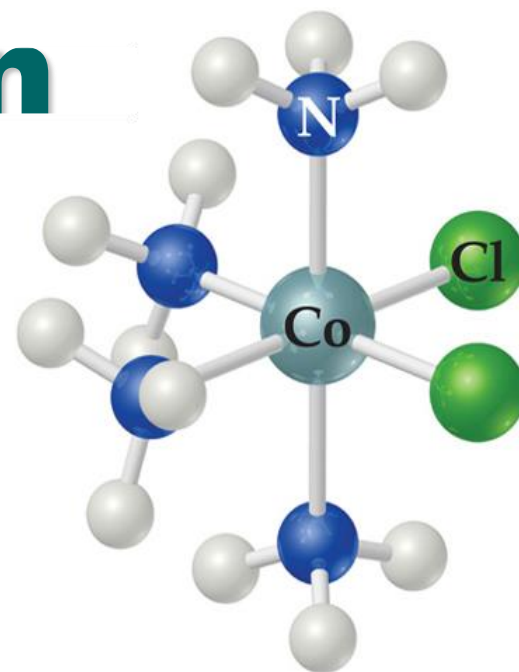


Chemistry of coordination complexes



Inorganic compounds

- **Simple salts**



- **Addition compounds** ---- formed when stoichiometric amounts of two or more stable compounds join together

Two types

- ❖ **Double salts**

Lose identity in solution



- ❖ **Coordination compounds**

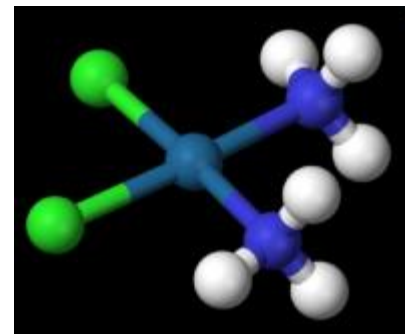
Retain identity in solution



Coordination Complex

**structure consisting of a central atom or ion,
bonded to a surrounding array of ligands**

atom within a ligand that is directly bonded
to the central atom or ion ---- **donor atom**



a ligand donates at least one pair of electrons to the central
atom/ion

compounds that contain a coordination complex -----
coordination compounds

Ligands

classified according to the number of donor atoms

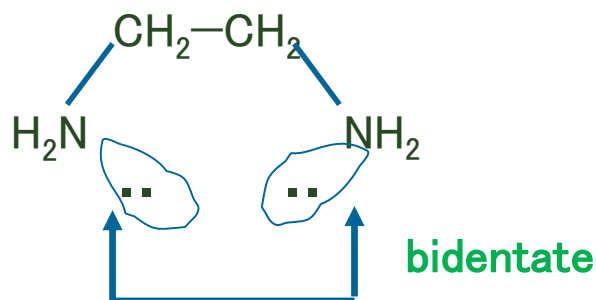
- monodentate = 1
- bidentate = 2
- tetradentate = 4
- hexadentate = 6

chelating agents

Monodentate

H_2O , CN^- , NH_3 , NO_2^- , SCN^- , OH^- , X^- (halides), CO , O^{2-}

- Some ligands have more than one coordination site — they form chelate complexes
- number electron donation sites by which the ligand “bites” the metal is called **denticity** of the ligand



STRUCTURE OF METAL COMPLEXES

Werner's work

- **Coordination complexes were long known – although not understood e.g. Prussian blue and copper vitriol.**
- **The key breakthrough occurred when Alfred Werner proposed his theory in 1893 to predict structure of these complexes.**
- **His brilliance showed the way to predict right structure even before the electron is known (was discovered by Thompson in 1896)**
- **He proposed two different valencies for coordination complexes**

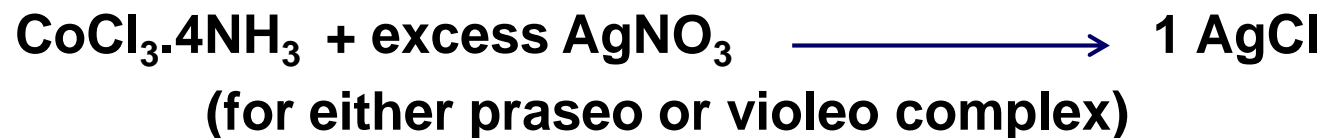
Metal Complexes used by Werner

Four different cobalt ammonium complexes were known, which were used by **Werner** to establish his theory

<u>Complex</u>	<u>Colour</u>	<u>early name</u>
$\text{CoCl}_3 \cdot 6\text{NH}_3$	Yellow	<i>Luteo</i> complex
$\text{CoCl}_3 \cdot 5\text{NH}_3$	Purple	<i>Purpureo</i> complex
$\text{CoCl}_3 \cdot 4\text{NH}_3$	Green	<i>Praseo</i> complex
$\text{CoCl}_3 \cdot 4\text{NH}_3$	<i>Violet</i>	<i>Violeo</i> complex

Experiments done by Werner

Treatment with excess AgNO_3 solution: resulted in different amount of precipitated AgCl



Werner's Conclusion

central metal atom in complex has two types of valencies,

Primary valency and **Secondary valency**.

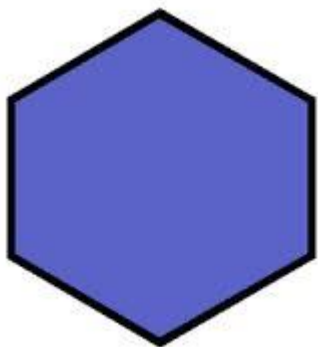
Primary valency: nondirectional

Secondary valency: directional

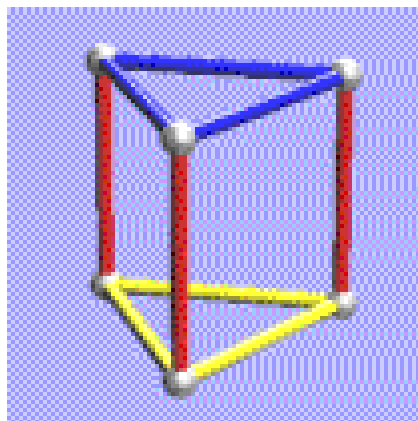
(Coordination number of the complex.

Number of ligand atoms coordinated to metal)

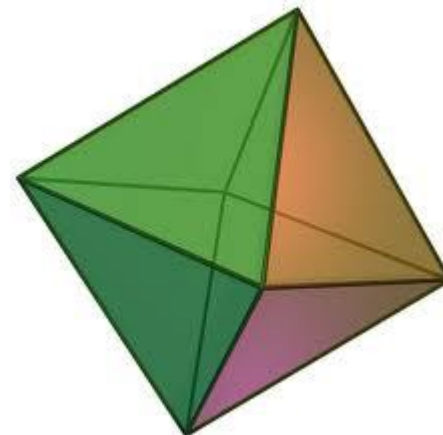
Possible structures - coordination number 6



Hexagonal



Triagonal prism

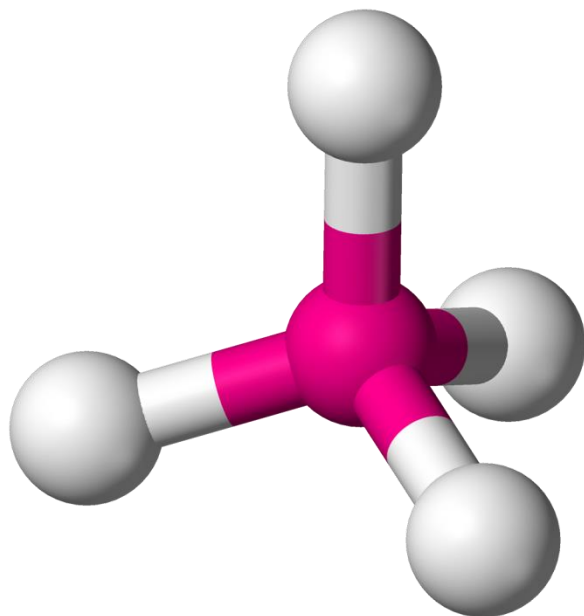


Octahedral

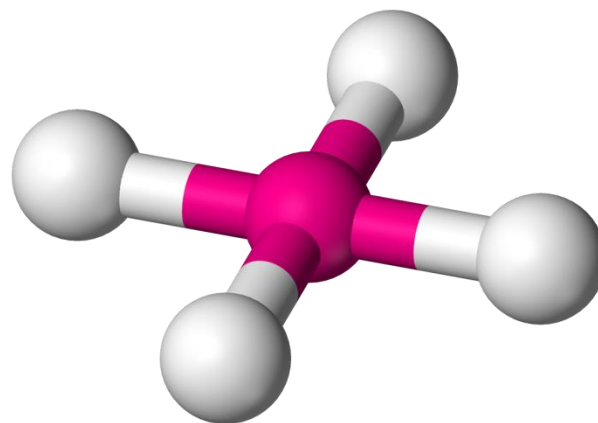
Number of isomers expected and found - coordination number 6

