin-orbit coupling mechanism. The ground terms, therefore, possess some orbital angular momentum, i.e., A or E term will possess some T character. Orbital contribution in octahedral & tetrahedral complexes summarized as follows:

$d^n$ Conf.:	High spin Octahedral Complexes.		Tetrahedral Complexes.	
	$d^1, d^2, d^6, d^7$	$d^3, d^4, d^5, d^8, d^9$	$d^1, d^2, d^5, d^6, d^7$	$d^3, d^4, d^8, d^9$
Orbital contribution:	Yes	No	No	Yes
Ground state:	$2T_{2g}, 3T_{1g}, 5T_{2g}, 4T_{1g}$	$4T_{2g}, 5E_g, 6A_{1g}, 3A_{2g}, 2E_g$	$2E, 3A_2, 6A_1, 5E, 4A_2$	$4T_1, 5T_2, 3T_1, 2T_2$

Magnetic moment value & crystal field splitting energy ( $\Delta$  or  $10Dq$ ) of a complex are related quantitatively as follows:

$$\mu_{eff} = \left( \frac{1-\alpha\lambda}{10Dq} \right) \mu_{spin\ only} = 2 \left( 1 - \frac{4\lambda}{10Dq} \right) \sqrt{s(s+1)} \quad \text{--- (1) [Since } \mu_{spin\ only} = 2\sqrt{s(s+1)} \text{]}$$

From equation (1), it follows that the greater the CFSE ( $10Dq$ ), smaller is the mixing effect and hence less is the orbital contribution. Strong donor ligands are likely to lessen the orbital contribution. Furthermore, depending on the sign of  $\lambda$ ,  $\mu_{eff}$  will be higher or lower than the  $\mu_{spin\ only}$  values. For  $d^7$  (tetrahedral)  $Co^{2+}$  complex ( $4A_2$ ),  $d^8$  (octahedral)  $Ni^{2+}$  complex ( $3A_{2g}$ ),  $\lambda$  is negative, so that the  $\mu_{eff}$  are higher than  $\mu_{spin}$ . For  $d^3$  (octahedral)  $Cr^{3+}$  complex ( $4A_{2g}$ ),  $\lambda$  is positive, so that lower  $\mu_{eff}$  than  $\mu_{spin\ only}$  moment are expected.

### Van Vleck Equation

In Van Vleck equation, changes in energies of molecules are considered when external magnetic field is applied. When magnetic field applied, the magnetic dipoles present in paramagnetic substances align along the direction of magnetic field. A multi electron system possesses several J levels. In an applied magnetic field (H), the J levels splits into (2J+1) levels. This splitting is known as first order Zeeman effect. 2nd order Zeeman effect arises due to mixing of the wave functions of a particular level with those of its neighbouring level and thus some characters of the excited state are introduced into the ground state. In van Vleck equation both these effects are included.

Derivation: Following assumptions are made in derivation of van Vleck equation:

- (i) The susceptibility does not depend on applied magnetic field (H).
- (ii) The energy of the nth level of the atom/ion can be given as  $W_n = W_n^0 + W_n^{(1)}(H) + W_n^{(2)}H^2 + \dots$   
(Where  $W_n^0$  = Energy of the nth level in absence of H,  $W_n^{(1)}$  = 1st order Zeeman coefficient,  $W_n^{(2)}$  = Second order Zeeman Coefficient).

On the application of external magnetic field (H), the energy of the magnetic dipole will be  $-\mu H$  given by the product of the magnetic moment in the direction of field and field strength. i.e.,  $W = -\mu H$  — (1)

On differentiating equation (1) w.r.to H, we get  $\frac{\partial W}{\partial H} = -\bar{\mu}$  — (2)

(Where  $\bar{\mu}$  = projection of  $\mu$  along H)

Considering the nth level, we have  $\bar{\mu}_n = -\frac{\partial W_n}{\partial H} = -\frac{\partial}{\partial H} [W_n^0 + W_n^{(1)}H + W_n^{(2)}H^2 + \dots]$  — (3)

Assuming that there are several states like n, each state is having its characteristic  $\bar{\mu}$  value. An average value  $\bar{\mu}$  can be taken, thus susceptibility ( $\chi_M$ ) is given as —

$$\chi_M = \frac{N \cdot \bar{\mu}}{H} \quad \text{--- (4)} \quad \bar{\mu} = \frac{\sum n_n \bar{\mu}_n}{N} \quad \text{--- (5)}$$

Population of these levels are given by Boltzmann's law

$$n_n = n_0 e^{\frac{-W_n}{kT}} \quad \text{(Where } n_n = \text{no. of molecules in the } n^{\text{th}} \text{ level, } n_0 = \text{no. of molecules in the ground level)}$$

$$\text{Since, } e^{\frac{-W_n}{kT}} = e^{\frac{-[W_n^0 + W_n^{(1)}H + W_n^{(2)}H^2]}{kT}} = e^{\frac{-W_n^0}{kT}} e^{\frac{-W_n^{(1)}H - W_n^{(2)}H^2}{kT}} \quad \text{--- (6)}$$

The energy difference between two successive levels is  $g\beta H$ . The product  $g\beta H$  is only  $\sim 1 \text{ cm}^{-1}$  at  $H = 10^4$  gauss so that  $g\beta H$  is quite small compared to  $kT \sim 200 \text{ cm}^{-1}$  at 298K;  $\sim 208 \text{ cm}^{-1}$  at 573K. Thus, the second order Zeeman susceptibility will be more less.

When the value of  $x$  is small,  $e^{-x} \approx (1-x)$   
 Thus,  $e^{\frac{-W_n}{kT}} = e^{\frac{-W_n^0}{kT}} [1 - \frac{W_n^{(1)}H}{kT}] \frac{(1 - \frac{W_n^{(2)}H^2}{kT})}{kT}$  — (8)

Since susceptibility is independent of applied field,  $\bar{\mu} = \frac{n_0 \sum_n \bar{\mu}_n e^{\frac{-W_n}{kT}}}{n_0 \sum_n e^{\frac{-W_n}{kT}}}$  — (9)

$$\text{Or, } \bar{\mu} = \frac{\sum_n [-W_n^{(1)} - 2W_n^{(2)}H] e^{\frac{-W_n^0}{kT}} (1 - \frac{W_n^{(1)}H}{kT})}{\sum_n [e^{\frac{-W_n^0}{kT}}] [1 - \frac{W_n^{(1)}H}{kT}]} \quad \text{--- (10)}$$

Since on the application of applied magnetic field, the J levels symmetrically split into different  $M_J$  levels (1st order Zeeman effect), we can have

$\sum_n W_n^{(1)} = 0$  and hence  $\sum_n W_n^{(1)} e^{\frac{-W_n^0}{kT}} = 0$ . Then, we can write

$$\bar{\mu} = \frac{H \sum_n [W_n^{(2)} - 2W_n^{(2)}] e^{\frac{-W_n^0}{kT}}}{\sum_n e^{\frac{-W_n^0}{kT}}} \quad \text{--- (11)}$$

$$\text{Thus, susceptibility, } \chi_M = \frac{N \sum_n \frac{W_n^{(2)} - 2W_n^{(2)}}{kT} e^{\frac{-W_n^0}{kT}}}{\sum_n e^{\frac{-W_n^0}{kT}}} \quad \text{--- (12)}$$

Calculation of magnetic susceptibility ( $\chi_M$ ) involves estimation of  $W_n^0, W_n^{(1)}$  &  $W_n^{(2)}$  values.

(6)

Van Vleck equation with large multiplet width:

Since in the case L & S vectors interact strongly, hence, Van Vleck equation can be represented taking  $\omega_n^{(1)} = 0$  considering second order Zeeman effect.  $\omega_n^0$  can be taken as zero, the  $n^{\text{th}}$  level in the absence of magnetic field being the ground state. So,

$$\chi_M = \frac{e^{-\frac{\omega_n^0}{kT}} \sum_n \left[ \frac{\omega_n^{(1)2}}{kT} \right] e^{-\frac{\omega_n^0}{kT}}}{\sum_n e^{-\frac{\omega_n^0}{kT}}} \quad (13)$$

Thus,

$$\begin{aligned} \chi_M &= \frac{N \sum_{M_J=-J}^J \frac{g^2 \beta^2 M_J^2}{(2J+1)}}{\sum_n e^{-\frac{\omega_n^0}{kT}}} = \frac{N g^2 \beta^2}{kT} \frac{1}{(2J+1)} \sum_{M_J=-J}^J M_J^2 = \frac{N g^2 \beta^2}{kT} \frac{1}{(2J+1)} 2[J^2(J+1)^2 + \dots + J^2] \\ &= \frac{N g^2 \beta^2}{kT} \frac{1}{(2J+1)} \frac{2J(J+1)(2J+1)}{6} = \frac{N \beta^2}{3kT} g^2 J(J+1) \Rightarrow \boxed{\mu = g_J \sqrt{J(J+1)}} \quad (14) \end{aligned}$$

