

NEET/JEE 2019

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UNIT - 4 : The *d*- and *f*-Block Elements | Coordination Compounds

THE *d*- AND *f*-BLOCK ELEMENTS

TRANSITION ELEMENTS

Their general electronic configuration is $(n-1)d^{1-10} ns^{0-2}$ where, n is the outermost shell.

Series	Element
First transition series (<i>3d</i> -series)	Sc (At. no. 21) to Zn (At. no. 30)
Second transition series (<i>4d</i> -series)	Y (At. no. 39) to Cd (At. no. 48)
Third transition series (<i>5d</i> -series)	La (At. no. 57), Hf (At. no. 72) to Hg (At. no. 80)
Fourth transition series (<i>6d</i> -series)	Ac (At. no. 89), Rf (At. no. 104) to Cn (At. no. 112)

Metallic Character

- Metallic bonding is due to possession of one or two electrons in the outermost shell and relatively low ionisation energies. All the transition elements are metals having *hcp*, *ccp* or *bcc* lattice except mercury which is a liquid.

Oxidation States

- They show variable oxidation states due to involvement of $(n-1)d$ and outer ns -electrons in bonding as the energies of ns and $(n-1)d$ subshells are nearly equal.
- When ns and $(n-1)d$ -electrons participate in bonding \rightarrow show higher oxidation state.

Magnetic Properties

- Magnetic moment, $\mu_{\text{eff}} = \sqrt{n(n+2)}$ B.M. (where, n = number of unpaired electrons)
- Magnetic character $\propto n$

Atomic and Ionic Radii

- Atomic radii decrease in the series with increase in atomic number because nuclear charge increases. After midway, decrease is small because of increased shielding effect of d -electrons. Ionic radii follow the same trend as the atomic radii.

Ionisation Energies

- $(IE)_1$ of $5d$ -elements are higher than those of the $3d$ and $4d$ -elements. This is due to greater effective nuclear charge acting on outer valence electrons because of the weak shielding of the nucleus by $4f$ -electrons.

Electrode Potential (E°)

- For the $3d$ -transition metals the $E^\circ(M^{2+}/M)$ values are :

V	Cr	Mn	Fe	Co	Ni	Cu
-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	0.34 (Volts)

The irregular trend is due to variation in ionisation energies and sublimation energies. Except copper $3d$ -elements are good reducing agents but weaker than s -block elements.

Melting and Boiling Points

- These metals have very high melting and boiling points due to stronger metallic bonding.
- The melting point of the transition elements first rise to a maximum and then fall as the atomic number increases.

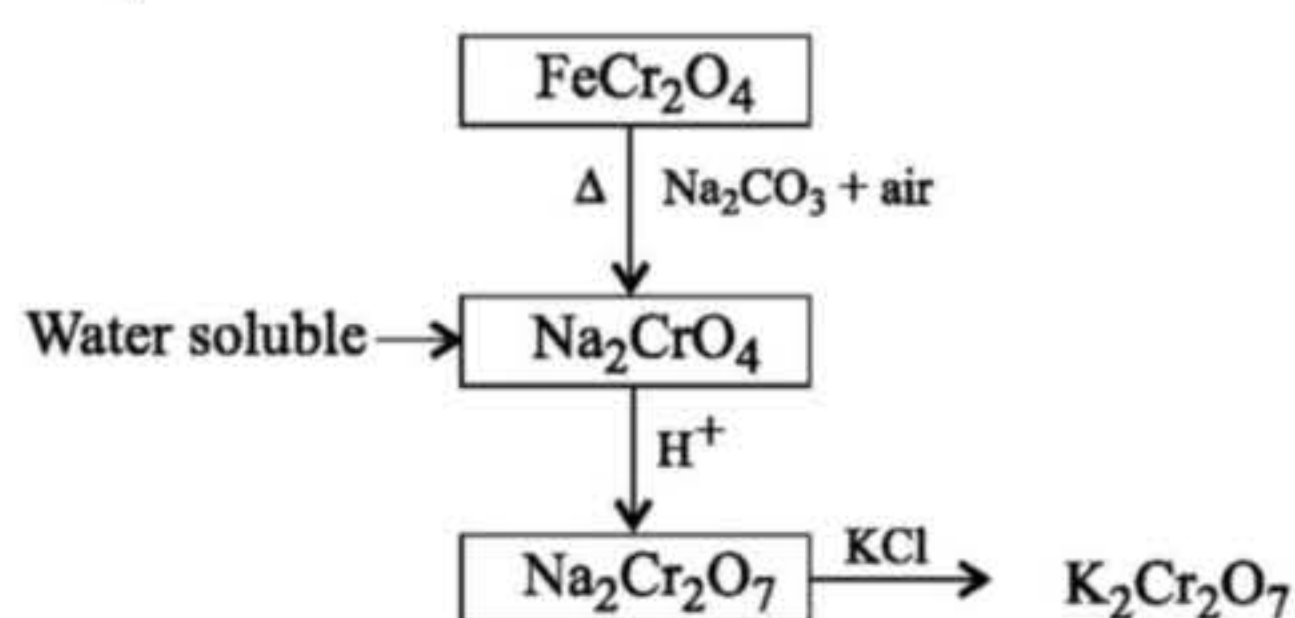
Alloy Formation

- Alloys are readily formed by these metals because of similar radii and other characteristics of transition metals.
- The alloys so formed are hard and have often high melting points and are also have considerable industrial importance.