Formula	Planar	Triagonal prism	Octahedral	Experimental
$[MX_6]$				1
$[MX_5Y]$				1
$[MX_4Y_2]$	 	 	 <i>cis</i> <i>trans</i>	2
$[MX_3Y_3]$	 	 	 <i>fac</i> <i>mer</i>	2

Possible structures - coordination number 4



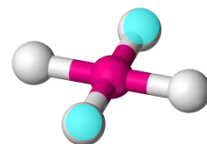
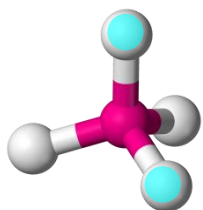
Tetrahedral



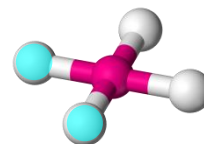
Square planar

No. of isomers expected and found – coordination number 4

Formula	Tetrahedral	square planar	experimental
---------	-------------	---------------	--------------



trans

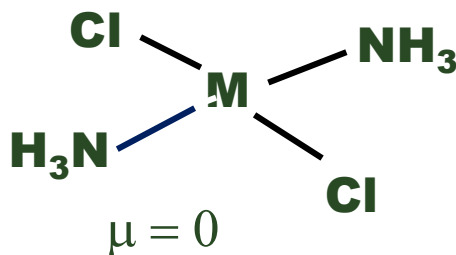
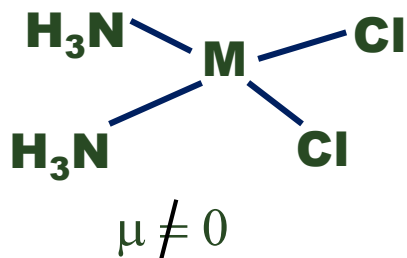


cis

2

- *trans structure has no dipole moment*
- *cis structure has dipole moment*

e.g. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and $[\text{Pd}(\text{NH}_3)_2\text{Cl}_2]$



Summary of Werner's Work

**The central metal atom in complex has two types of valencies,
Primary valency and Secondary valency.**

Primary valencies are ionizable whereas secondary valencies non-ionizable

**In complexes, the ligands are projected in space about the central metal
atom to give a specific shape to the complex.**

Recent methods of studying complexes

Simultaneous measurement of molar conductivity and freezing point depression

Molar conductivity measurement

Depends on (a) concentration of solute

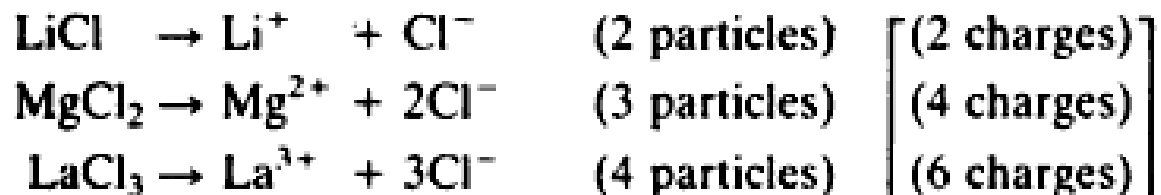
(b) number of charges on the species formed on dissolution

Molar conductivities of salt and complexes (at 0.001M concentration)

			ohm ⁻¹ cm ² mol ⁻¹
LiCl	Li ⁺ Cl ⁻	Total of 2 charges	112.0
CaCl ₂	Ca ²⁺ 2Cl ⁻	Total of 4 charges	260.8
CoCl ₃ .5NH ₃			261.3
CoBr ₃ .5NH ₃			257.6
LaCl ₃	La ³⁺ 3Cl ⁻	Total of 6 charges	393.5
CoCl ₃ .6NH ₃			431.6
CoBr ₃ .6NH ₃			426.9

Cryoscopic measurement

- It involves measurement of how much freezing point is lowered
- Depends on the number of particles present in solution



Establishment of structure of complexes

Formula	Cryoscopic measurement	Molar conductivity	Structure
$\text{CoCl}_3 \cdot 6\text{NH}_3$	4 particles	6 charges	$[\text{Co}(\text{NH}_3)_6]^{3+} \quad 3\text{Cl}^-$
$\text{CoCl}_3 \cdot 5\text{NH}_3$	3 particles	4 charges	$[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} \quad 2\text{Cl}^-$
$\text{CoCl}_3 \cdot 4\text{NH}_3$	2 particles	2 charges	$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ \quad \text{Cl}^-$
$\text{CoCl}_3 \cdot 3\text{NH}_3$	1 particle	0 charge	$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$
$\text{Co}(\text{NO}_2)_3 \cdot \text{KNO}_2 \cdot 2\text{NH}_3$	2 particles	2 charges	$\text{K}^+ \quad [\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4]^-$
$\text{Co}(\text{NO}_2)_3 \cdot 2\text{KNO}_2 \cdot \text{NH}_3$	3 particles	4 charges	$2\text{K}^+ \quad [\text{Co}(\text{NH}_3)(\text{NO}_2)_5]^{2-}$
$\text{Co}(\text{NO}_2)_3 \cdot 3\text{KNO}_2$	4 particles	6 charges	$3\text{K}^+ \quad [\text{Co}(\text{NO}_2)_6]^{3-}$

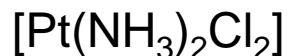
Other methods

Measurement of magnetic moment

Information about the number of unpaired electron spins present in a complex

Possible to decide how the electrons are arranged and which orbitals are occupied

Measurement of dipole moment



cis form have dipole moment

trans form does not have any dipole moment

Single Crystal X-ray diffraction

most powerful and modern technique for the determination of crystal structure

Oak Ridge Thermal Ellipsoid Plot (ORTEP)

Effective Atomic Number

Sidgwick suggested that electron pairs from ligands were added until the central metal was surrounded by the same number of electrons as the next noble gas