Van Vleck equation with small multiplet width:

Taking  $\omega_n^{(2)} = 0$ , the Van Vleck equation can be represented as

$$\chi_M = \frac{N \sum_n \left[ \frac{\omega_n^{(1)2}}{kT} \right] e^{-\frac{\omega_n^0}{kT}}}{\sum_n e^{-\frac{\omega_n^0}{kT}}} \quad (15)$$

This can be broken into two portions to show the first and second order Zeeman effects. For first order Zeeman effect,  $\chi_M$  is given as—

$$\chi_M = \frac{N \sum_n \left[ \frac{\omega_n^{(1)2}}{kT} \right] e^{-\frac{\omega_n^0}{kT}}}{\sum_n e^{-\frac{\omega_n^0}{kT}}} \quad (16)$$

Since  $\omega_n^0 = 0$ ,

$$\chi_M = \frac{N \sum_n \frac{\omega_n^{(1)2}}{kT}}{(2J+1)} \quad (17)$$

for Second order Zeeman effect  $\chi_M$  is given as

$$\chi_M = \frac{-2N \sum_n \omega_n^{(2)} e^{-\frac{\omega_n^0}{kT}}}{\sum_n e^{-\frac{\omega_n^0}{kT}}} \quad (18)$$

Since  $\omega_n^0 = 0$ ,

$$\chi_M = \frac{-2N \sum_n \omega_n^{(2)}}{(2J+1)}$$

$$\chi_M = N \alpha = \frac{-2N \sum_n \omega_n^{(2)}}{(2J+1)} \quad (19)$$

$$\therefore \boxed{\alpha = \frac{2}{(2J+1)} \sum_n \omega_n^{(2)}} \quad (20)$$

From above equations, following conclusions can be drawn:

- Dependence of temperature: The 1st order Zeeman susceptibility equation contains  $kT$ , so it is dependent on temp.  $\chi_M \propto 1/T$ . The second order susceptibility does not carry  $kT$ , so it is independent of temp. Thus it is also called temperature independent paramagnetism or Van Vleck paramagnetism or residual paramagnetism.

The second order Zeeman effect arises from mixing of wave functions of a particular level with those of neighbouring level. Thus, the degree of second order Zeeman effect is inversely proportional to energy difference between the two levels.

(7)  
Magnetic properties of Inner transition (f-block) elements

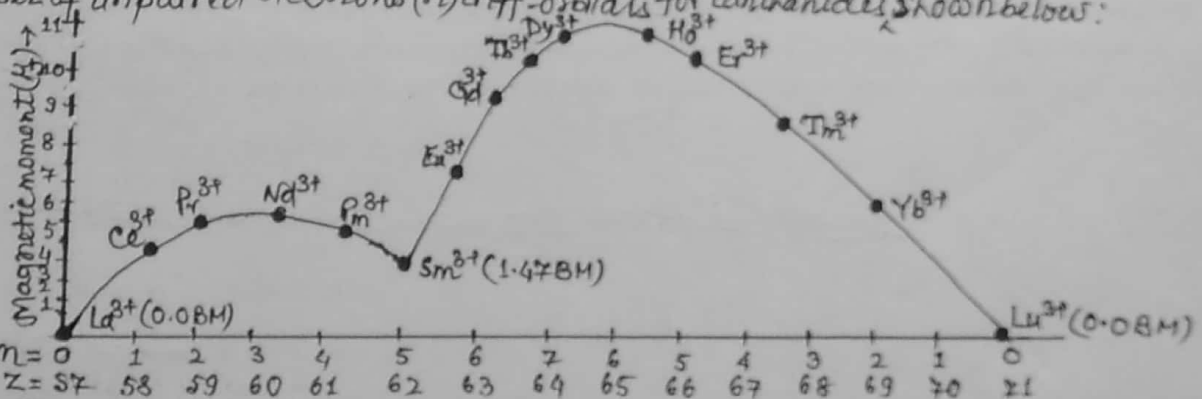
We know that magnetic behaviour in chemical substances arises due to the presence of unpaired electrons. An electron may be regarded as an elementary or tiny magnetic. The origin of magnetism is most easily described in prewave mechanical terms where we take picture the electron as negatively charged particle, possesses both spinning motion on its axis and revolving motion about a nucleus. The former motion gives rise to spin moment and the later to orbital moment. The combination of these two moments results in the paramagnetic moment (i.e., paramagnetism) for certain atom/ion.

In the 4f series (i.e., Lanthanides),  $\text{La}^{3+}$  ion is empty (i.e.,  $4f^0$  conf.) and  $\text{Lu}^{3+}$  is completely filled (i.e.,  $4f^{14}$  conf.). These ions are diamagnetic as there is no unpaired electron. The remaining  $M^{3+}$  ( $4f^1 - f^{13}$  conf.) ions are paramagnetic, since they are partly filled, i.e., presence of one or more unpaired electrons.

The magnetic behaviour of the f-block elements (Lanthanides/Actinides) is fundamentally different from that of d-block elements (transition metals). The reason for the difference is that the electrons responsible for the properties of the  $M^{3+}$  ions are 4f or 5f orbital which are effectively shielded from the influence of external forces by overlain s & p-orbitals. Due to this, it is not possible to explain the magnetic moment in terms of unpaired electron atom. The orbital contribution which is ignored in the case of d-block elements, cannot be ignored in the case of f-block elements.

The simple relation for calculating magnetic moment is given by  $\mu = \sqrt{n(n+2)} BM$  (where  $n = \text{no. of unpaired electrons}$ ) cannot be valid in f block elements. In the case of f block elements, the total paramagnetism is due to both spin<sup>(S)</sup> & Orbital<sup>(L)</sup> moments, given as  $\mu_{\text{eff}} = g \sqrt{J(J+1)} BM$  (where  $g = \text{a constant, called Lande Splitting factor} = 1.5 + \frac{S(S+1) - L(L+1)}{2J(J+1)}$ ;  $J = \text{total or resultant angular momentum}$ ).  $\mu_J$  values of  $M^{3+}$  ions calculated from above formula, e.g., for  $\text{Ce}^{3+}$  ( $4f^1$  conf.) ground state term is  $2F_{5/2}$ .  $S = 1/2, L = 3, J = 5/2, g = 6/7$   
 $\mu_J$  or  $\mu_{\text{eff}} = g \sqrt{J(J+1)} BM = \frac{6}{7} \sqrt{5/2(5/2+1)} = 2.54 BM$ . Experimental value lie in the range 2.3-2.5 BM.

The experimental values of  $\mu_J$  (in BM) of  $M^{3+}$  ions are plotted against their atomic no. / number of unpaired electrons ( $n$ ) in f-orbitals for Lanthanides as shown below:



From the graph, it is evident that  $\text{La}^{3+}$  ( $4f^0$ ) &  $\text{Lu}^{3+}$  ( $4f^{14}$ ) are diamagnetic ( $\mu_J = 0$ ).  $\mu_J$  value increases upto  $\text{Nd}^{3+}$  and then decreases to  $\text{Sm}^{3+}$  ion. It starts rising again and becomes maximum at  $\text{Dy}^{3+}$  (10.5 BM), and then decreases to  $\text{Lu}^{3+}$  (0.0 BM).

In actinides (5f-series), 5f-orbitals are not completely shielded from external ligand field due to their greater spatial extension. Thus, 5f electrons in actinides are more exposed to crystal field and are less effectively shielded. As a result, the orbital contribution to magnetic moment is quenched in actinides. Magnetic moment values of tri positive actinides ( $M^{3+}$ ) ions decrease from  $\text{U}^{3+}$  ( $5f^3, n=3$ ) to give minimum value at  $\text{Pu}^{3+}$  ( $5f^5, n=5$ ) and then increase to show a maximum value at  $\text{Cf}^{3+}$  ( $5f^9, n=5$ ). Thereafter it decreases at  $\text{Es}^{3+}$  ( $5f^{10}, n=4$ ).

Unit-4 Reaction mechanism of Transition metal complexes.

4.1 Inert & Labile Complexes: The rate at which replacement/substitution of one ligand by other ligands takes place refers kinetic stability of the complexes. On kinetic stability complexes can be classified into two types: (1) Labile complexes (2) Inert complexes.

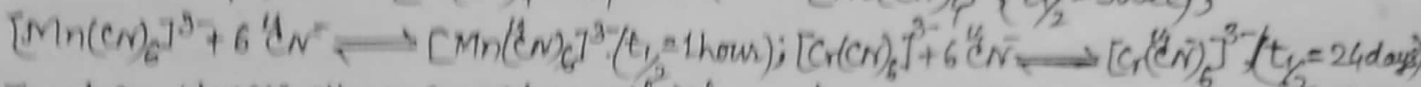
1. Labile complexes: The ability of a particular complex ion to engage in substitution of one or more ligands in its coordination sphere [ ] by other ligands is called its lability. Those complexes which are highly reactive (i.e. complexes in which ligands can be readily replaced/substituted by other ligands) are called labile complexes.