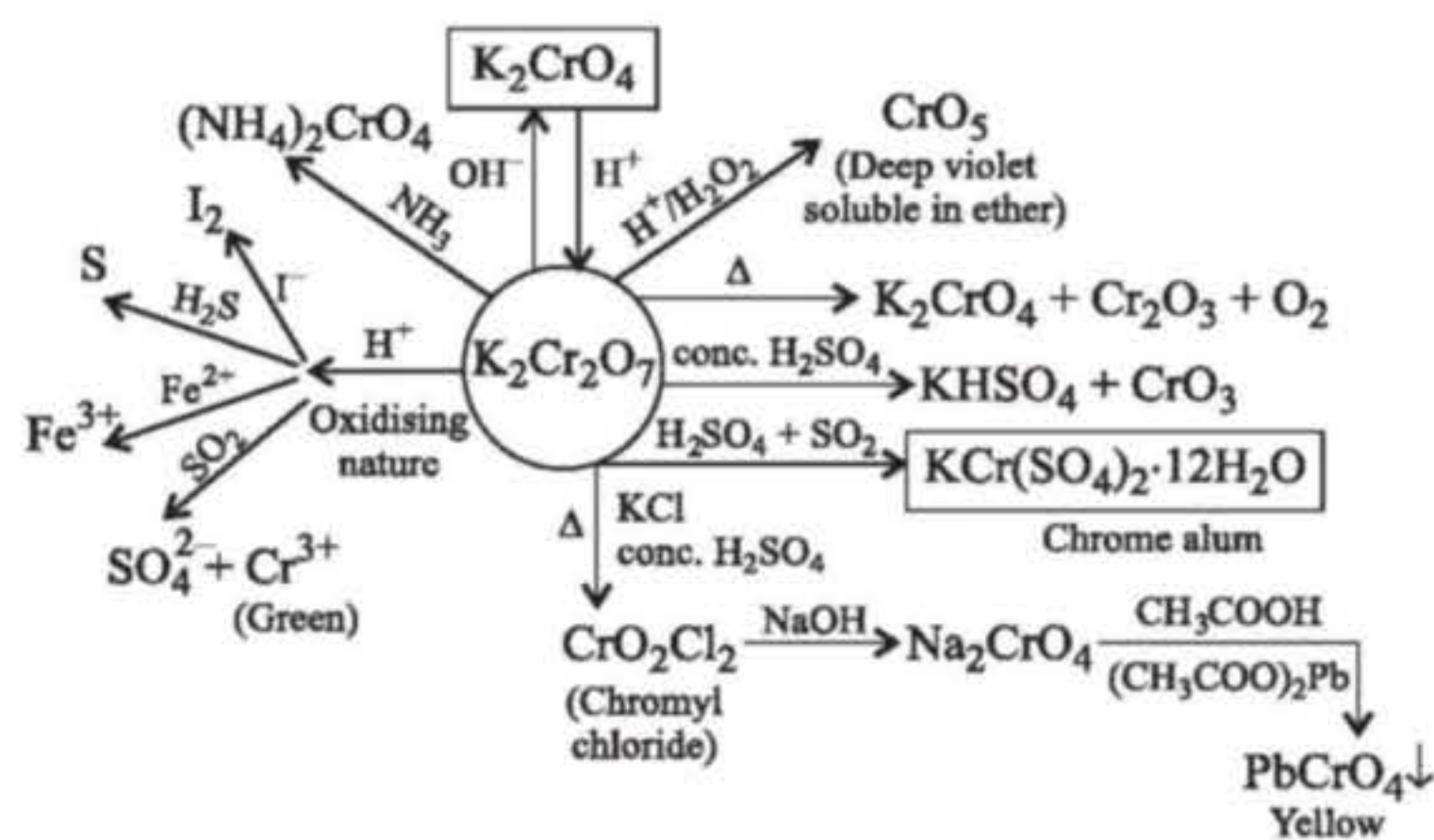
Some Important Compounds of Transition Elements

Potassium Dichromate ($K_2Cr_2O_7$)

- Preparation :



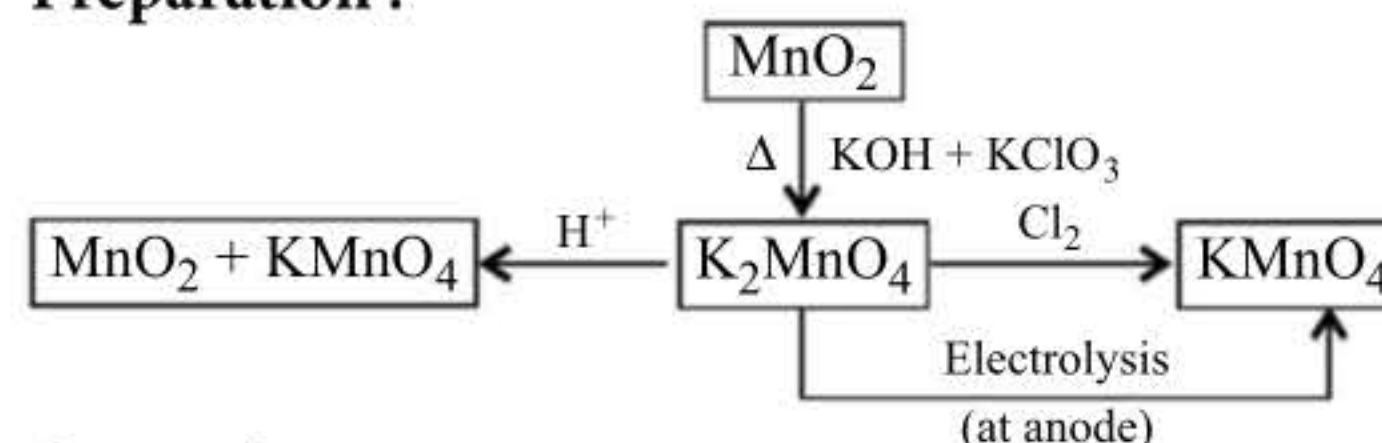
- Properties :