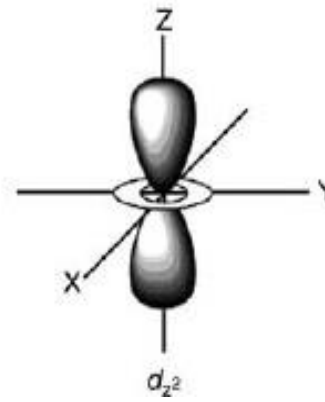
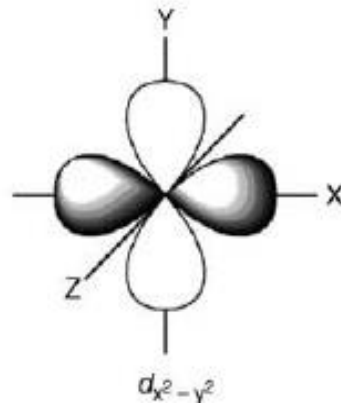
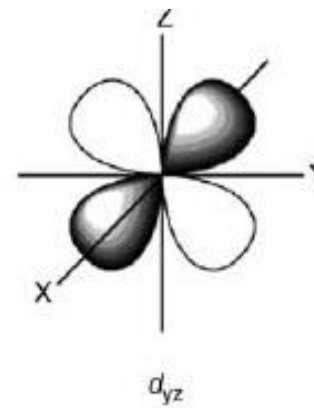
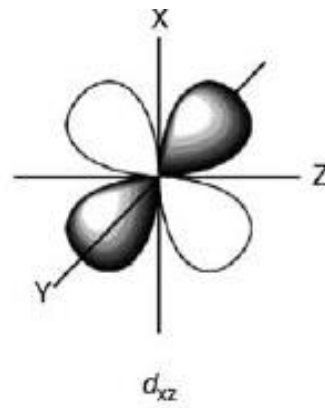
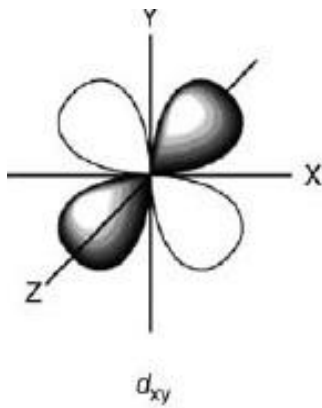
Atom	Atomic number	Complex	Electrons lost in ion formation	Electrons gained by coordination	EAN	
Cr	24	$[\text{Cr}(\text{CO})_6]$	0	12	36	} (Kr)
Fe	26	$[\text{Fe}(\text{CN})_6]^{4-}$	2	12	36	
Fe	26	$[\text{Fe}(\text{CO})_5]$	0	10	36	
Co	27	$[\text{Co}(\text{NH}_3)_6]^{3+}$	3	12	36	
Ni	28	$[\text{Ni}(\text{CO})_4]$	0	8	36	
Cu	29	$[\text{Cu}(\text{CN})_4]^{3-}$	1	8	36	} (Xe)
Pd	46	$[\text{Pd}(\text{NH}_3)_6]^{4+}$	4	12	54	
Pt	78	$[\text{PtCl}_6]^{2-}$	4	12	86	
Fe	26	$[\text{Fe}(\text{CN})_6]^{3-}$	3	12	35	exceptions
Ni	28	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	2	12	38	
Pd	46	$[\text{PdCl}_4]^{2-}$	2	8	52	
Pt	78	$[\text{Pt}(\text{NH}_3)_4]^{2+}$	2	8	84	

Significant number of exceptions where the EAN is not that of a noble gas

If the original metal ion has an odd number of electrons, adding of electron pairs cannot result in noble gas structure

Tendency to attain the noble gas configuration is a significant factor but not a necessary condition for complex formation

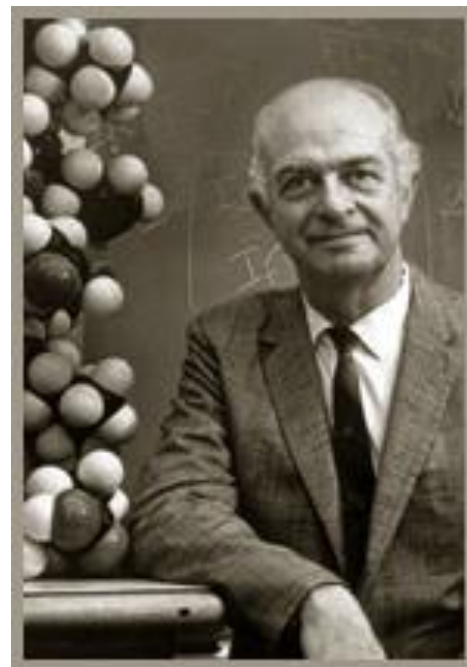
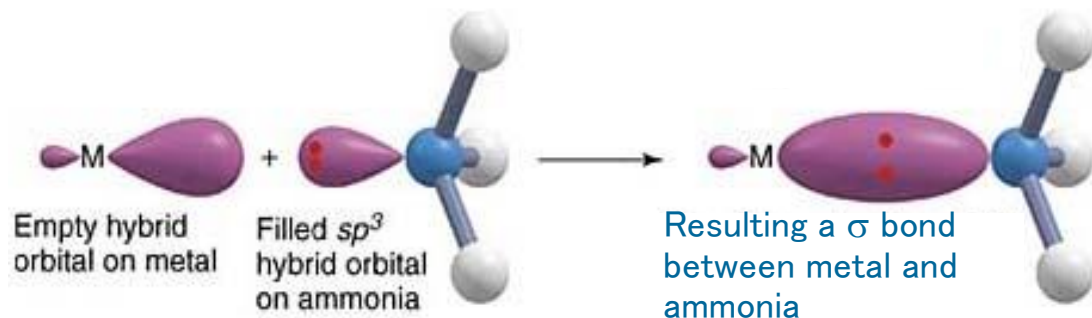
d orbitals



Valence bond theory for coordination complexes

metal form coordination bond with the ligand

bonding is due to donation of a pair of electron
of ligand to metal



Linus Carl Pauling
(1901-1994)

Nobel prizes: 1954, 1962

**VB theory can explain SHAPE and MAGNETIC PROPERTY
of the metal complexes**

Valence Bond Theory

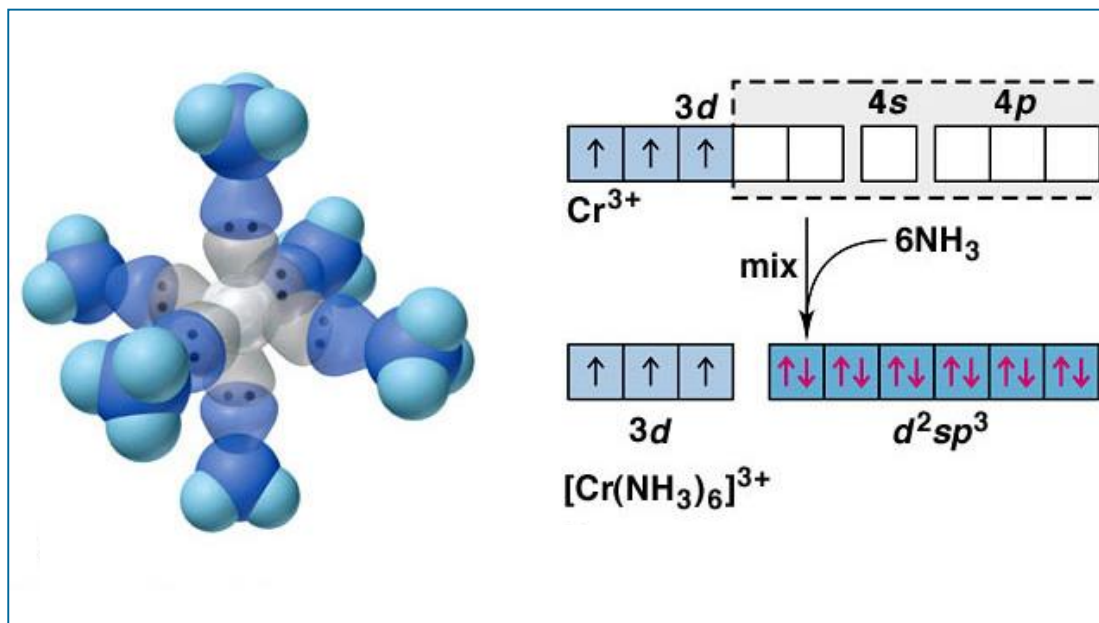
- Metal or metal ion: Lewis acid
- Ligand: Lewis base
- Hybridization of orbitals

<i>C.N. Geometry</i>		<i>Hybrids</i>
4	tetrahedral	sp^3
4	square planar	dsp^2
5	trigonal bipyramidal	dsp^3 or sp^3d
6	octahedral	d^2sp^3 or sp^3d^2