According to Taube, the complexes for which replacement of ligands takes place in time less than 1 minute at 25°C & 1M solution are referred as Labile complexes.

The labile octahedral complexes are given by  $M^{n+}$  ions for which there is little or no loss in CFSE (Crystal field stabilisation energy). Octahedral complexes of  $d^0, d^1, d^2$  &  $d^{10}$  both in high & low spin are labile. Order of lability of the ions:  $d^3, d^4, d^5$  &  $d^6$  is  $d^6 > d^3 > d^4 > d^5$ . In thermodynamic sense, stable and unstable terms are used, which shows the extent to which complex will persist in the solution under suitable conditions.

Examples of labile complexes are  $[Ni(CN)_4]^{2-}$ ,  $[Hg(CN)_4]^{2-}$ ,  $[Mn(CN)_6]^{3-}$  etc.

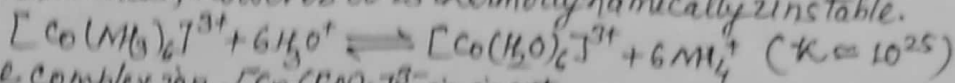
Cyano complexes of Ni(II), Mn(II) & Cr(III) are extremely stable thermodynamically, yet kinetically they provides very different picture. If the rate of exchange of  $^{14}CN^-$  (labelled) is measured, it found  $[Ni(CN)_4]^{2-}$  is labile,  $[Mn(CN)_6]^{3-}$  is moderately labile &  $[Cr(CN)_6]^{3-}$  is inert complex ion.



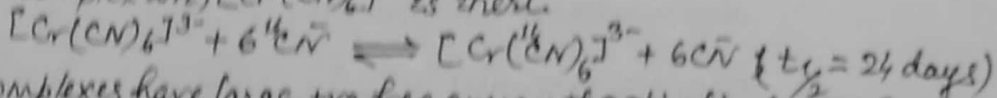
2. Inert complexes: Those complexes which are less reactive (i.e. complexes which ligands cannot be readily replaced/substituted by other ligands) are called Inert complexes. According to Taube, the complexes in which substitution of ligands takes place in more than one hour at 25°C & 1M conc<sup>n</sup> are called inert complexes.

The inert octahedral complexes are given by  $M^{n+}$  ions for which there is a large loss in CFSE. Low spin <sup>Octahedral</sup> complexes of  $d^3, d^4, d^5$  &  $d^6$  ion are inert, and order of inertness of these is  $d^6 > d^3 > d^4 > d^5$ . Examples of inert complexes:  $[Co(NH_3)_6]^{3+}$ ,  $[Cr(CN)_6]^{3-}$  etc.

The complex ion,  $[Co(NH_3)_6]^{3+}$  can be stored for long time in acidic medium due to kinetic inertness, however it is thermodynamically unstable.



The complex ion,  $[Cr(CN)_6]^{3-}$  is inert.



Inert complexes have large +ve free energy of activation ( $\Delta G^\ddagger$ ) while thermodynamically stable complexes have large +ve free energy of reaction ( $\Delta G$ ).

4.2 Kinetic applications of VBT & CFT

Kinetic application of valence bond theory (VBT): According to valence bond theory octahedral complexes can be divided into two types: (i) Outer orbital complexes (ii) Inner orbital complexes.

(i) Outer Orbital complexes: Those complexes in which outer orbit(n) d-orbitals involve of in hybridisation (i.e.  $sp^3d^2$  hybridisation) are called outer orbital complexes.



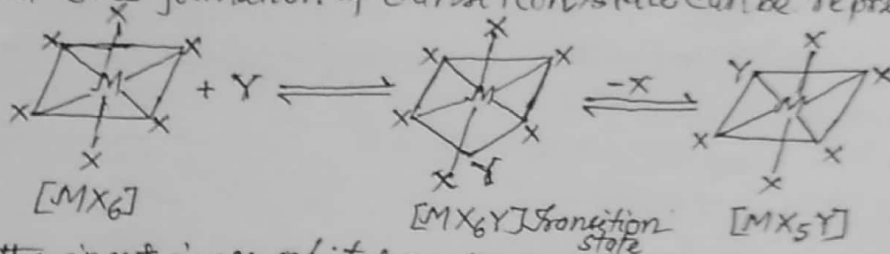
(2)

For examples,  $[FeF_6]^{3-}$ ,  $[Co(H_2O)_6]^{2+}$  etc. These complexes are generally labile.

In outer orbital complexes of  $Cr^{2+}(d^4)$ ,  $Mn^{2+}(d^5)$ ,  $Fe^{2+}(d^6)$ ,  $Fe^{3+}(d^5)$ ,  $Co^{2+}(d^7)$ ,  $Ni^{2+}(d^8)$ ,  $Cu^{2+}(d^9)$ , substitution of the ligands occurs rapidly. This can be explained by VBT, as the metal-ligand ( $M-L$ ) bonds, formed by  $sp^3d^2$  hybrid orbitals (vacant) of metal and filled orbital of ligand ( $L$ ), are weaker. Hence, ligand can be replaced or substituted easily. The  $d^8$  system ( $Ni^{2+}$ ) should form outer orbital complexes which will be labile, i.e.  $d_{xy}^2 \cdot d_{xz}^2 \cdot d_{yz}^2 \cdot d_{x^2-y^2}^1 \cdot d_{z^2}^1$ .

(ii) Inner orbital complexes: Those complexes in which inner  $(n-1)d$  orbitals involved in hybridisation (i.e.  $d^2sp^3$  hybridisation) are called inner orbital complexes. For examples,  $[Co(NH_3)_6]^{3+}$ ,  $[Cr(CN)_6]^{3-}$ ,  $[Fe(CN)_6]^{4-}$  etc.

In the labile inner orbital octahedral complexes, there should be at least one  $d$ -orbital of  $t_{2g}$  set empty, so that this empty  $d$ -orbital may be accept the electron pair from the ligand, and the transition state with coordination number 7 is formed. The formation of transition state can be represented as -



In the inert inner orbital complexes three  $d$ -orbitals of  $t_{2g}$  set occupy at least one electron. Hence, they cannot be used to accept the electron pair given by ligand for the formation of transition state.

Kinetic application of Crystal field theory (CFT): An octahedral complex can be converted into product either by  $SN^1$  dissociation (i.e. via 5 coordinated square pyramidal intermediate) or by  $SN^2$  association (i.e. via 7 coordinated pentagonal bipyramidal intermediate). The symmetry is lowered and CFSE decreases during the intermediate formation. The decrease of CFSE is called activation energy ( $E_a$ ). Thus, activation energy is change in CFSE during transformation of octahedral complex into intermediate species (square pyramidal or pentagonal bipyramidal).

The inert octahedral complexes are formed by the metal ions ( $d^3, d^4, d^5$  &  $d^6$  conf.) for which there is large loss in CFSE values while the labile octahedral complexes are formed by the metal ions ( $d^0, d^1, d^2$  &  $d^{10}$  conf.) for which there is little or no loss in the CFSE values.

Some conclusions can be drawn here: (a) Both high & low spin octahedral complexes of  $d^0, d^1$  &  $d^2$  ions are labile as there is no loss in CFSE values are found for these metal ions by  $SN^1$  or  $SN^2$  mechanism. (b) High spin octahedral complexes of  $d^3$  ion is inert as there is appreciable loss in CFSE value is found by  $SN^1$  (-2.0  $\Delta_0$ ) or  $SN^2$  (-4.26  $\Delta_0$ ) mech. (c) High spin octahedral complexes of  $d^5$  ion are labile complexes because there is no loss in CFSE is found. (d) Both high & low spin octahedral complexes of  $d^8$  ion are inert since for any mechanism, there is substantial loss of CFSE value is found. (e) Both high & low spin octahedral complexes of  $d^{10}$  metal ion are labile as substitution reactions are fast (f) The low spin complexes of  $d^3, d^4, d^5$  &  $d^6$  ions are inert as there is substantial loss in CFSE value is found by both  $SN^1$  &  $SN^2$  mechanism.

(3)

The order of inertness of low spin complexes formed by  $d^3, d^4, d^5$  &  $d^6$  ions is :

Order of inertness :  $d^6 > d^3 > d^4 > d^5$

Loss of CFSE for  $SN^1(X_2)$  :  $-4.00 \quad -2.00 \quad -1.43 \quad -0.86$

Loss of CFSE for  $SN^2(X_2)$  :  $-8.52 \quad -4.26 \quad -2.98 \quad -1.40$

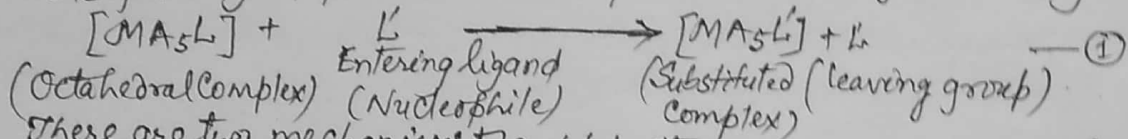
Hence,  $d^6$  ion form the most inert complex.