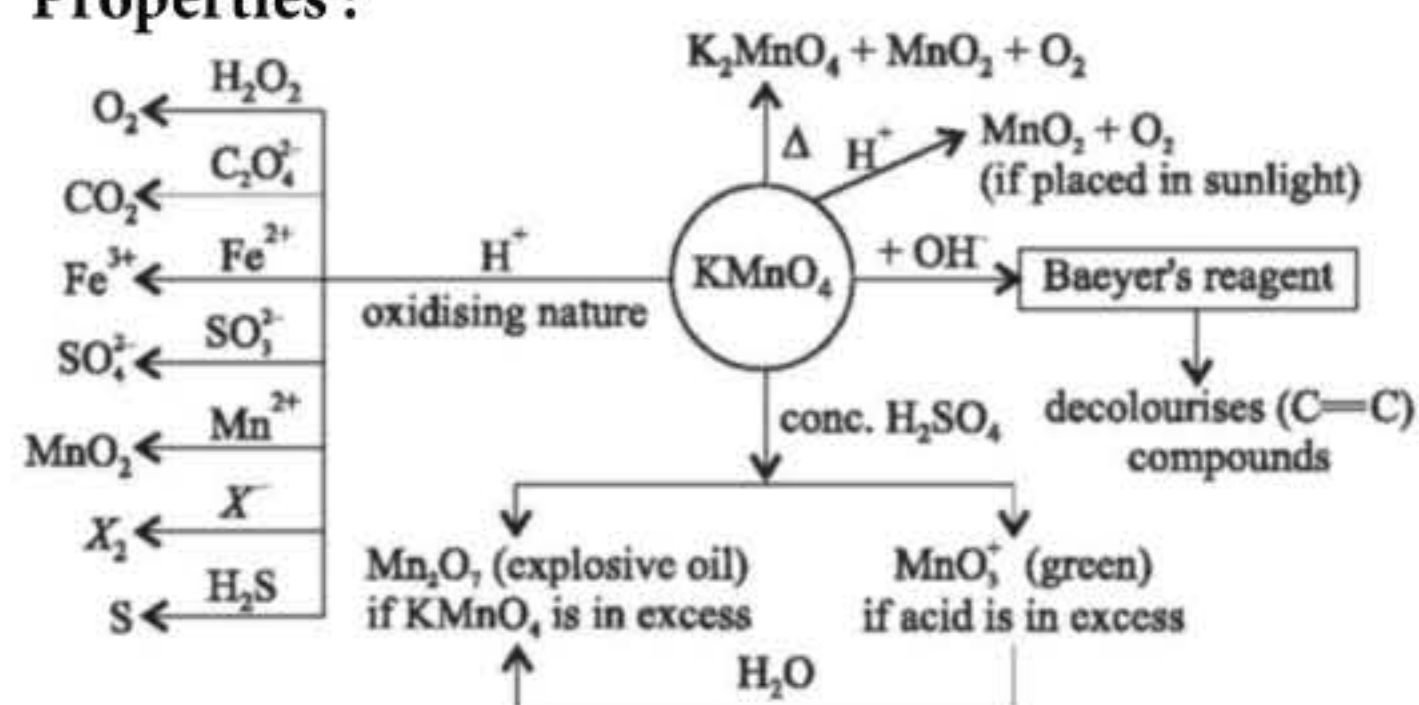
- Uses : It is used
 - in dyeing and calico printing,
 - in chrome tanning in leather industry,
 - as a volumetric reagent in laboratory for the estimation of ferrous ions, iodide ions, etc.

Potassium Permanganate ($KMnO_4$)

- Preparation :



- Properties :



- Uses : It is used
 - as an oxidising agent in the laboratory and industry,
 - as a disinfectant and germicide,
 - in qualitative and quantitative analysis.

INNER TRANSITION ELEMENTS

- Elements in which last electron enters into *f*-orbital are called *f*-block elements. *f*-block elements are also known as inner transition elements. There are two series of inner transition elements.
 - Lanthanoids
 - Actinoids

Electronic Configuration

Element	Electronic configuration	Element	Electronic configuration
La (57)	$[\text{Xe}]5d^16s^2$	Ac (89)	$[\text{Rn}]6d^17s^2$
Ce (58)	$[\text{Xe}]4f^15d^16s^2$	Th (90)	$[\text{Rn}]6d^27s^2$
Pr (59)	$[\text{Xe}]4f^36s^2$	Pa (91)	$[\text{Rn}]5f^26d^17s^2$
Nd (60)	$[\text{Xe}]4f^46s^2$	U (92)	$[\text{Rn}]5f^36d^17s^2$
Pm (61)	$[\text{Xe}]4f^56s^2$	Np (93)	$[\text{Rn}]5f^46d^17s^2$
Sm (62)	$[\text{Xe}]4f^66s^2$	Pu (94)	$[\text{Rn}]5f^67s^2$
Eu (63)	$[\text{Xe}]4f^76s^2$	Am (95)	$[\text{Rn}]5f^77s^2$
Gd (64)	$[\text{Xe}]4f^75d^16s^2$	Cm (96)	$[\text{Rn}]5f^76d^17s^2$
Tb (65)	$[\text{Xe}]4f^96s^2$	Bk (97)	$[\text{Rn}]5f^97s^2$
Dy (66)	$[\text{Xe}]4f^{10}6s^2$	Cf (98)	$[\text{Rn}]5f^{10}7s^2$
Ho (67)	$[\text{Xe}]4f^{11}6s^2$	Es (99)	$[\text{Rn}]5f^{11}7s^2$
Er (68)	$[\text{Xe}]4f^{12}6s^2$	Fm (100)	$[\text{Rn}]5f^{12}7s^2$
Tm (69)	$[\text{Xe}]4f^{13}6s^2$	Md (101)	$[\text{Rn}]5f^{13}7s^2$
Yb (70)	$[\text{Xe}]4f^{14}6s^2$	No (102)	$[\text{Rn}]5f^{14}7s^2$
Lu (71)	$[\text{Xe}]4f^{14}5d^16s^2$	Lr (103)	$[\text{Rn}]5f^{14}6d^17s^2$

Lanthanoids Contraction

- A unique feature of lanthanoids is the decrease in atomic and ionic radii from lanthanum to lutetium. The gradual and steady decrease across the period is called Lanthanoid contraction.
- The difference in radii between two successive elements is not large but cumulative effect over 14 elements is nearly 14 pm in atomic radii and 20 pm in ionic radii of tripositive ions.
- **Cause of lanthanoid contraction :** From La to Lu atomic number increases, number of protons in the nucleus increases and electrons are added to 4f orbitals which have very poor shielding power. It shields the growing nuclear charge imperfectly. As a result effective nuclear charge increases and radius decreases.

