

M.Sc Semester I
Paper I, Inorganic Chemistry



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**TOPIC:- Valence Bond (VBT) And Crystal
Field (CFT) Applications**

.2.2 Valence Bond (VBT) And Crystal Field (CFT) Applications

(a) VBT Application

According to VBT Octahedral Complex are of two types:

- i. Outer-Orbital Complexes which involve sp^3d^2 hybridisation.
- ii. Inner-Orbital Complexes which involve d^2sp^3 hybridisation.

The two d-orbitals involved in sp^3d^2 and d^2sp^3 hybridisation are dx^2-y^2 and dz^2 eg set orbitals.

1. Outer-Orbital Octahedral Complexes

Outer-orbital octahedral complexes (sp^3d^2 hybridisation) are generally labile for example the octahedral complexes of $Mn^{2+}(3d^5)Fe^{2+}$, $Fe^{3+}(3d^5)Co^{2+}(3d^7)Ni^{2+}(3d^8)Cu^{2+}(3d^9)$ and Cr^{2+}

$(3d^4)$ exchange ligands rapidly and hence are labile. This is because, the use of outer d-orbitals does not make effective overlap between metal and ligand orbitals resulting in weaker bonds.

2. Inner-Orbital Octahedral Complexes

The six d^2sp^3 hybrid orbitals are filled with the six electron pairs denoted by the 6 ligands. d^n electrons of the central metal will occupy d_{xy} , d_{yz} and d_{xz} orbitals. These complexes are inert as the use of inner d-orbitals results in an effective overlap between metal

and ligand orbitals giving stronger bonds. Inner orbital octahedral complexes are given in the Table 6.1 which explain the following observations:

- a. In the labile inner-orbital octahedral complexes there is at least one d-orbital of t_{2g} set empty, so that this empty d-orbital may be used to accept the electron pair from the incoming ligand in forming the transition state with coordination number seven (unstable), which finally stabilise in to an octahedral complex (Coordn. No. 6), removing one ligand (Fig 6.1).

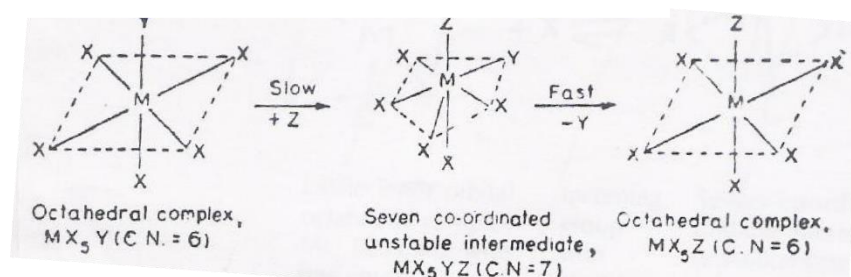


Fig. 6.1

- b. In the inert-orbital octahedral complexes every d-orbital of t_{2g} set (i.e. d_{xy} , d_{yz} and d_{xz}) contains at least one electron, and have no vacant orbital to link an extra ligand.

Table 6.1 Distribution of d^n -electrons in various t_{2g} orbitals for labile and inert inner-orbital octahedral complexes (according to VBT)

Type of the complex	d^n configuration	Distribution of d^n electron (shown by arrows) in t_{2g} orbitals. Electrons shown by crosses in e_g orbitals have been donated by six ligands to enter d^2sp^3 hybrids and are in opposite spins.									Example of central metal ions
		d					s	p			
		t_{2g}			e_g			px	py	pz	
		xy	yz	zx	x^2-y^2	z^2					
inner orbital labile octahedral complexes	d^0				xx	xx	xx	xx	xx	xx	Sc(+3), Y(+3), rare earth (+3), Te(+4), Zr(+4), Hf(+4), Ce(+4), Th(+4), Nb(+5), Ta(+5), Mo(+6), W(+6)
	d^1	↑			xx	xx	xx	xx	xx	xx	Ti(+3), V(+4), Mo (+5), W Re(+6)
	d^2	↑	↑		xx	xx	xx	xx	xx	xx	Ti(+2), V(+3), Nb (+3), Ta(+3), W(+4), Re(+5), Ru(+6)
inner orbital inert octahedral complexes	d^3	↑	↑	↑	xx	xx	xx	xx	xx	xx	V(+2), Cr(+3), Mo(+3), W(+3), Mn(+4), Re(+4)
	d^4	↓↑	↑	↑	xx	xx	xx	xx	xx	xx	$[\text{Cr}(\text{CN})_6]^{4-}$, $[\text{Mn}(\text{CN})_6]^{1-}$ Re(+3), Os(+3), Ir(+4)
	d^5	↓↑	↓↑	↑	xx	xx	xx	xx	xx	xx	$[\text{Mn}(\text{CN})_6]^{4-}$, Re(+2), $[\text{Fe}(\text{CN})_6]^{3-}$ Ru(+3), Os(+3), Ir(+4)
	d^6	↓↑	↓↑	↓↑	xx	xx	xx	xx	xx	xx	$[\text{Fe}(\text{CN})_6]^{4-}$, Ru(+2), Os(+2), Co(+3) (except Co Fe_3^{4-}) Rh (+3), Ir (+3)