### Substitution reactions in Octahedral Complexes

Substitution reactions in which a ligand present in the coordination sphere [ ] of the complex compounds is replaced by another ligand (nucleophile) are called nucleophilic or ligand substitution reactions ( $SN$  reactions).  $[ML_6] + L' \xrightarrow{(SN^1)}$   $[ML_5L'] + L$   
(Nucleophile or Lewis base)

### Kinetics/Mechanism of Nucleophilic Substitution reactions in Octahedral Complexes:

Nucleophilic Substitution ( $SN$ ) reaction in an octahedral complex is a reaction in which one of the ligands present in the complex is replaced by another ligand, e.g.



There are two mechanisms to explain the occurrence of the above ligand substitution reaction: 1. Unimolecular nucleophilic substitution ( $SN^1$ ) or dissociative mechanism:

When nucleophilic substitution reactions in octahedral complex proceeds with dissociative and associative steps, it is said  $SN^1$  mechanism/dissociative mechanism.

(a) Dissociative step: In this step, loss of leaving group by dissociation of octahedral complex occurs.  $[MA_5L] \xrightarrow{k} [MA_5] + L$  [ $k$  = rate constant of dissociation reaction]

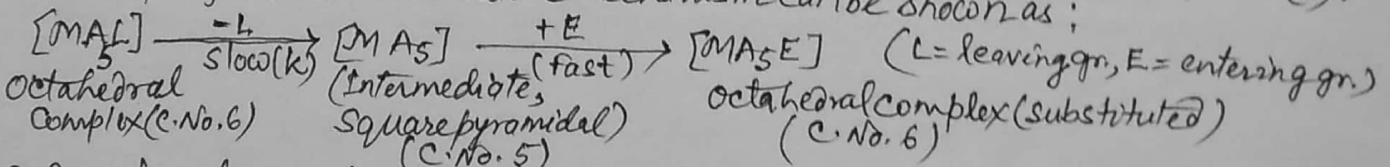
(b) Associative step: In this step, addition of entering group (nucleophile or Lewis base) by association occurs.  $[MA_5] + L' \xrightarrow{\text{fast step}} [MA_5L']$   
Intermediate (square pyramidal) (Substituted octahedral complex)

Since the dissociative step (a) is a slow step, it is the rate determining step. The reaction of this step is unimolecular since it involves only one reacting species,  $[MA_5L]$ . The rate of this reaction depends on the concentration of  $[MA_5L]$  only, i.e.,

$$\text{Rate (r)} = k_1 [MA_5L]; \text{ Order} = \text{molecularity} = 1, \text{ so it is } SN^1 \text{ mechanism.}$$

In this mechanism, since the octahedral complex,  $[MA_5L]$  dissociates in rate determining step (slow step), the mechanism is called dissociative mechanism.

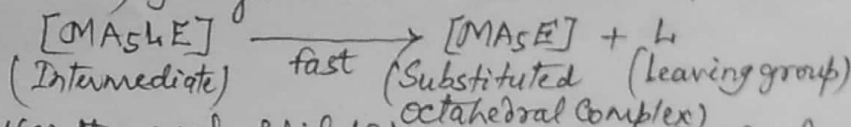
Above discussion indicates that the rate of reaction (1) is directly proportional to concentration of  $[MA_5L]$  and is independent of the conc<sup>2</sup> of nucleophile ( $E$ ). Steps of  $SN^1$  or dissociative mechanism can be shown as:



2. Bimolecular nucleophilic substitution ( $SN^2$ ) or Associative mechanism: When nucleophilic reaction (substitution) in an octahedral complex proceeds with associative and dissociative steps, it is said  $SN^2$  or Associative mechanism. Reaction (2) proceeds through following steps:

(a) Associative step: In this step, addition of entering group (nucleophile) by association of complex (octahedral) occurs.  $[MA_5L] + E \xrightarrow[\text{(slow)}]{k_2} [MA_5LE]$   
(Octahedral complex) (Nucleophile) (7 coordinated intermediate)

(b) Dissociative step: In this step, loss of leaving group by dissociation of intermediate (7-coordinated) giving substituted octahedral complex.

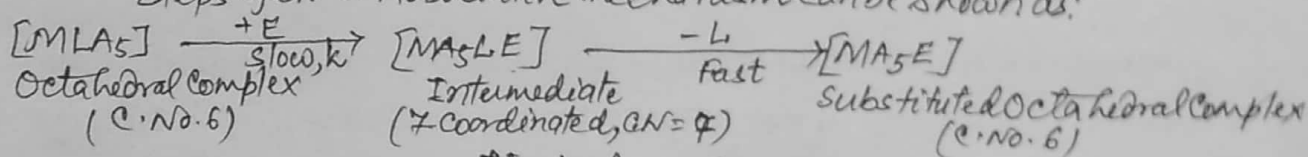


In step (a), the nucleophile (E) attacks the octahedral complex (MA<sub>5</sub>L) and gets associated with it to form seven-coordinated intermediate (MA<sub>5</sub>LE). Thus, in this step a new bond (M-E) is formed, called bond making step. This is slow, and hence rate determining step.

This is bimolecular, since it involves two species: MA<sub>5</sub>L & E. The rate of this reaction depends on the concentration of the complex (MA<sub>5</sub>L) as well as on the conc<sup>n</sup> of nucleophile (E).  
i.e., Rate (r) = k [MA<sub>5</sub>L]<sup>1</sup> [E]<sup>1</sup>; Order = molecularity = 2, So it is S<sub>N</sub><sup>2</sup> mechanism.

In this mechanism, since the entering group (E) gets associated with the complex, [MA<sub>5</sub>L] is rate determining step (slow step) to form 7-coordinated intermediate, this mechanism is also called associative mechanism.

Steps of S<sub>N</sub><sup>2</sup> or Associative mechanism can be shown as:



### Hydrolysis Reactions

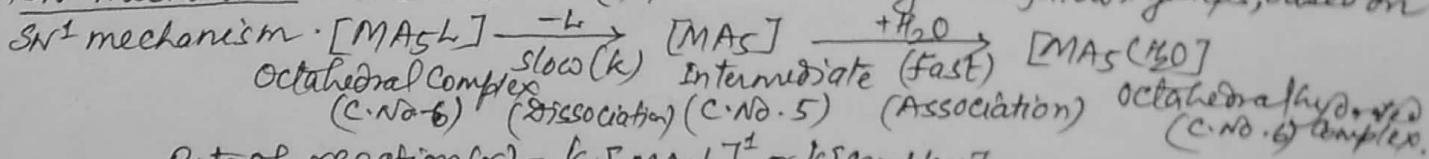
These are the nucleophilic substitution reactions in which a ligand present in a complex compound is replaced or substituted by H<sub>2</sub>O (water, aqua) or by -OH group. Hydrolysis reactions are of two types: (1) Acid hydrolysis

(2) Base hydrolysis.

(1) Acid hydrolysis: The nucleophilic substitution reaction in which a ligand present in a complex species is replaced/substituted by H<sub>2</sub>O (aqua) molecule is called acid hydrolysis or aquation of the complex. It takes place in neutral or acidic medium (pH < 3). e.g., [Co(MH<sub>2</sub>)<sub>5</sub>Cl]<sup>2+</sup> + H<sub>2</sub>O → [Co(MH<sub>2</sub>)<sub>5</sub>(H<sub>2</sub>O)]<sup>3+</sup> + Cl<sup>-</sup>

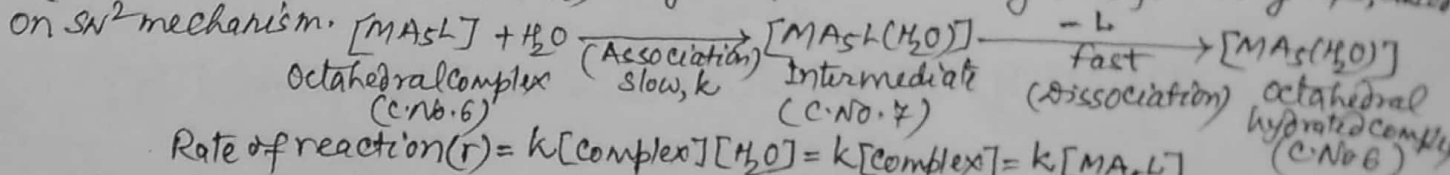
Mechanism of Acid hydrolysis of octahedral complexes: Let us consider the acid hydrolysis of [MLA<sub>5</sub>] in which A & L are inert ligands. The hydrolysis of [MA<sub>5</sub>L] can be represented as: [MLA<sub>5</sub>] + H<sub>2</sub>O → [MA<sub>5</sub>(H<sub>2</sub>O)] + L — (1)

(a) S<sub>N</sub><sup>1</sup> mechanism: The reaction (1) proceeds through the following steps, based on S<sub>N</sub><sup>1</sup> mechanism.