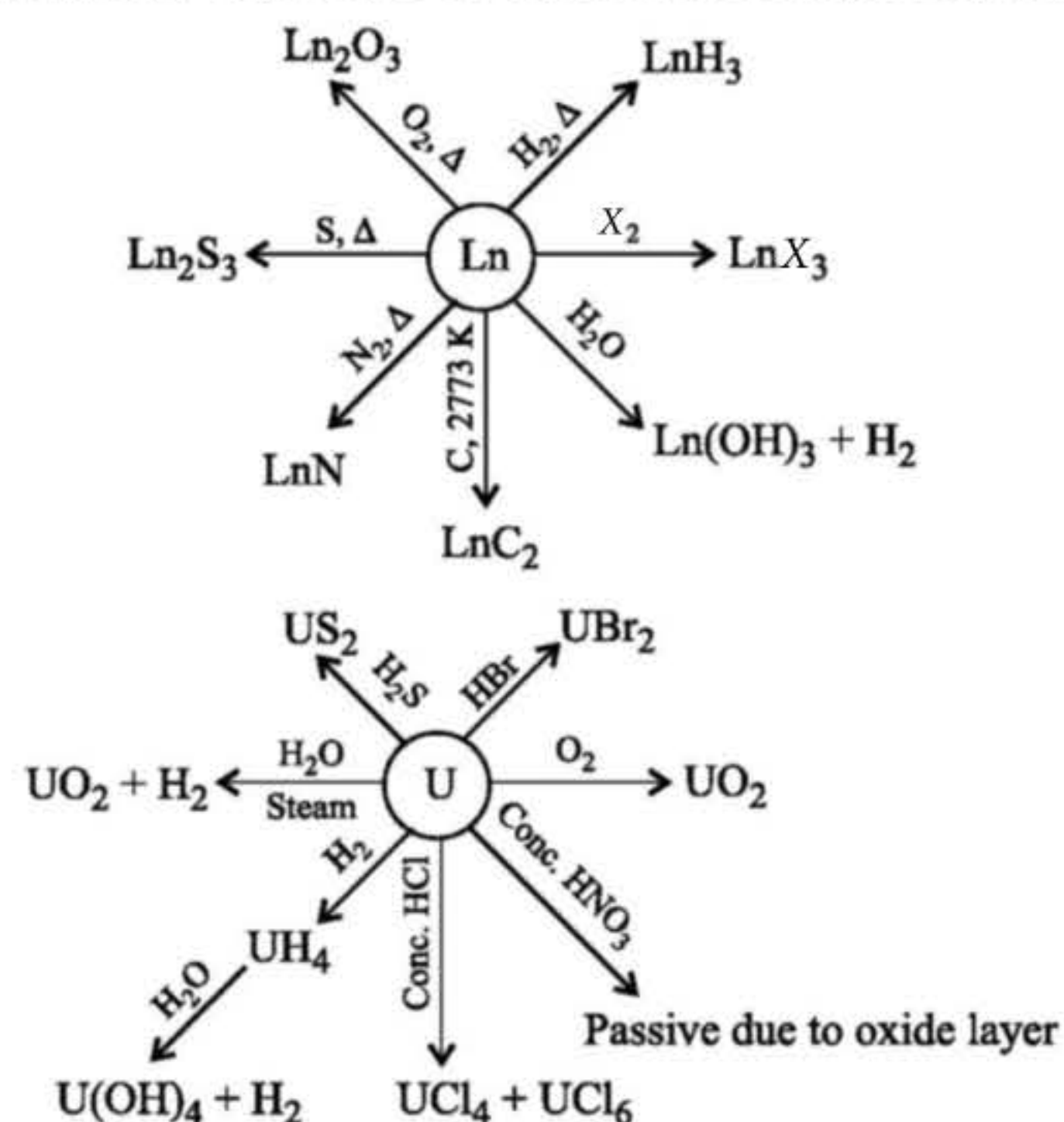
The decrease in atomic radii is irregular due to irregular electronic configuration. But ionic radii decrease in a regular manner.

- **Consequences of lanthanoid contraction :**
 - Atomic radii of 2nd and 3rd transition series elements are almost identical due to lanthanoid contraction. e.g., Zr = 160 pm, Hf = 159 pm. As a result they occur in nature together and their separation from their mixture is difficult.
 - The slight difference in size of lanthanoids is responsible for difference in their properties like solubility, complex ion formation. This difference is utilised in their separation from the mixture of lanthanoids by solvent extraction or ion exchange.

Comparison of Lanthanoids and Actinoids

- Actinoid metals display greater variety of structures than lanthanoids. This is because irregularities in metallic radii are far greater than in lanthanoids.
- Magnetic susceptibility of actinoids vary with the number of 5f unpaired electrons roughly parallel to the corresponding lanthanoids. However magnetic susceptibility of lanthanoids are higher than those of actinoids.
- Actinoids resemble the lanthanoids in showing close similarities with each other and gradual variation in properties except oxidation state.

Chemical Properties of Lanthanoids and Actinoids



COORDINATION COMPOUNDS

TERMS RELATED TO COORDINATION COMPOUNDS

The diagram illustrates the components of a coordination compound using the example $[\text{Cu}(\text{NH}_3)_4]^{2+} \text{SO}_4^{2-}$. Labels with arrows point to the following parts:

- Central metal atom :** Metal atom to which ligands are attached.
- Ligands :** The donor atoms, molecules or anions which donate a pair of electrons to the metal atom or ion and form a coordinate bond.
- Counter ions :** The ionizable groups written outside the bracket.
- Coordination number :** The total number of ligands attached to the central metal ion through coordinate bond.
- Coordination sphere :** Square bracket enclosing the central atom and the ligands directly attached to it.