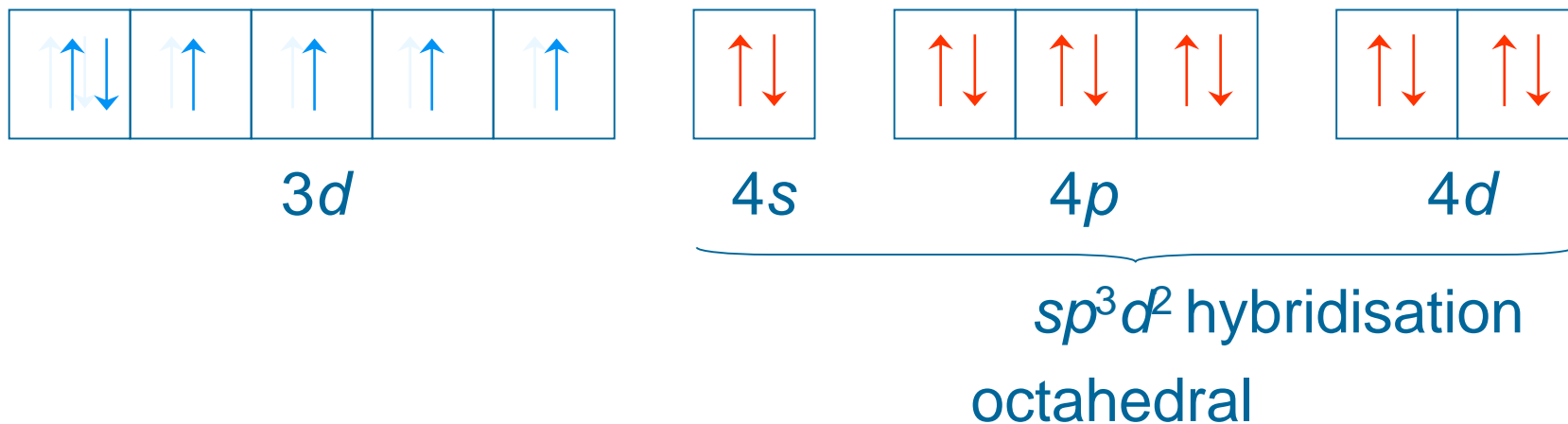
Explanation of structures by VB theory

s, p and d orbitals **mix** to give hybrid orbitals with specific geometries

Octahedral Complex $[\text{Cr}(\text{NH}_3)_6]^{3+}$



Explanation of structures by VB theory

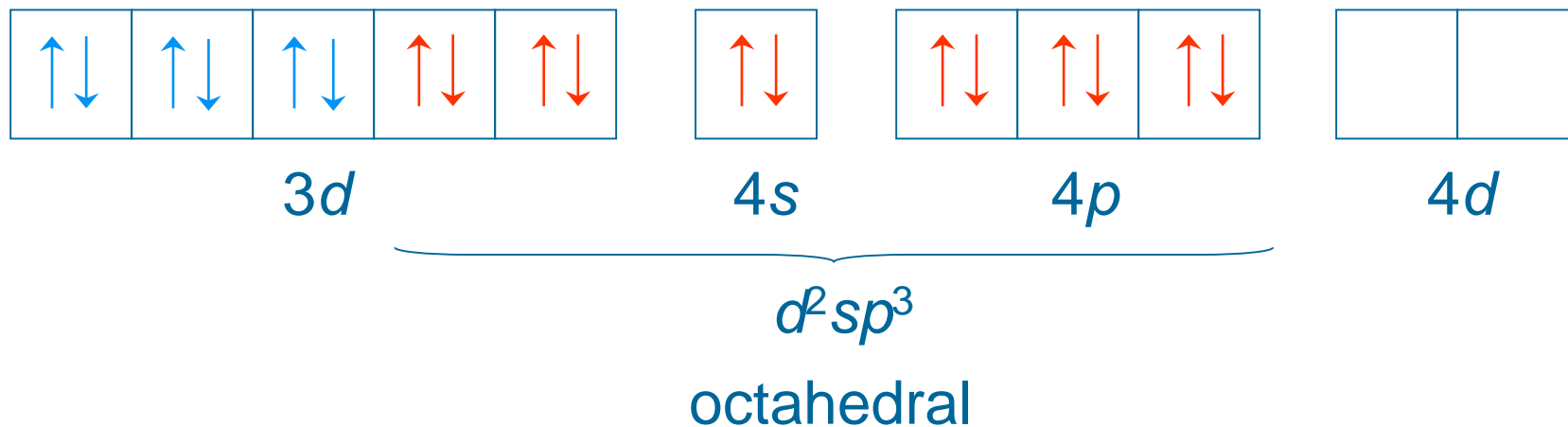


complex is paramagnetic

Explanation of structures by VB theory



Inner orbital complex

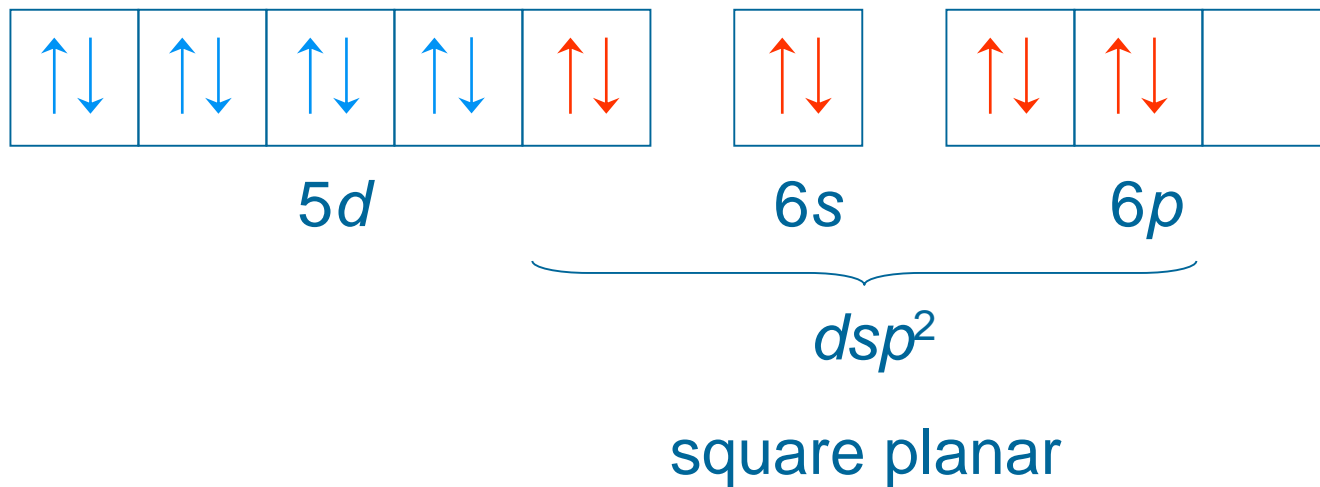


complex is diamagnetic

Explanation of structures by VB theory

$[\text{PtCl}_4]^{2-}$, diamagnetic

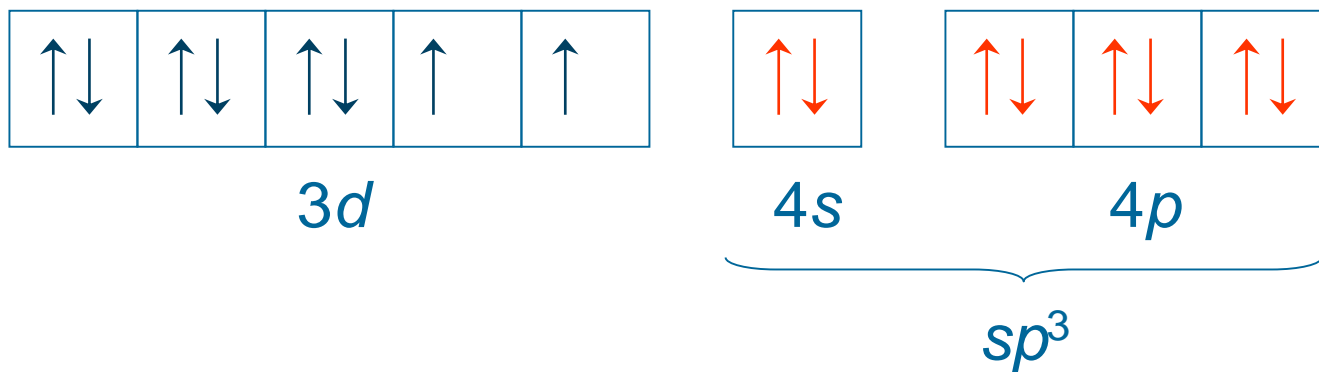
$\text{Pt}^{2+} [\text{Xe}] 4f^{14} 5d^8$



Explanation of structures by VB theory

$[\text{NiCl}_4]^{2-}$, tetrahedral

$\text{Ni}^{2+} [\text{Ar}] 3d^8$



paramagnetic

Limitations of VB theory

- Colour of the metal complex can not be explained
- Can not explain why the magnetic property vary with temperature