Rate of reaction (r) = k [MA<sub>5</sub>L]<sup>1</sup> or k [complex]

(b) S<sub>N</sub><sup>2</sup> mechanism: The reaction (1) may also proceed through the following steps, based on S<sub>N</sub><sup>2</sup> mechanism.



Rate of reaction (r) = k [complex] [H<sub>2</sub>O] = k [complex] = k [MA<sub>5</sub>L]

It is clear from the above discussion that both the mechanisms predict that rate of hydrolysis reaction (1) is dependent only on the conc<sup>n</sup> of the complex, [MA<sub>5</sub>L], whatever be the mechanism (S<sub>N</sub><sup>1</sup> or S<sub>N</sub><sup>2</sup>).

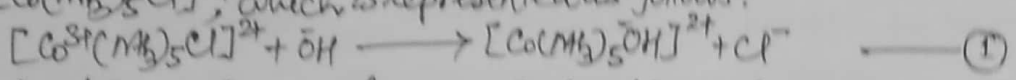
Consequently we will have to look to some other factors to decide the mechanism given below:

(i) Charge on the complex: The reaction rate of hydrolysis of several octahedral complexes of Co<sup>3+</sup> & other metal ions decreases with the increase in the charge on the complex.



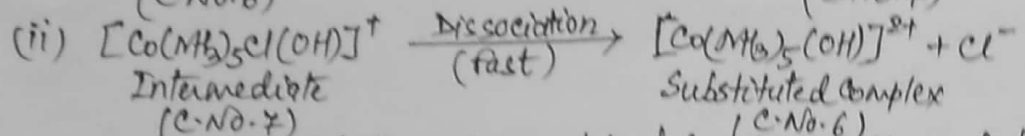
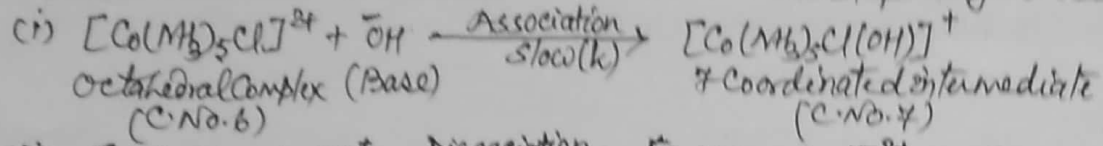
(6)  
 2. Base hydrolysis: The nucleophilic substitution reaction in which the anion of water (i.e., OH<sup>-</sup> ion) replaces the coordinated ligand from a complex species is known as base hydrolysis of the complex species. For example,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + \text{OH}^- \longrightarrow [\text{Co}(\text{NH}_3)_5(\text{OH})]^{2+} + \text{Cl}^-$ . In this reaction, the coordinated ligand (Cl<sup>-</sup>) is replaced by OH<sup>-</sup> ion. Thus, Cl<sup>-</sup> is leaving group and OH<sup>-</sup> ion is the entering group.

Mechanism of Base hydrolysis: Let us consider base hydrolysis of octahedral Co(III) ammine complex,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ , which is represented as follows:

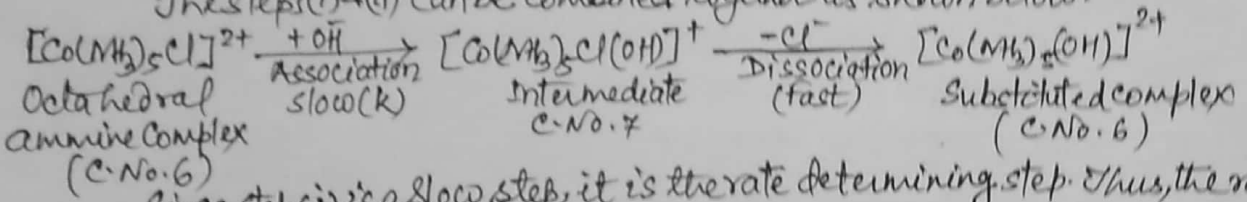


Following two mechanisms have been proposed to explain above reaction (1):

(a) SN<sup>2</sup>/Associative mechanism: This involves two steps as given below:



The steps (i) & (ii) can be combined together as shown below:



Since step (i) is a slow step, it is the rate determining step. Thus, the rate law for reaction (1) is given as:  $\text{Rate}(r) = k[\text{Complexion}][\text{OH}^-] = k[\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}][\text{OH}^-] = k[\text{Complex}][\text{Base}]$

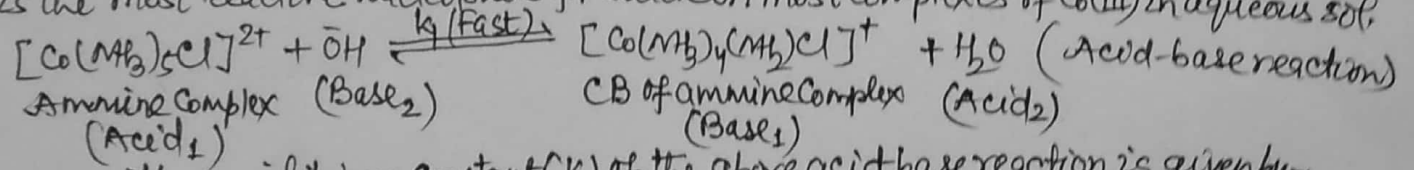
Order = Molecularity = 2, so it is SN<sup>2</sup> mechanism, and since slower step is association, hence associative mechanism.

Limitation of SN<sup>2</sup> mechanism: SN<sup>2</sup> mechanism is not able to explain following experimental observations:

- (i) The rate law equation shows, rate of hydrolysis is dependent on conc<sup>n</sup> of OH<sup>-</sup>. However, at high concentration of OH<sup>-</sup> ions, the reaction rate becomes independent of [OH<sup>-</sup>]. Hence, at high concentration of OH<sup>-</sup> ions, it is first order (SN<sup>1</sup>) w.r. to  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ .
- (ii) Although  $\text{NCs}^-$ ,  $\text{NO}_2^-$ ,  $\text{N}_3^-$  etc. nucleophiles are as strong as OH<sup>-</sup>, their concentration does not affect the rate of hydrolysis of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  ion. Thus, SN<sup>2</sup> mechanism cannot explain why the rate of reaction depends on [OH<sup>-</sup>] and not on the concentration of other  $\text{X}^-$ .

SN<sup>1</sup> Conjugate Base (CB) mechanism: This mechanism was proposed by Garrick (1937) for base hydrolysis reaction. SN<sup>1</sup>(CB) stands for substitution nucleophilic unimolecular conjugate base.

According to this mechanism, the reacting complex,  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  which acts as a Bronsted acid donates the proton (H<sup>+</sup>) from the non-leaving NH<sub>2</sub> (amino) group, and it thus gets converted into its conjugate base amido (NH<sub>2</sub>) complex,  $[\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]^+$ , and OH<sup>-</sup> ion which is a base is converted into conjugate acid (H<sub>2</sub>O). The hydroxide ion (OH<sup>-</sup>) is the most reactive nucleophile for attack on most complexes of Co(III) in aqueous sol.



The equilibrium constant (K) of the above acid base reaction is given by-

$$K = \frac{[\text{CB}][\text{H}_2\text{O}]}{\text{Conc. of } [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} [\text{OH}^-]} \quad \left\{ \text{where } [\text{CB}] = \text{conc}^2 \text{ of conjugate base, } [\text{Co}(\text{NH}_3)_4(\text{NH}_2)\text{Cl}]^+ \right\}$$

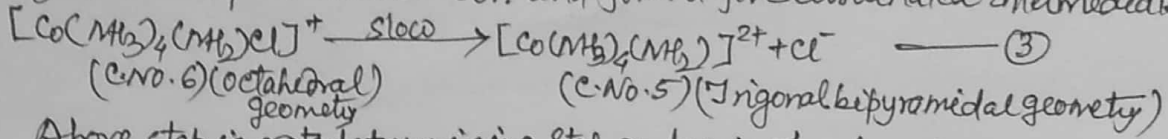
--- (1)

(7)

∴ [CB] = K × Conc<sup>2</sup> of [Co(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup> × [OH<sup>-</sup>] (Since [H<sub>2</sub>O] = a constant)

Or, [CB] = K<sub>B</sub>[Complex][Base] ——— (2)

Since conjugate base, [Co(NH<sub>3</sub>)<sub>4</sub>(NH<sub>2</sub>)Cl]<sup>+</sup> is formed by the removal of H<sup>+</sup> (proton) from the complex, it is more reactive than the reacting complex and hence undergoes S<sub>N</sub><sup>1</sup> mechanism by a slow step to lose Cl<sup>-</sup> ion and form a five coordinated intermediate species.