WERNER'S THEORY

Proposed by Alfred Werner. The main postulates are :

- Primary valency corresponds to the oxidation state of the central metal. It is ionisable and satisfied by negative ions.
- Secondary valency is equal to the number of groups bound directly to the metal ion and is fixed for a metal. It is non-ionisable and is satisfied by neutral or negative ions.
- The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements (called coordination polyhedra) corresponding to different coordination numbers.

IUPAC RULES FOR NAMING COMPLEXES

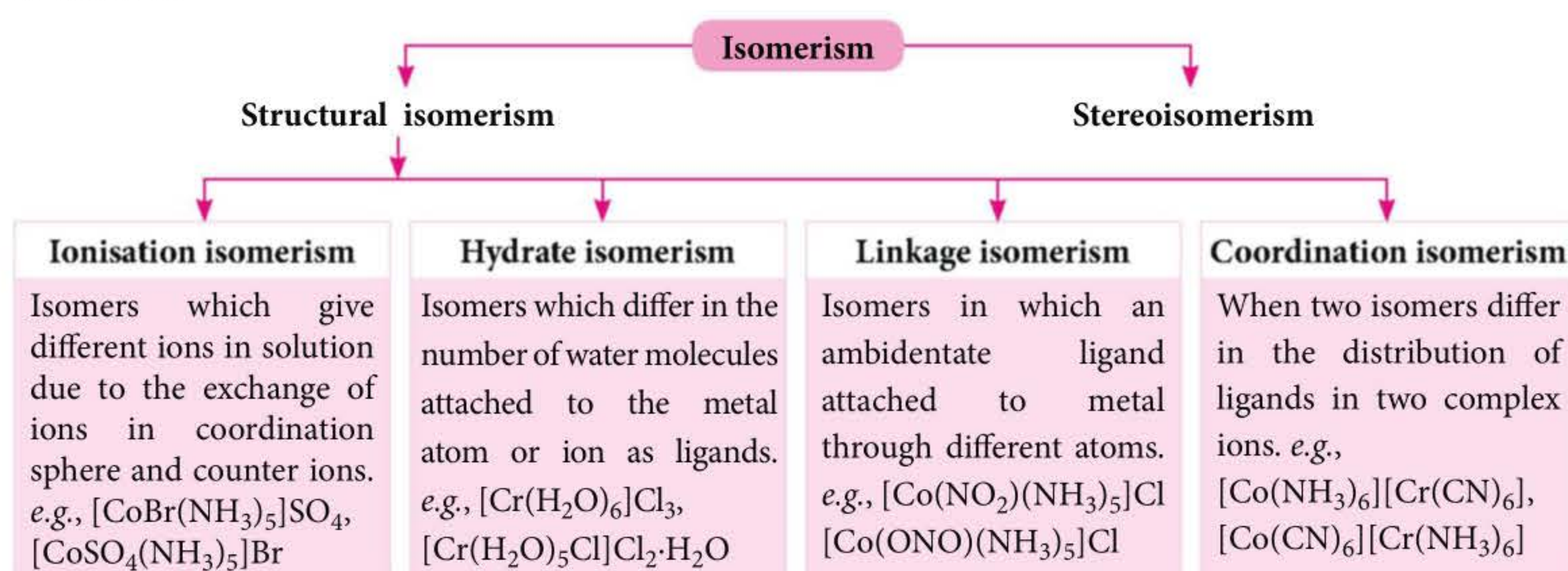
- The cations are named first.
- Within the coordination entity names are written in the following sequence :
Number of ligands, Name of ligand, Name of central atom/ion, Oxidation state of central atom/ion.
- Number of ligands of each kind is indicated by numerical prefix di, tri, tetra, penta, hexa etc. for 2, 3, 4, 5, 6

- For ligands containing any of these prefixes in their names, the number is indicated by prefix bis, tris, tetrakis etc. for 2, 3, 4, ligands respectively.
- Names of ligands are written in alphabetical order. The names of anionic ligands end as *o*. The suffix *ide*, *ite* or *ate* is replaced by *o* or suffix *-e* is replaced by *-o*.
- Names of neutral ligands are used as such. Some neutral ligands have special names. *e.g.*, *en* = ethylene diamine (ethane-1,2-diamine)
- **Names of central atom/ion :** When coordination entity is neutral or positive (cationic) then name of metal remains same. If the complex is anion, the name of central metal atom is made to end in *-ate*.
- Oxidation number of central atom is indicated in roman numerals just after name of central atom or ion in parenthesis.
- In case of ambidentate ligand the symbol of donor atom is indicated just after the name of metal.

Examples :