Crystal Field Theory

Proposed by Bethe and van Vleck

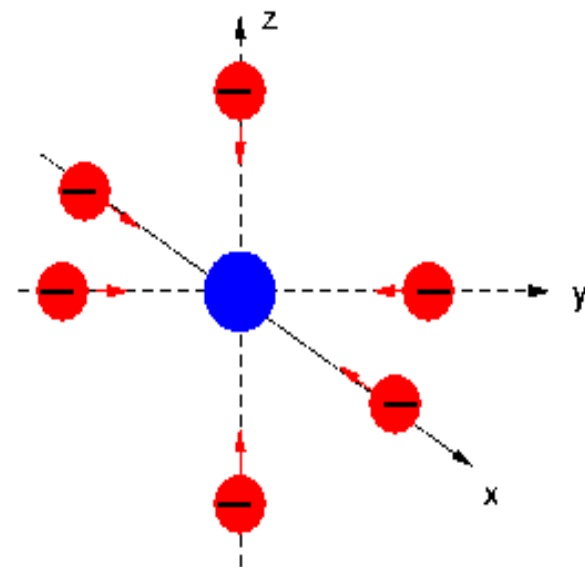
Interaction between metal and ligand is purely electrostatic
i.e., bonding is due to **ion-ion attraction** if ligand is ionic or **ion-dipole attraction** if ligand is neutral

Explain the electronic spectra and magnetism of the transition metal complexes

Assumptions

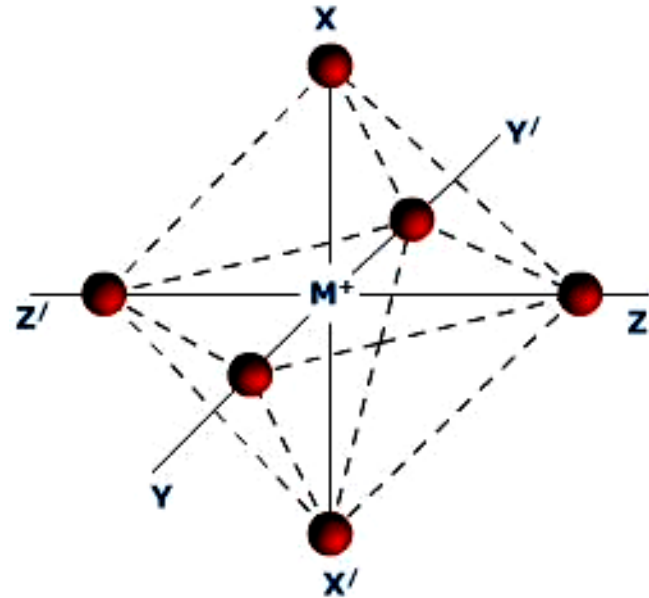
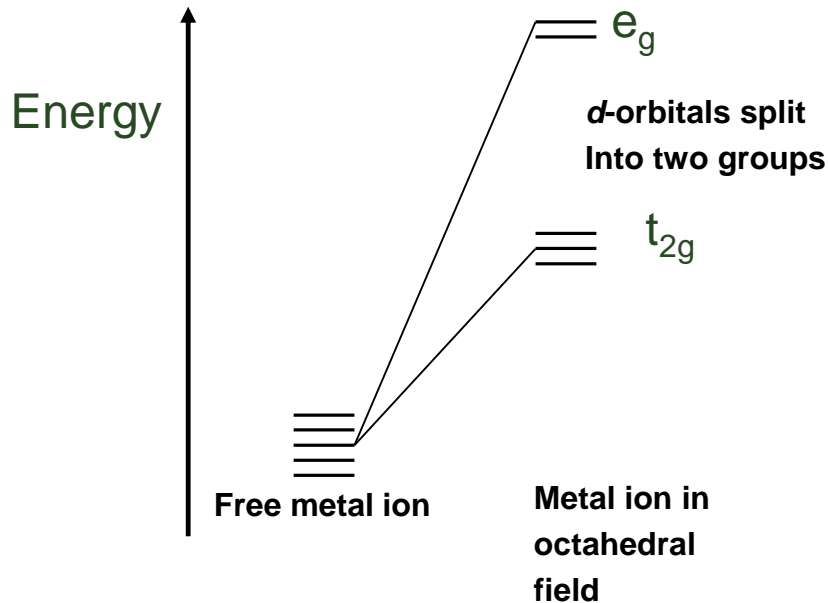
- ❖ The ligands are considered as **point charges**
- ❖ There is **no overlap** between metal and ligand orbitals
- ❖ All the *d* orbitals on the metal have **same energy** in the free atom.
The ligands destroy the degeneracy of these orbitals

Approach of ligands in an octahedral complex



To the metal ion, it looks like negative charges (electrons) are approaching

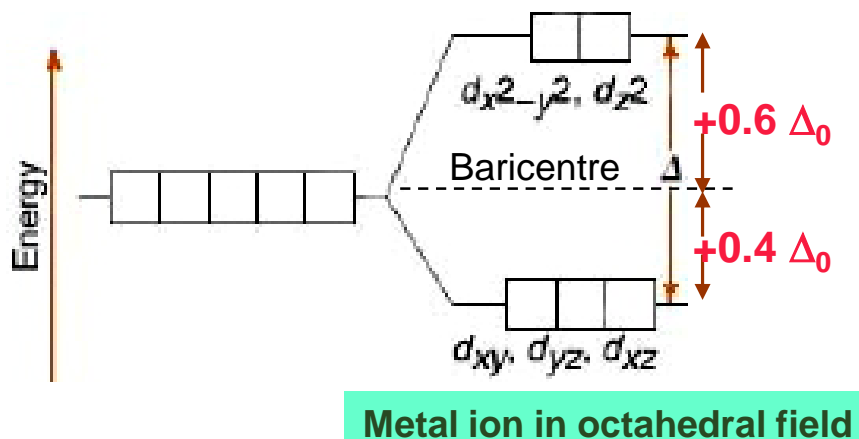
Splitting of d -orbitals in an octahedral field



In an isolated gaseous metal ion, the five d orbitals are **degenerate**

If a **spherically symmetrical field** of negative charges surrounds the metal ion, the d orbitals remain degenerate ----- energy of the orbitals is raised because of the **repulsion** between the field and the electrons on the metal

Energy level of *d* orbitals in an octahedral field



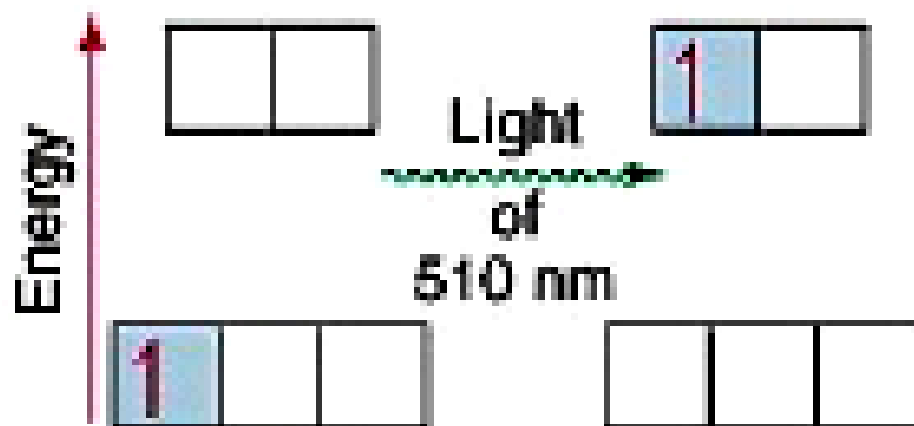
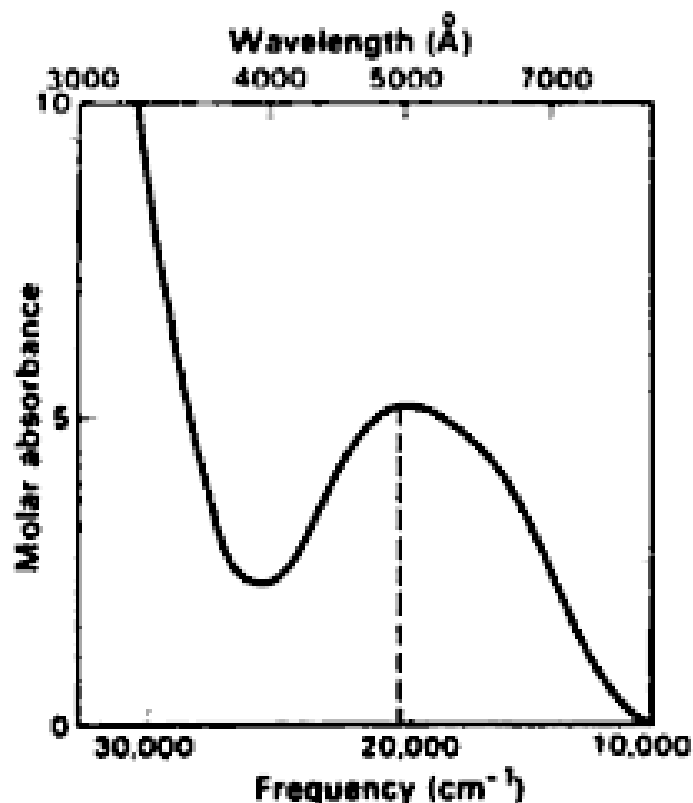
Approach of **six ligands** along *x*, *y*, *z*, *-x*, *-y* and *-z* directions will increase the energy of the $d_{x^2-y^2}$ and d_{z^2} orbitals (which point along the axes) much more than it increases the energy of the d_{xy} , d_{yz} and d_{xz} orbitals (which point between the axes)