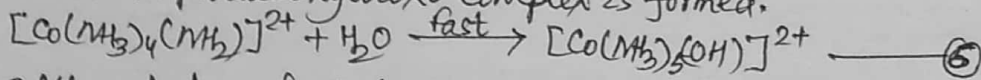


Above step is rate determining step and unimolecular. Thus,

Rate(r) = k<sub>1</sub>[Co(NH<sub>3</sub>)<sub>4</sub>(NH<sub>2</sub>)Cl]<sup>+</sup> = k<sub>1</sub> × K [Co(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup> [OH<sup>-</sup>] / [H<sub>2</sub>O] ——— (4)

∴ Rate(r) = K<sub>B</sub>[Co(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup> [OH<sup>-</sup>] (where K<sub>B</sub> = k<sub>1</sub> K / [H<sub>2</sub>O]) ——— (5)

The intermediate species formed as above reacts with the free H<sub>2</sub>O molecules and hence the product hydroxo complex is formed.

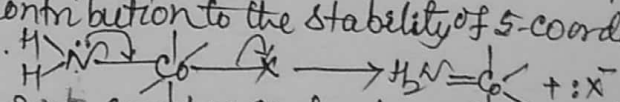


Although base hydrolysis reaction involves an S<sub>N</sub><sup>1</sup> mechanism (formation of 5-coordinated intermediate), but the order of reaction is 2.

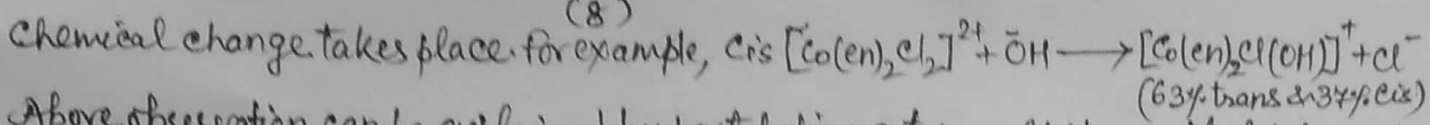
Evidences in favour of S<sub>N</sub><sup>1</sup>CB mechanism: The base hydrolysis of Co(III) complexes are generally very much faster than acid hydrolysis, i.e., K<sub>B</sub> ≫ K<sub>A</sub>. The fact which clearly opposes a simple S<sub>N</sub><sup>2</sup> mechanism and therefore provides evidence in favour of the S<sub>N</sub><sup>1</sup>CB mechanism. The validity of a S<sub>N</sub><sup>1</sup>CB mechanism can be studied in terms of following aspects:

(i) The acid-base behaviour of the reacting complex: It has been observed that rate of H<sup>+</sup> transfer from reacting complex (Bronsted base) to OH<sup>-</sup> in many complexes, such as [Co(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup>, [Co(en)<sub>2</sub>(NH<sub>3</sub>)Cl]<sup>2+</sup> is nearly 10<sup>5</sup> times faster than the rate of hydrolysis. Thus, a reacting complex with no proton (i.e., no N-H) hydrogen should react with OH<sup>-</sup> ligand much more slowly and the rate of reaction should be independent of [OH<sup>-</sup>]. In the absence of an acidic proton (H<sup>+</sup>) on non-leaving ligands in the complexes, an S<sub>N</sub><sup>1</sup>CB mechanism is not possible. The failure of such complexes to proceed a faster base hydrolysis supports the S<sub>N</sub><sup>1</sup>CB mechanism, and it can be said that the acid-base properties of the complexes are more important to the rate of reaction than the nucleophilic properties of OH<sup>-</sup> ligand.

(ii) The reactivity & stability of intermediate species: Since the coordinated amines have very low acidity, the concentration of the conjugate base is a very small portion of the total concentration of the complex. Thus, its reactivity is very much greater by a factor far in excess of the simple ratio of K<sub>B</sub>/K<sub>A</sub>. Rate of reaction of [Co(NH<sub>3</sub>)<sub>4</sub>(NH<sub>2</sub>)Cl]<sup>+</sup> must be 10<sup>6</sup> times greater than that of [Co(NH<sub>3</sub>)<sub>5</sub>Cl]<sup>2+</sup>. Two features of the CB have been considered to explain its reactivity: (a) The CB has a charge, one unit less positive than the starting complex. But the charge effect cannot account for the enormous rate difference involved. (b) It has been proposed that the amide (NH<sub>2</sub>) ligand could labilise the leaving group by a combination of electron repulsion in the ground state and a π-bonding contribution to the stability of 5-coordinate intermediate. However, it is not certain.



(iii) The structure of 5-coordinated intermediate species: It has been observed that in the base hydrolysis reaction of Co(III) ammine complexes, there is considerable stereo-

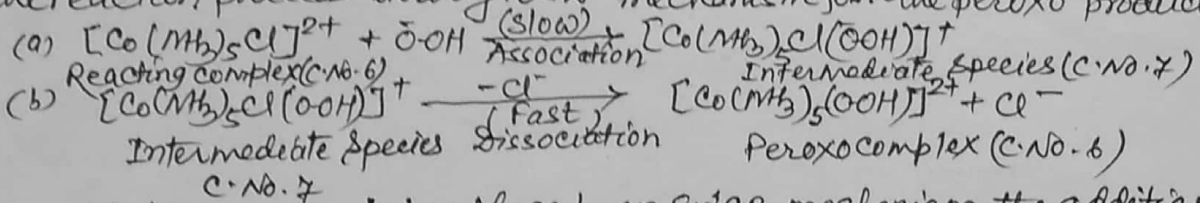


Above observation can be explained by postulating a trigonal bipyramidal intermediate species, upon which the attack of water ( $\text{H}_2\text{O}$ ) can take place in different ways, each of which leading to one of these isomers. If loss of ligand from conjugate base results in the formation of a square pyramidal intermediate species, it seems more likely that there would be complete retention of stereochemistry. The trans-configuration is, in fact, fully retained in the product.

(iv) Base hydrolysis in presence of nucleophilic reaction: The reaction of  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  &  $\text{OH}^-$  ion in aqueous solution of  $\text{H}_2\text{O}_2$  is studied. When  $\text{H}_2\text{O}_2$  is added to the reaction mixture, a decrease in the rate constant is observed. It is found addition of 0.018 M  $\text{H}_2\text{O}_2$  to a reaction mixture containing 0.029 M  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  & 0.029 M  $\text{OH}^-$  in equal amounts, a decrease in the value of rate constant by a factor of 3.6 is obtained, i.e.,  $k_A/k_B = 3.6$  (where  $k_A$  = rate constant in the absence of  $\text{H}_2\text{O}_2$ ,  $k_B$  = rate constant in the presence of  $\text{H}_2\text{O}_2$ ). This can be explained as follows:

Since peroxo ( $\text{O-OH}$ ) ion is a weaker base, but a better nucleophile towards metal ions than  $\text{OH}^-$  ion, the reaction of  $\text{H}_2\text{O}_2$  with  $\text{OH}^-$  reduces the concentration of  $\text{OH}^-$  ion and increase that of  $\text{H}_2\text{O}$ .  $\text{OH}^- + \text{H}_2\text{O}_2 \longrightarrow \text{H}_2\text{O} + \text{O-OH}^-$ .

Since the  $\text{O-OH}^-$  ion is better nucleophile as compared to  $\text{OH}^-$  ion, addition of  $\text{H}_2\text{O}_2$  should increase the rate of base hydrolysis reaction as compared to  $\text{OH}^-$  if the reaction proceeds through  $\text{S}_\text{N}2$  mechanism from the peroxo product.

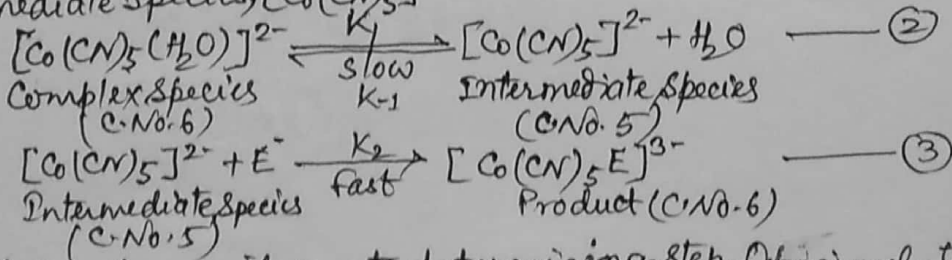


If the reaction takes place by an  $\text{S}_\text{N}1\text{CB}$  mechanism, the addition of  $\text{H}_2\text{O}_2$  to the reaction mixture should reduce the rate of base hydrolysis compared to  $\text{OH}^-$ . Because of the reduction in the concentration of  $\text{OH}^-$  ions, rate of reaction decreases. Experimental data show an agreement with the  $\text{S}_\text{N}1\text{CB}$  mechanism.