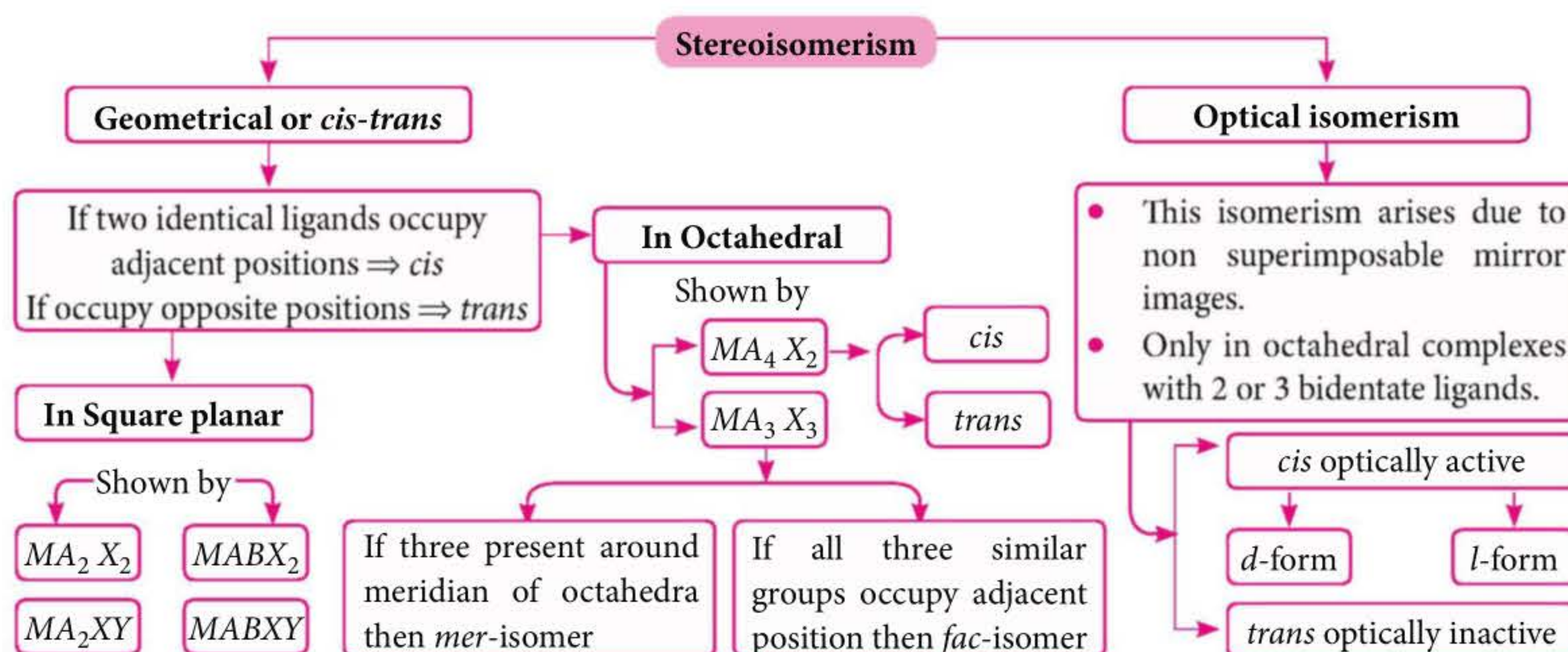
$[\text{Cu}(\text{NH}_3)_4] \text{SO}_4$: Tetraamminecopper(II) sulphate
 $[\text{Ni}(\text{dmg})_2]$: *bis*(dimethylglyoximate)nickel(II)

ISOMERISM



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* Geometrical isomerism is not shown by tetrahedral complexes.

VALENCE BOND THEORY (VBT)

- Main postulates of this theory are
 - The central metal ion makes available as many number of empty orbitals as its coordination number in compound formation.
 - Appropriate vacant orbitals of metal undergoes hybridisation to give a definite geometry such as square planar(dsp^2), tetrahedral (sp^3), octahedral(d^2sp^3), etc.
 - Empty hybrid orbital of metal overlap with filled orbital of ligands containing lone pair to form $M \leftarrow L$ coordinate bond.

Coordination Number	Type of Hybridisation	Geometry	Examples
2	sp	Linear	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$
3	sp^2	Trigonal planar	$[HgI_3]^-$
4	sp^3	Tetrahedral	$Ni(CO)_4$, $[NiX_4]^{2-}$, $[ZnCl_4]^{2-}$, $[CuX_4]^{2-}$ where, $X = Cl^-, Br^-, I^-$
	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$ $[Ni(NH_3)_4]^{2+}$
5	dsp^3	Trigonal bipyramidal	$Fe(CO)_5$, $[CuCl_5]^{3-}$
	sp^3d	Square pyramidal	$[SbF_5]^{2-}$
6	d^2sp^3	Octahedral (Inner orbital)	$[Cr(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$
	sp^3d^2	Octahedral (Outer orbital)	$[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$

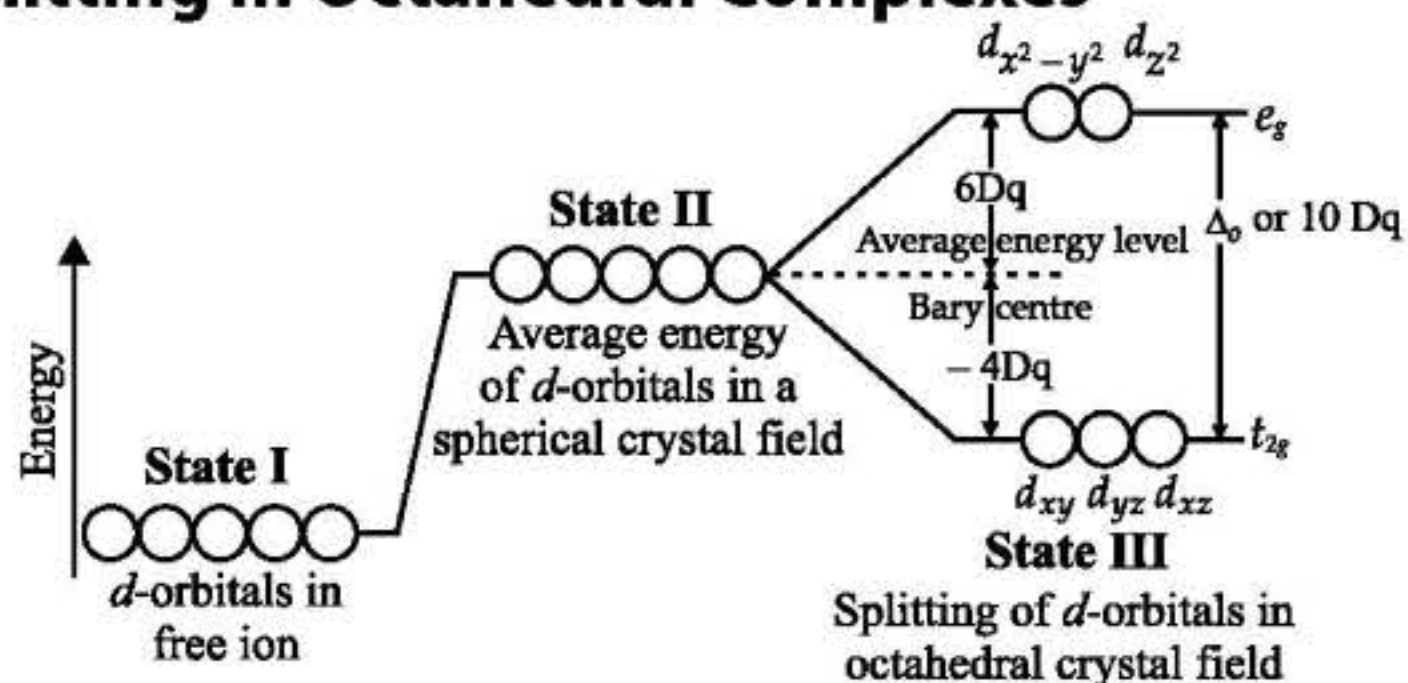
CRYSTAL FIELD THEORY (CFT)