Rather than referring to the energy level of an isolated metal atom, the weighted mean of these two sets of perturbed orbitals is taken as the zero ----- **Baricentre**

Difference in energy between the two *d* levels is given either of the symbols Δ_o or **$10Dq$**

e_g orbitals are $0.6\Delta_o$ above the average level and t_{2g} orbitals are $0.4\Delta_o$ below the average

Colour of the complexes



d-d transition gives a single broad peak with maxima at 20300 cm^{-1}

value of Δ_o is **243 kJ/mol**
(1 kJ/mol = 83.7 cm^{-1})

convenient way of measuring Δ_o

UV-visible absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

Crystal Field Stabilization Energy (CFSE)

CFSE is obtained from Δ_o

For $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ the single electron is situated at the t_{2g} level

$$\begin{aligned}\text{CFSE} &= -0.4 \times \Delta_o \\ &= -0.4 \times 243 = -97 \text{ kJ/mol}\end{aligned}$$

For $[\text{Cr}(\text{CN})_6]^{3-}$ what is CFSE if it absorbs at 26280 cm^{-1} ?

All three electrons are situated at the t_{2g} level

$$\begin{aligned}\text{CFSE} &= -3 \times 0.4 \times \Delta_o \\ &= -3 \times 0.4 \times 26280 / 83.7 = -376.77 \text{ kJ/mol}\end{aligned}$$

$$\text{CFSE}_{\text{Oh}} = (-n_{(t_{2g})} \times 0.4 + n_{(e_g)} \times 0.6) \times \Delta_o$$

Magnitude of Δ_0

Depends on following major factors

- Nature of the ligands
- Charge on the central metal ion
- Whether the metal is in the 1st, 2nd or 3rd row of transition elements

Nature of the ligands

Crystal field splitting of various ligands with same metal ion

Complex	Absorption peak	
	(cm ⁻¹)	(kJ mol ⁻¹)
$[\text{Cr}^{\text{III}}\text{Cl}_6]^{3-}$	13 640	163
$[\text{Cr}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$	17 830	213
$[\text{Cr}^{\text{III}}(\text{NH}_3)_6]^{3+}$	21 680	259
$[\text{Cr}^{\text{III}}(\text{CN})_6]^{3-}$	26 280	314

Spectrochemical series

Possible to arrange ligands in a series that reflects their ability to split the d-orbitals

Weak field ligands $\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{Cl}^- < \text{NO}_3^- < \text{F}^- < \text{OH}^-$
 $< \text{EtOH} < \text{oxalate} < \text{H}_2\text{O} < \text{EDTA} < (\text{NH}_3 \text{ and pyridine})$
 $< \text{en} < \text{dipyridyl} < \text{o-phenanthroline} < \text{NO}_2^- < \text{CN}^-$
 $< \text{CO}$ **Strong field ligands**

Ligands which cause only a small degree of crystal field splitting
--- **weak field ligands**

order remain practically constant for different metals

pattern of increasing σ donation

Halide donors $<$ O donors $<$ N donors $<$ C donors

Charge on the central metal ion

Table 7.9 Crystal field splittings for hexa-aqua complexes of M^{2+} and M^{3+}

Oxidation state		Ti	V	Cr	Mn	Fe	Co	Ni	Cu
(+II)	Electronic configuration	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9
	Δ_o in cm^{-1}	–	12 600	13 900	7 800	10 400	9 300	8 500	12 600
	Δ_o in kJ mol^{-1}	–	151	(166)	93	124	111	102	(151)
(+III)	Electronic configuration	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8
	Δ_o in cm^{-1}	20 300	18 900	17 830	21 000	13 700	18 600	–	–
	Δ_o in kJ mol^{-1}	243	226	213	(251)	164	222	–	–

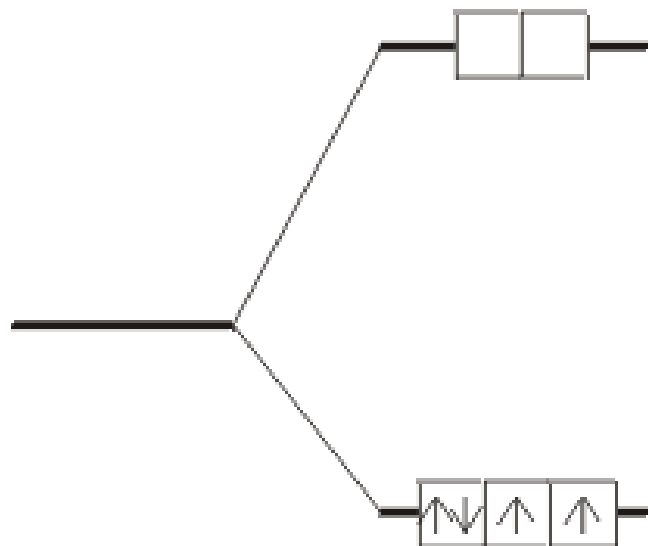
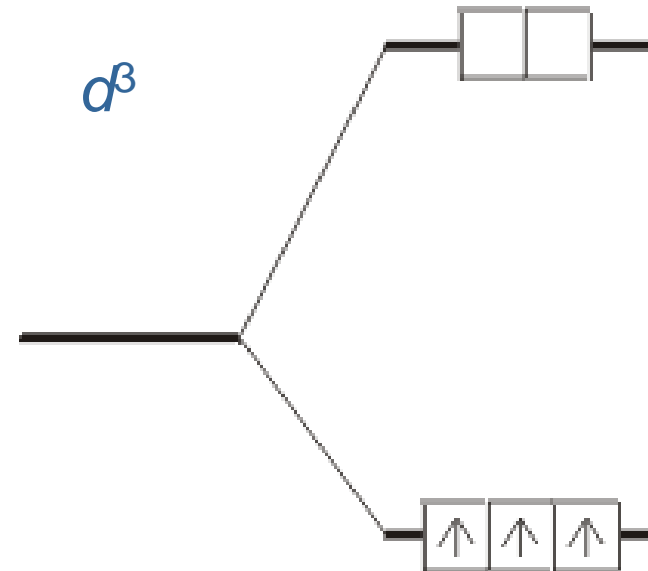
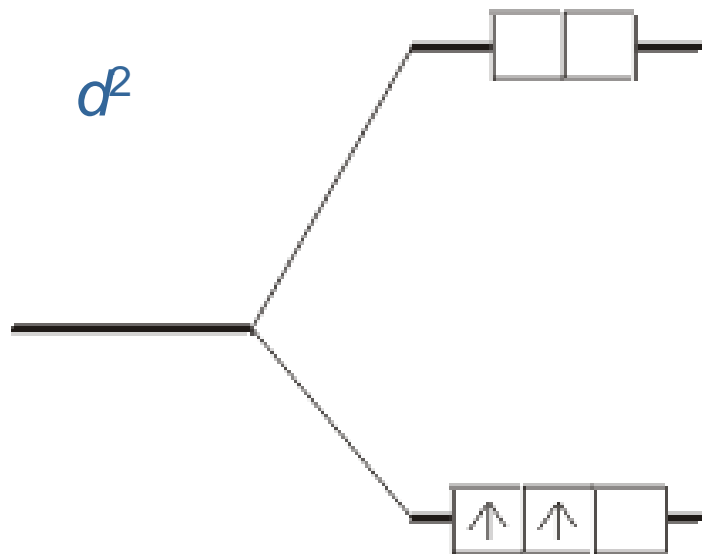
Values for d^4 and d^9 are approximate because of tetragonal distortion.