Anation reactions: Nucleophilic substitution reactions in which  $\text{H}_2\text{O}$  molecule present in the coordination sphere of a complex species is replaced by an anionic ligand is called anation reaction. for example,  $[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-} + \text{E}^- \longrightarrow [\text{Co}(\text{CN})_5\text{E}]^{3-} + \text{H}_2\text{O}$   
 is anation reaction in which  $\text{H}_2\text{O}$  is the leaving ligand and  $\text{E}^-$  ion is the entering ligand.

An anation reaction can be considered as the reverse of acid hydrolysis reaction (aquation reaction), in which L is leaving ligand &  $\text{H}_2\text{O}$  is the entering ligand. shown below:  $[\text{MA}_5\text{L}] + \text{H}_2\text{O} \longrightarrow [\text{MA}_5(\text{H}_2\text{O})] + \text{L}$

Mechanism: The anation reaction (1) given above proceeds by a purely limiting  $\text{S}_\text{N}1$  mechanism with the formation of sufficiently long lived 5-coordinate intermediate species,  $[\text{Co}(\text{CN})_5]^{2-}$



First step (2) is slow, so it is rate determining step. Obviously, the rate of reaction (1) is given as:

(9)

$$\text{Rate} = \frac{d[\text{Co}(\text{CN})_5\text{E}]}{dt} = k [\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-} \quad \text{--- (4) [where } k = \frac{k_1 k_2 [\text{E}^-]}{k_{-1} [\text{H}_2\text{O}] + k_2 [\text{E}^-]} \text{]}$$

values of  $k_1$  and  $k_{-1}/k_2$  can be obtained from a graph of  $1/k$  against  $1/[\text{E}^-]$  for various concentration of  $\text{E}^-$ . For  $[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$ ,  $k_1$  was found to be nearly constant at constant ionic strength, and was very much nearly the same as the rate constant found for the exchange of coordinated water with  $\text{H}_2\text{O}$ .

Kinetic studies of the reacting complex,  $[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-}$  in aqueous solution show that there are bimolecular reactions with a rate which shows dependence on the concentration of reacting complex & incoming ligand ( $\text{E}^-$ ). Since in aqueous solution, water ( $\text{H}_2\text{O}$ ) also behave as ligand, and hence  $\text{E}^-$  competes of ~~complex~~ (with the solvent water for the active intermediate species  $[\text{Co}(\text{CN})_5]^{2-}$ , the rate of formation of complex,  $[\text{Co}(\text{CN})_5\text{E}]^{3-}$  will be dependent on the concentration of  $\text{E}^-$  also. If the ligand ( $\text{E}^-$ ) is present in high concentration, the rate of substitution of water no longer depends on the concentration of  $\text{E}^-$ . The rate of formation of product,  $[\text{Co}(\text{CN})_5\text{E}]^{3-}$  at this concentration should be equal to the rate of formation of intermediate species species,  $[\text{Co}(\text{CN})_5]^{2-}$  and also equal to the rate of formation of intermediate species. is given by

$$\frac{d[\text{Co}(\text{CN})_5]^{2-}}{dt} = k_1 [\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-} - k_{-1} [\text{Co}(\text{CN})_5]^{2-} [\text{H}_2\text{O}] - k_2 [\text{Co}(\text{CN})_5]^{2-} [\text{E}^-] \quad \text{--- (5)}$$

At the steady state,  $d[\text{Co}(\text{CN})_5]^{2-}/dt = 0$ . Thus,  $[\text{Co}(\text{CN})_5]^{2-} = k_1 [\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-} / (k_{-1} [\text{H}_2\text{O}] + k_2 [\text{E}^-])$  --- (6)

$$\therefore \frac{d[\text{Co}(\text{CN})_5\text{E}]^{3-}}{dt} = \frac{k_1 k_2 [\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-} [\text{E}^-]}{k_{-1} [\text{H}_2\text{O}] + k_2 [\text{E}^-]} \quad \text{--- (7)}$$

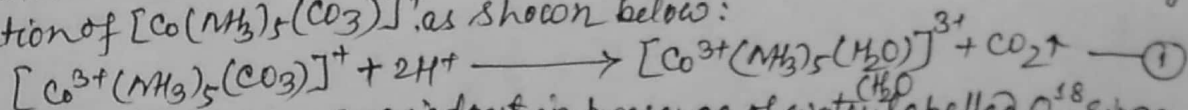
$$\text{If } k_{-1} [\text{H}_2\text{O}] \gg k_2 [\text{E}^-]; \frac{d[\text{Co}(\text{CN})_5\text{E}]^{3-}}{dt} = \frac{k_1 k_2 [\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-} [\text{E}^-]}{k_{-1}} \quad \text{--- (8)}$$

The reaction is second order observed.

$$\text{If } k_2 [\text{E}^-] \gg k_{-1} [\text{H}_2\text{O}]; \frac{d[\text{Co}(\text{CN})_5\text{E}]^{3-}}{dt} = k_1 [\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{2-} \quad \text{--- (9)}$$

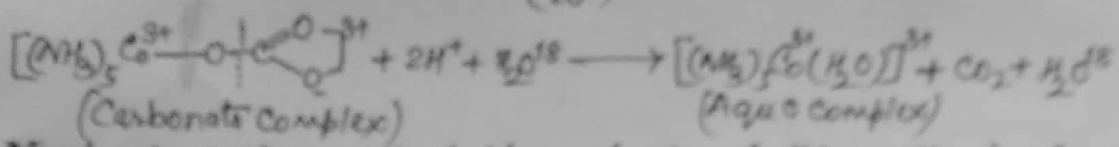
The reaction is first order observed. first order rate constant is equal to that for the dissociation of the aquo complex. If  $\text{E}^-$  represent a group of nucleophiles, the same limiting rate law should be applicable to all.

⇒ Substitution reactions without breaking/cleavage of M-L bond: Generally nucleophilic/ligand substitution reactions undergo metal-ligand cleavage. However, there are a quite few nucleophilic/ligand substitution reactions occur without cleavage of M-L bond for example, Aquation of carbonate complex,  $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]^+$  by excess of acid ( $\text{H}^+$ ) leading to formation of aquo complex,  $[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$  is a nucleophilic substitution reaction in which  $\text{Co}^{3+}-\text{O}$  bond is not broken. This bond remains intact during the aquation of  $[\text{Co}(\text{NH}_3)_5(\text{CO}_3)]^+$  as shown below:



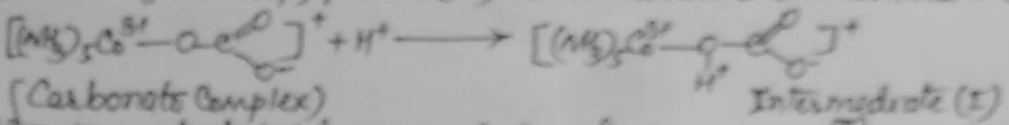
Above reaction (1) was carried out in presence of water labelled  $\text{O}^{18}$ . Since neither aquo complex nor  $\text{CO}_2$  formed in the above reaction contains any  $\text{O}^{18}$ , C-O bond in  $\text{CO}_3^{2-}$  is broken and  $\text{Co}^{3+}-\text{O}$  bond remains unbroken.  $\text{CO}_2$  is produced by the cleavage of C-O bond. In presence of  $\text{H}_2\text{O}^{18}$ , reaction (1) can thus be shown as:



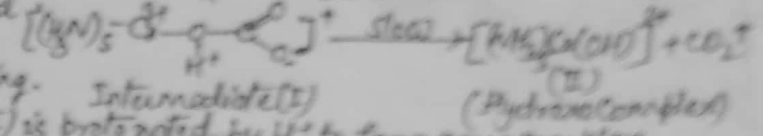


Mechanism: The most probable mechanism for this reaction involves the following steps:

(a) In the first step, proton (H<sup>+</sup>) attacks on the O-atom bonded to Co<sup>3+</sup> forming an intermediate

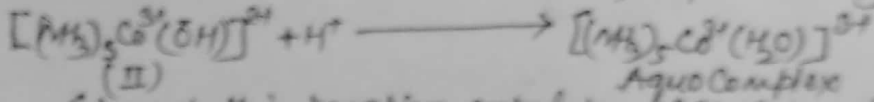


(b) Intermediate (I) loses CO<sub>2</sub> to form hydroxo complex,  $[(NH_3)_5Co^{3+}(OH)]^{2+}$ . In this step, C-O bond is broken and CO<sub>2</sub> gas is liberated



It is slow & step and hence rate determining.

(c) In the final step, hydroxo complex (II) is protonated by H<sup>+</sup> to form aquo complex.