- Main postulates of crystal field theory are
 - In a coordination compound there are electrostatic interaction between metal atom/ion and ligands.
 - In an isolated metal atom or ion all five d -orbitals have equal energy *i.e.*, they are degenerate.
 - When metal atom/ion gets surrounded by ligands, there occur interaction between d -electron cloud of metal atom/ion and ligands.
 - If the field due to ligand around metal atom is spherically symmetrical, the d -orbitals of metal remain degenerate.
 - If the field due to ligand surrounding metal is unsymmetrical (as in octahedral and tetrahedral complexes) the degeneracy of d -orbitals is splitted into two sets of orbitals.
 - Orbitals lying in the direction of ligands (point charges) are raised to higher energy state than

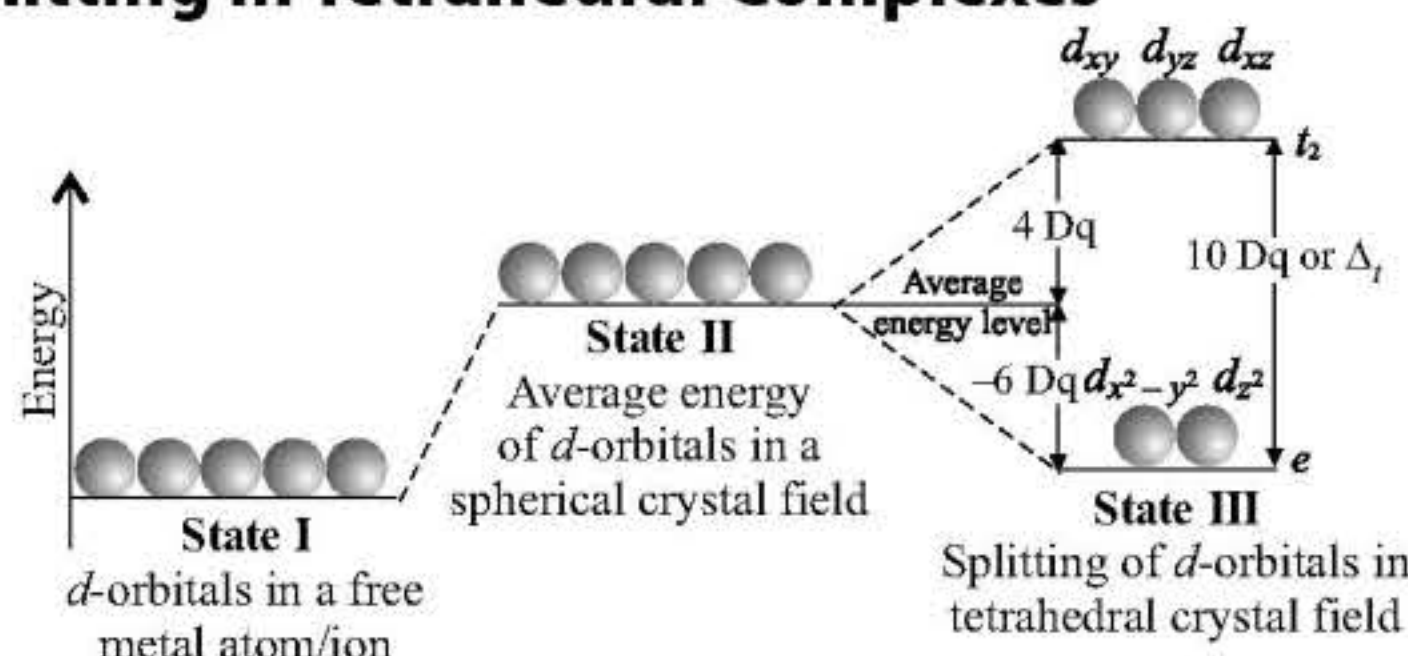
those orbitals lying between the ligands (point charges).

- The energy difference between two sets of orbitals is denoted by Δ_o and Δ_t for octahedral and tetrahedral complexes respectively.
- The magnitude of Δ_o or Δ_t depends upon the field strength of ligand around the metal.
- Ligands which cause large splitting (large Δ) are called strong field ligands while those which cause small splitting (small Δ) are called weak field ligands.

Splitting in Octahedral Complexes



Splitting in Tetrahedral Complexes



Calculation of CFSE

- $CFSE = (-0.4x + 0.6y)\Delta_o$
where,
 x = number of electrons occupying t_{2g} orbitals.
 y = number of electrons occupying e_g orbitals.