Table 6.2 Loss in CFSE, E_{α} (in the units of Dq) in the formation of a pentagonal bipyramidal intermediate in octahedral substitution reactions on the basis of S_N2 associated mechanism

SN2 association mechanism Octahedral (oct.)→Pentagonal bipyramidal (pent.bipy.)						
(C.N. = 6)			(C.N. = 7)			
d^n ion	Strong ligand field (spin-paired or low-spin complexes)			Weak ligand field (spin-paired or low-spin complexes)		
	Oct. (C.N.= 6)	pent.bipy. (C.N.= 7)	E_{α}	Oct. (C.N.= 6)	pent.bipy. (C.N.= 7)	E_{α}
d^0	0 Dq	0 Dq	0 Dq	0 Dq	0 Dq	0 Dq
d^1	4	5.28	0	4	5.28	0
d^2	8	10.56	0	8	10.56	0
d^3	12	17.74	-4.26	12	7.74	-4.26
d^4	16	13.02	-2.98	6	4.93	-2.07
d^5	20	18.30	-1.70	0	00	0
d^6	24	15.48	-8.52	4	5.28	0
d^7	18	12.66	-5.34	8	10.56	0
d^8	12	7.74	-4.26	12	7.74	-4.26
d^9	6	4.93	-1.07	6	4.93	-1.07
d^{10}	0	0.00	0	0	0.00	0

Table 6.3 Loss in CFSE, E_{α} (in the units of Dq) in the formation of a pentagonal bipyramidal intermediate in octahedral substitution reactions on the basis of S_N1 associated mechanism

SN1 association mechanism Octahedral (oct.) → Square Pyramidal (Squ. pyi) (C.N. = 6) (C.N. = 5)						
d ⁿ ion	Strong ligand field (spin-paired or low-spin complexes)			Weak ligand field (spin-paired or low-spin complexes)		
	Oct. (C.N.= 6)	pent.bipy. (C.N.=5)	E _α	Oct. (C.N.= 6)	pent.bipy. (C.N.= 5)	E _α
d ⁰	0 Dq	0 Dq	0 Dq	0 Dq	0 Dq	0 Dq
d ¹	4	4.57	0	4	4.57	0
d ²	8	9.14	0	8	9.14	0
d ³	12	10.00	-2.00	12	10.00	-2
d ⁴	16	14.57	-1.43	6	9.14	0
d ⁵	20	19.14	-0.86	0	00	0
d ⁶	24	20.00	-4.00	4	4.57	0
d ⁷	18	19.14	0	8	19.14	0
d ⁸	12	10.00	-2.00	12	10.00	-2
d ⁹	6	9.14	0	6	9.14	0
d ¹⁰	0	0.00	0	0	0.00	0

The value of CFSE mentioned are in the units of Dq and have been given for both the fields viz. strong field and weak field and for both the mechanism (S_N1, and S_N2).

Negative values of E denotes a loss of CFSE when octahedral complex is changed into an activated complex which may be square pyramidal or pentagonal bipyramidal. If the CFSE of the activated complex is greater than that of octahedral complex. E_α has been given zero value which shows that these complexes do not lose CFSE when they are changed into activated complexes.

The octahedral complexes formed by the ions for which there is large loss in CFSE are least labile i.e. such complexes are inert.

On the other hand octahedral complexes given by ions for which there is little or no loss in CFSE are labile i.e. such complexes react rapidly. Thus we see:

- i Both high spin and low spin octahedral complexes of d^0 , d^1 and d^2 ions will react rapidly, i.e. these are labile complexes, in which there is no loss in CFSE.
- ii. According to VBT inner-orbital octahedral complexes of d^3 , d^4 , d^5 , and d^6 ion are inert while these are called low spin or spin paired complexes according to CFT.

CFT predicts that low spin complexes of these ions are also inert whether the mechanism is assumed to be SN^1 or SN^2 in which CFSE values decreases.

The ion with maximum loss of CFSE will form the most inert complex. Thus the order of inertness of low spin complexes formed by d^3 , d^4 , d^5 and d^6 ions is:

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

Loss of CFSE for SN^1 mechanism : $-4.00 > -2.00 > -1.43 > -0.86$ Loss
of CFSE for SN^2 mechanism : $-8.52 > -4.26 > -2.98 > -1.70$

The order of reactivity will be reverse of the above i.e. the order of reactivity will be $d^6 > d^3 > d^4 > d^5$ it is supported by the following facts:

- i. High spin octahedral complexes of d^3 ion will react slowly, i.e. these are inert complexes because for this ion there is substantial loss in CFSE whether the substitution mechanism is SN^1 or SN^2 .

- ii. High spin octahedral complexes of d^5 ion react rapidly i.e. these are labile complexes, since there is no loss in CFSE.
- iii. Both high spin and low spin octahedral complexes of d^8 ion are inert.

According to VBT d^8 ion [$3d_{xy}^2, 3yz^2, 3dxz^2, 3d(x^2-y^2), 3dz^2$] will form outer orbital complexes and will be labile. Therefore in case d^8 ion VBT & CFT gives different predictions.

- iv. Both high spin and low spin octahedral complexes of d^{10} ion are labile.