Since in this reaction, expulsion of CO<sub>2</sub> takes place and thus it can be called decarboxylation reaction rather than an acid hydrolysis reaction.

⇒ Nucleophilic/Ligand substitution reactions in Square planar complexes:

Metal atoms/ions of d<sup>8</sup> conf. (e.g. Ni<sup>2+</sup>, Pt<sup>2+</sup>, Pd<sup>2+</sup>, Ir<sup>3+</sup>, Rh<sup>3+</sup>, Co<sup>3+</sup>, Au<sup>3+</sup>) usually form square planar complexes (C.No. 4). Among these, Pt(II) complexes are the most studied complexes due to high stability, relatively easy to synthesize and slower ligand substitution reactions. In square planar complexes, ligand substitution reactions takes place by the following means: (i) Nucleophilic substitution, (ii) Electrophilic substitution, (iii) Oxidative addition followed by reductive elimination.

(i) Nucleophilic substitution: In this reaction, nucleophile (X<sup>-</sup>) replaces ligand of a complex species. e.g.,  $[PtCl(R)(PR_3)_2]^{+} + X^{-} \longrightarrow [PtX(R)(PR_3)_2]^{+} + Cl^{-}$

(Reacting complex) Nucleophile ligand (Product)

(ii) Electrophilic substitution: In this reaction, an electrophile ligand attacks and replaces another ligand (L) of a complex species.

e.g.,  $[PtCl(R)(PR_3)_2]^{+} + HgCl_2 \longrightarrow [PtClHgCl(PR_3)_2]^{+} + R_2HgCl$

(iii) Oxidative addition followed by reductive elimination: In this reaction, fast oxidation of central metal and then elimination of a molecule producing expansion of coordination no.

e.g.,  $[Pt^{II}Cl(R)(PR_3)_2]^{+} + Cl_2 \xrightarrow{oxidative\ addition} [Pt^{IV}Cl_2(R)(PR_3)_2]^{+} \xrightarrow{-RCl} [Pt^{II}Cl_2(R)(PR_3)_2]^{+}$

(O. state of Pt = +2, C.N. = 4) Intermediate (O. state = +4, C.N. = 6) (Reductive elimination) Product (O. state = +2, C.N. = 4)

Here complex (I) is oxidized to intermediate (O. state of Pt = +4 & C.N. = 6) and intermediate gets reduced with the elimination of RCl into (II) in which O. state of Pt = +2, C.N. = 4.

Kinetics of the substitution reaction: The first step of explaining mechanism for reaction is to determine the rate law experimentally let us consider following reaction:  $[ML_2TX] + X \xrightarrow{k_1} [ML_2TX] + X$  [where X = entering ligand, X = leaving ligand/group, T = ligand trans to ligand X]. The rate law of above reaction

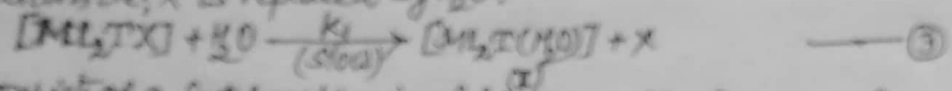
$$Rate = -\frac{d[ML_2TX]}{dt} = k_1[ML_2TX] + k_2[ML_2TX][X] \quad \text{--- (1)}$$

The second term  $k_2[ML_2TX][X]$  corresponds to S<sub>N</sub><sup>2</sup> reaction of X with the formation of 5-coordinated intermediate species, while the first term  $k_1[ML_2TX]$  shows a

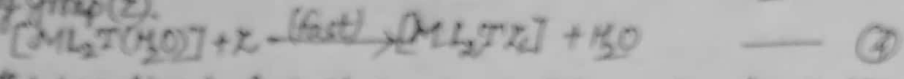
two step reaction in which leaving ligand is first substituted by H<sub>2</sub>O (water) as the rate determining step followed by relatively fast replacement of water by incoming ligand (Z).

The reaction (1) can proceed through the following two paths:

(i) Solvent path: This path proceeds through the following steps: (a) This step consists of slow aquation reaction, i.e. X is replaced by H<sub>2</sub>O.



(b) This step consists of a fast reaction in which the coordinated H<sub>2</sub>O molecule in (3) is replaced by the entering group (Z).

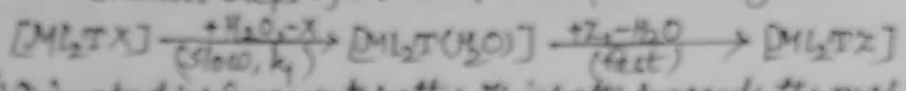


Since this reaction is fast, it is not rate determining step. On the other hand, since reaction (3) is a slow reaction, it is rate determining step. The rate of reaction (3) is given as

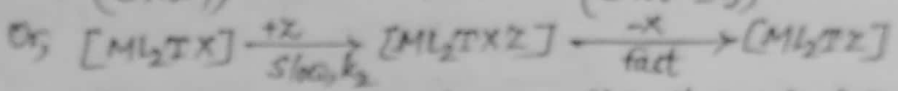
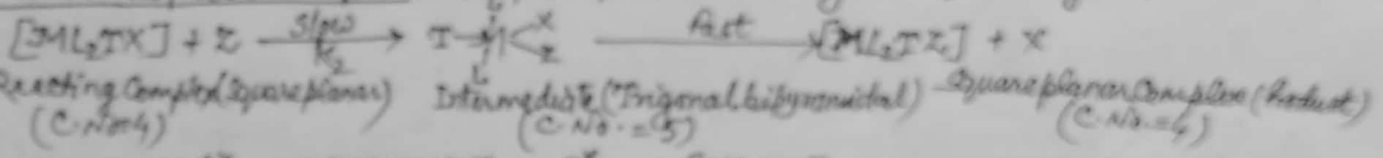
$$r_1 = k_1 [ML_2TX] [H_2O], \text{ Now since } H_2O \text{ is present in large excess, } [H_2O] = \text{a constant.}$$

$$\text{So, } r_1 = k_1 [ML_2TX] \quad \text{--- (5)}$$

The two steps of solvent path represented by reactions (3) & (4) can be combined as follows:



(ii) Direct displacement path: This path proceeds through the following steps:



Since first step is a slow reaction, it is rate determining step. The rate (r<sub>2</sub>) of this slow reaction is given as - r<sub>2</sub> = k<sub>2</sub> [ML<sub>2</sub>TX] [Z] --- (6)

This equation shows that rate determining step is bimolecular and the mechanism involved is S<sub>N</sub><sup>2</sup>.

Above discussion shows that the rate (r) of the substitution reaction (1) is given by

$$r = r_1 + r_2 = k_1 [ML_2TX] + k_2 [ML_2TX] [Z] = [ML_2TX] \{ k_1 + k_2 [Z] \}$$
$$= [\text{Complex}] \{ k_1 + k_2 (\text{entering group}) \} \quad \text{--- (7)}$$

This relation shows that the substitution reactions in square planar complexes follow a two-term rate law.

In relation (7), k<sub>1</sub> is the first order rate constant for solvent controlled reaction and k<sub>2</sub> is the second order rate constant for reaction with Z and corresponds to S<sub>N</sub><sup>2</sup> mechanism.

Factors affecting the rate of substitution reactions in square planar complexes: Some of the important factors which affect the rate of substitution reactions in square planar complexes:

(1) Steric effect: Cis blocking is more effective than the trans blocking. This result supports the assumption that the intermediate formed during S<sub>N</sub><sup>2</sup> mechanism has trigonal bipyramidal geometry. In [Pt(dien)Cl]<sup>+</sup>, the four Cl groups are halved above the plane and block the access to central metal. Thus, it is a hindered system. The reaction of hindered systems is largely dissociative while that of unhindered e.g. [Pt(dien)Cl]<sup>+</sup> is associative.

(2) Effect of leaving group: It is observed that the rate of reaction decrease in the order of the leaving group X<sup>-</sup> of complex species [Pt<sup>2+</sup>(dien)X]<sup>+</sup> by NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, SCN<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Cl<sup>-</sup>.

In the square planar complex [Pt(dien)X]<sup>+</sup> three coordination positions are always occupied by the inert dien & fourth by X (maybe NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup> etc).

(3) Effect of solvent: The order k<sub>2</sub> values for solvents viz DMSO, H<sub>2</sub>O, EtOH, MeOH etc is: DMSO > H<sub>2</sub>O > MeOH > EtOH. While the order of reactivity for non-conductivity solvents has been found as: CCl<sub>4</sub> > CH<sub>2</sub>Cl<sub>2</sub> > m-cresol > tert-butanol > ethyl acetate > acetone > DMF. The exchange reaction: trans [Pt(Ph)<sub>2</sub>Cl]<sup>+</sup> + Cl<sup>-</sup> → [Pt<sup>2+</sup>(Ph)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> + Cl<sup>-</sup> has been studied.