Colour

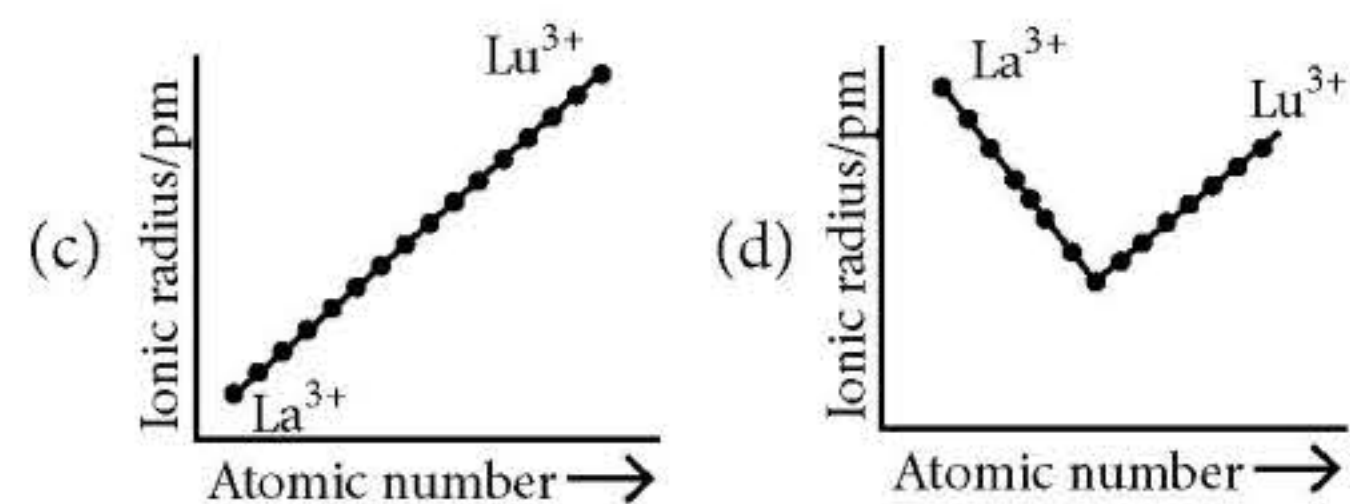
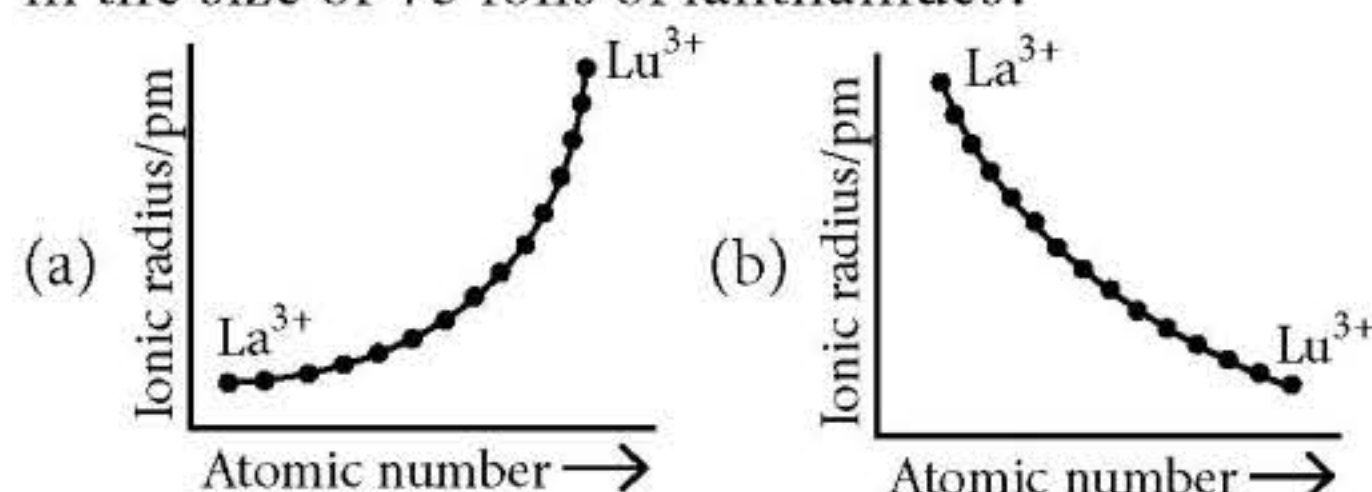
- The energy difference for the first transition series generally falls in the visible region. Absorption of one colour in the visible spectrum results in the ion having the complementary colour.
- The amount of d -orbital splitting depends on the ligands, thus different ligands have different splitting energies (Δ_o values) and different colours result.

APPLICATIONS OF COORDINATION COMPOUNDS

- Coordination compounds are of great importance in biological system. *e.g.*, chlorophyll, haemoglobin, myoglobin, etc. are coordinate compounds of Mg, Fe and Co respectively.
- The platinum complex, *cis*-[PtCl₂(NH₃)₂] known as *cis*-platin is used in cancer treatment.
- EDTA is often used for treatment of lead poisoning.
- Coordination compounds are used as catalyst, *e.g.*, Wilkinson's catalyst, (Ph₃P)₃RhCl is used for dehydrogenation of alkenes, Ziegler-Natta catalyst, [TiCl₄ + (C₂H₅)₃Al] is used for polymerisation of ethene.

SPEED PRACTICE

1. What is the ratio of uncomplexed to complexed Zn²⁺ ion in a solution, *i.e.*, 10 M NH₃, if the stability constant of [Zn(NH₃)₄]²⁺ is 3 × 10⁹?
(a) 3.3 × 10⁹ (b) 3.3 × 10⁻¹⁴
(c) 3.3 × 10¹⁴ (d) 3.3 × 10⁻⁹
2. Which of the following graphs shows correct trends in the size of +3 ions of lanthanides?



3. $K_{\text{instability}}$ values for [Ag(NO₂)₂]⁻ and [Ag(CN)₂]⁻ are 1.3 × 10⁻³ and 8 × 10⁻²¹ respectively. If C₁ and C₂ are the concentrations of Ag⁺ ion in equimolar solutions of these two complexes respectively, then
(a) C₁ > C₂ (b) C₁ = C₂
(c) C₁ < C₂ (d) C₁ = 2C₂