Whether the metal is in the 1st, 2nd or 3rd row of transition elements

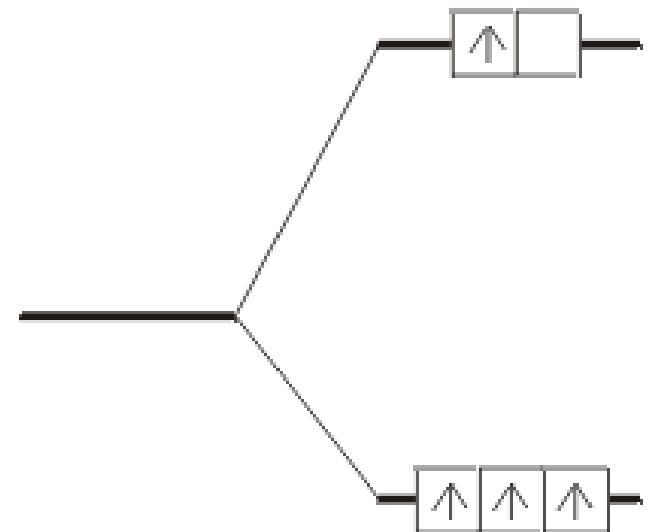
Table 7.10 Δ_o , crystal field splittings in one group

	cm^{-1}	kJ mol^{-1}
$[\text{Co}(\text{NH}_3)_6]^{3+}$	24 800	296
$[\text{Rh}(\text{NH}_3)_6]^{3+}$	34 000	406
$[\text{Ir}(\text{NH}_3)_6]^{3+}$	41 000	490

Distribution of electrons



d^4



Crystal Field Stabilization: Weak Field and Strong Field

For d^4 two configurations are possible (i) $t_{2g}^3 e_g^1$ or (ii) $t_{2g}^4 e_g^0$

Which arrangement occurs for any particular complex depends on whether the energy to promote an electron to the upper e_g level (crystal field splitting Δ_o) is greater than the energy to pair electrons (P) in the lower t_{2g} level

In weak field

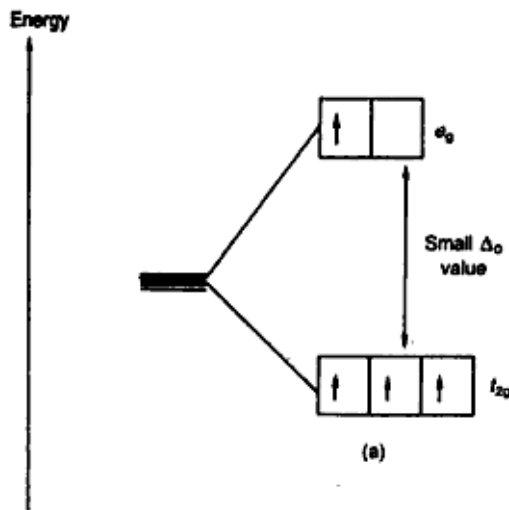
$$CFSE = -3 \times 0.4 \times \Delta_o + 1 \times 0.6 \times \Delta_o = -0.6 \Delta_o$$

In strong field

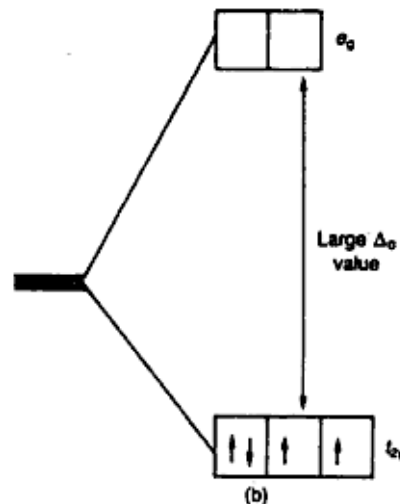
$$CFSE = -4 \times 0.4 \times \Delta_o = -1.6 \Delta_o$$

$$\text{Total SE} = -1.6 \Delta_o + P$$

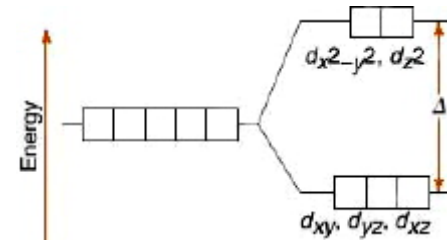
P = pairing energy



(a)



(b)



d^4 high-spin arrangement

d^4 low-spin arrangement

Pairing energy

Depends on two factors

- (i) Electronic repulsion in metal d -orbitals forcing two electrons to occupy same orbital
- (ii) Exchange energy to reverse the spin

For a given metal ion P is constant

CFSE and pairing energy for some complexes

Complex	Configuration	Δ_o (cm^{-1})	P (cm^{-1})	Predicted	Found
$[\text{Fe}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$	d^6	10 400	17 600	high spin	high spin
$[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$	d^6	32 850	17 600	low spin	low spin
$[\text{Co}^{\text{III}}\text{F}_6]^{3-}$	d^7	13 000	21 000	high spin	high spin
$[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+}$	d^7	23 000	21 000	low spin	low spin

CFSE and electronic arrangement of octahedral complexes

Number of d electrons	Arrangement in weak ligand field				Arrangement in strong ligand field			
	t_{2g}	e_g	CFSE Δ_o	Spin only magnetic moment $\mu_s(D)$	t_{2g}	e_g	CFSE Δ_o	Spin only magnetic moment $\mu_s(D)$
d^1	$\uparrow \square \square$	$\square \square$	-0.4	1.73	$\uparrow \square \square$	$\square \square$	-0.4	1.73
d^2	$\uparrow \uparrow \square$	$\square \square$	-0.8	2.83	$\uparrow \uparrow \square$	$\square \square$	-0.8	2.83
d^3	$\uparrow \uparrow \uparrow$	$\square \square$	-1.2	3.87	$\uparrow \uparrow \uparrow$	$\square \square$	-1.2	3.87
d^4	$\uparrow \uparrow \uparrow$	$\uparrow \square$	-1.2 +0.6 = -0.6	4.90	$\uparrow \downarrow \uparrow \uparrow$	$\square \square$	-1.6	2.83
d^5	$\uparrow \uparrow \uparrow$	$\uparrow \uparrow$	-1.2 +1.2 = -0.0	5.92	$\uparrow \downarrow \uparrow \downarrow \uparrow$	$\square \square$	-2.0	1.73
d^6	$\uparrow \downarrow \uparrow \uparrow$	$\uparrow \uparrow$	-1.6 +1.2 = -0.4	4.90	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\square \square$	-2.4	0.00
d^7	$\uparrow \downarrow \uparrow \downarrow \uparrow$	$\uparrow \uparrow$	-2.0 +1.2 = -0.8	3.87	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \square$	-2.4 +0.6 = -1.8	1.73
d^8	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \uparrow$	-2.4 +1.2 = -1.2	2.83	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \uparrow$	-2.4 +1.2 = -1.2	2.83
d^9	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \downarrow \uparrow$	-2.4 +1.8 = -0.6	1.73	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \downarrow \uparrow$	-2.4 +1.8 = -0.6	1.73
d^{10}	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \downarrow \uparrow \downarrow$	-2.4 +2.4 = 0.0	0.00	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow$	$\uparrow \downarrow \uparrow \downarrow$	-2.4 +2.4 = 0.0	0.00

Magnetism

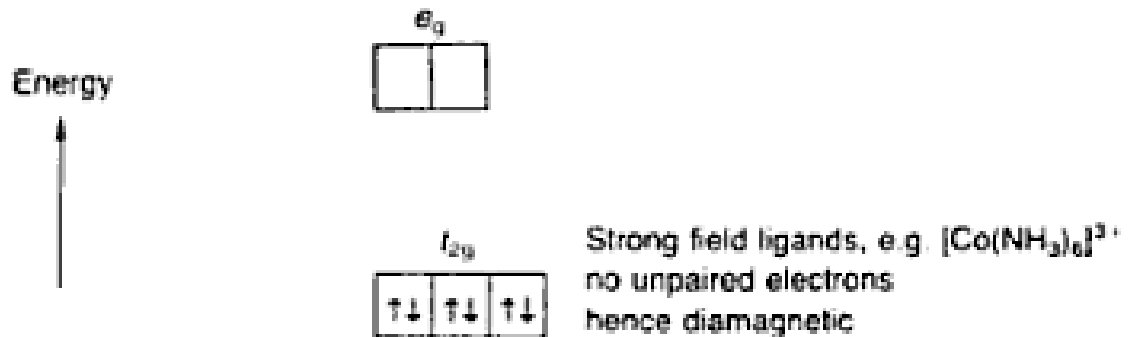
If there is n number of unpaired electrons, spin only magnetic moment,

$$\mu_s = \sqrt{n(n + 2)}$$

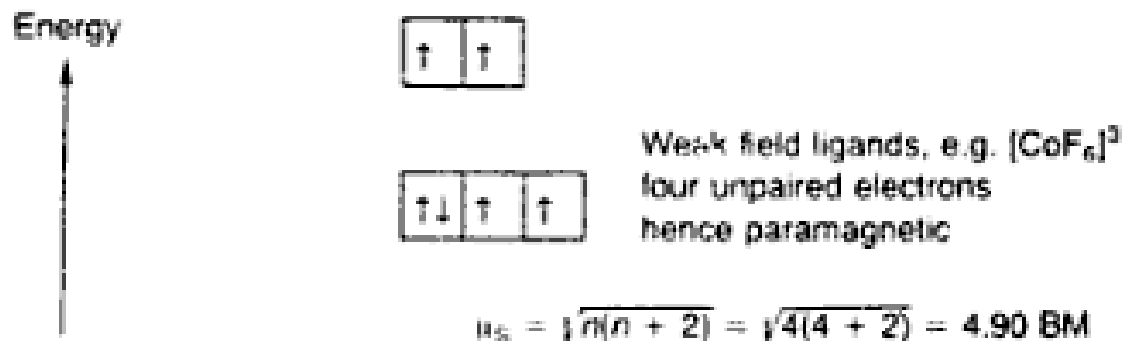
Spin only moment is valid for
1st row transition elements

Temperature dependence is
explained by spin-orbit
coupling

Co^{3+} octahedral complex with strong field ligands



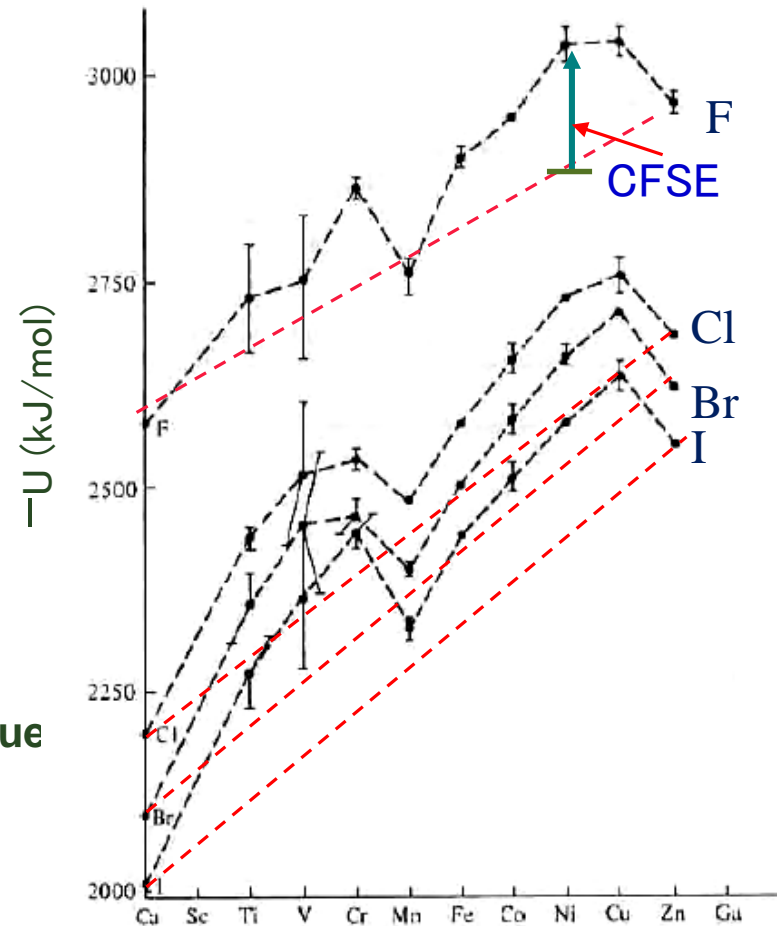
Co^{3+} octahedral complex with weak field ligands



Effects of Crystal Field Splitting

Lattice energies of metal complexes vary due to crystal field stabilization

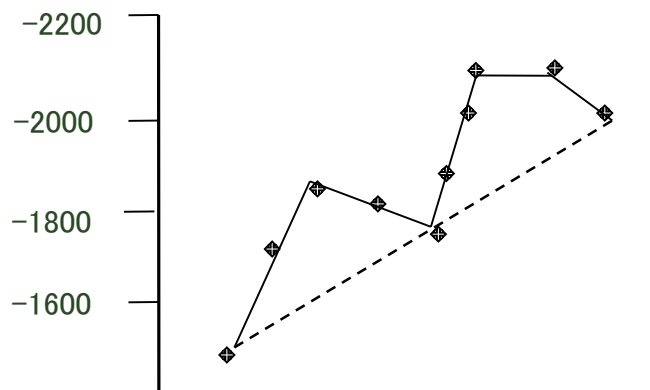
Lattice energies of the metal halides (MX_2) of the first transition series. Vertical bars indicates uncertainties in experimental value



Effects of Crystal Field Splitting contd....

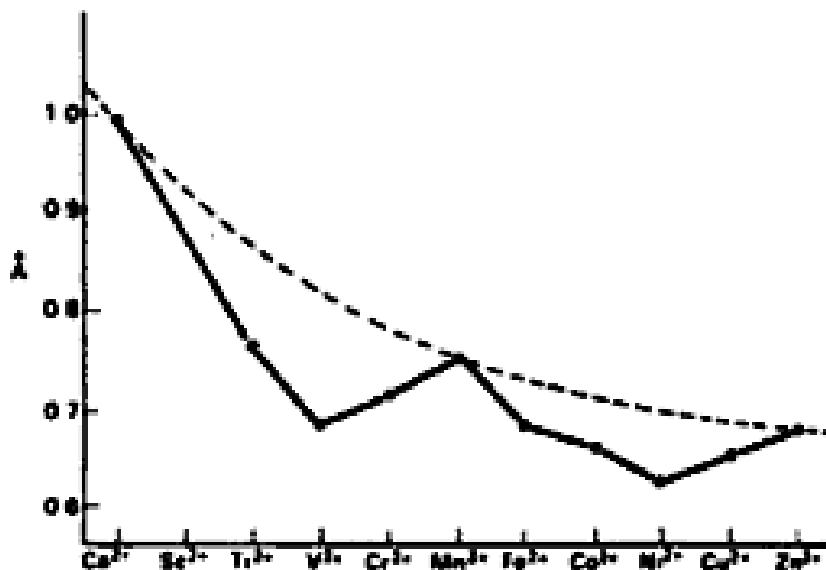
Enthalpy of hydration

Enthalpies of hydration for M^{2+}



Effects of Crystal Field Splitting contd....

Octahedral ionic radii of M^{2+} vary with crystal field splitting



Effects of Crystal Field Splitting contd....

