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CHAPTER ONE

Chemistry of d-block elements

- Iron, copper, silver and gold are among the transition elements that have played important roles in the development of human civilization.

- The d–block occupies the large middle section flanked by s– and p– blocks in the periodic table.

- The terms *transition metal (or element)* and *d block element* are sometimes used as if they mean the same thing, but ‘d-block metal’ and ‘transition element’ are not interchangeable.

- A transition element is defined as the one which has incompletely filled *d-orbitals in its* ground state or in any one of its oxidation states.

- Zinc, cadmium and mercury of group 12 have full d^{10} configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals.

- However, being the end members of the three transition series, their chemistry is studied along with the chemistry of the transition metals.
- The presence of partly filled *d or f-orbitals in their* atoms sets the study of the transition elements and their compounds apart from that of the main group elements.

- Various precious metals such as silver, gold and platinum and industrially important metals like iron, copper and titanium form part of the transition metals.
- The d–orbitals of the penultimate energy level in their atoms receive electrons giving rise to the three rows of the transition metals, i.e., 3d, 4d and 5d.
- The fourth row of 6d is still incomplete.

Electronic Configurations of the d-Block Elements

- In general the electronic configuration of these elements is $(n-1)d^{1-10}ns^{1-2}$.

- The (n–1) stands for the inner d-orbitals which may have one to ten electrons and the outermost ns orbital may have one or two electrons.

- However, this generalization has several exceptions because

of very little energy difference between (n-1)*d and ns orbitals*.

- Furthermore, half and completely filled sets of orbitals are relatively more stable.

- A consequence of this factor is reflected in the electronic configurations of Cr and Cu in the 3d series.
- Consider the case of Cr, for example, which has $3d^5 4s^1$ instead of $3d^4 4s^2$;
- the energy gap between the two sets (3d and 4s) of orbitals is small enough to prevent electron entering the 3d orbitals.
- Similarly in case of Cu, the configuration is $3d^{10} 4s^1$ and not $3d^9 4s^2$.
- This is something that you are just going to have to accept.
- There is no *simple* explanation for it which is usable at this level.

- Any simple explanation which is given is faulty!
- People sometimes say that a half-filled d level as in chromium is stable, and so it is - *sometimes*!
- But you then have to look at *why* it is stable.
- But you only have to look at the electronic configuration of tungsten (W) to see that this apparently simple explanation doesn't always work.
- Tungsten has the same number of outer electrons as chromium, but its outer structure is different, $5d^4 6s^2$.

- ➢ The obvious explanation is that chromium takes up this structure because separating the electrons minimizes the repulsions between them,
- ✓ otherwise it would take up some quite different structure.
- ➢ But you only have to look at the electronic configuration of tungsten (W) to see that this apparently simple explanation doesn't always work.
- ➢ Tungsten has the same number of outer electrons as chromium, but its outer structure is different, $5d^4 6s^2$.

- Again the electron repulsions must be minimised - otherwise it wouldn't take up this configuration.
- But in this case, it *isn't* true that the half-filled state is the most stable - it doesn't seem very reasonable, but it's a fact!
- The real explanation is going to be much more difficult than it seems at first sight.

Transition metal ions

- You have already come across the fact that when the Periodic Table is being built, the 4s orbital is filled before the 3d orbitals.

- This is because before filling orbitals, 4s orbitals have a lower energy than 3d orbitals.
- However, once the electrons are actually in their orbitals,
- ✓ the energy order changes, and in all the chemistry of the transition elements, the 4s orbital behaves as the outermost, highest energy orbital.
- To write the electronic structure for Co^{2+}:

$$\mathrm{Co: [Ar]3d^7 4s^2}$$

$$\mathrm{Co^{2+}: [Ar]3d^7}$$

- The 2+ ion is formed by the loss of the two 4s electrons.

- To write the electronic structure for V^{3+}:

V: [Ar] $3d^3 4s^2$, V^{3+}: [Ar] $3d^2$

- The 4s electrons are lost first followed by one of the 3d electrons.

- To write the electronic structure for Cr^{3+}:

Cr: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$

Cr^{3+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$

- The 4s electron is lost first followed by two of the 3d electrons.

General properties of Transition Metals Physical

General physical properties of the elements

- ➢ Nearly all the transition elements display typical metallic properties such as high tensile strength, ductility,
- ✓ malleability, high thermal and electrical conductivity and metallic lustre.
- ➢ With the exceptions of Zn, Cd, Hg and Mn, they have one or more typical metallic structures at normal temperatures.


Scandium, Sc; 3B(3)


Titanium, Ti; 4B(4)


Vanadium, V; 5B(5)


Manganese, Mn; 7B(7)


Cobalt, Co; 8B(9)


Nickel, Ni; 8B(10)

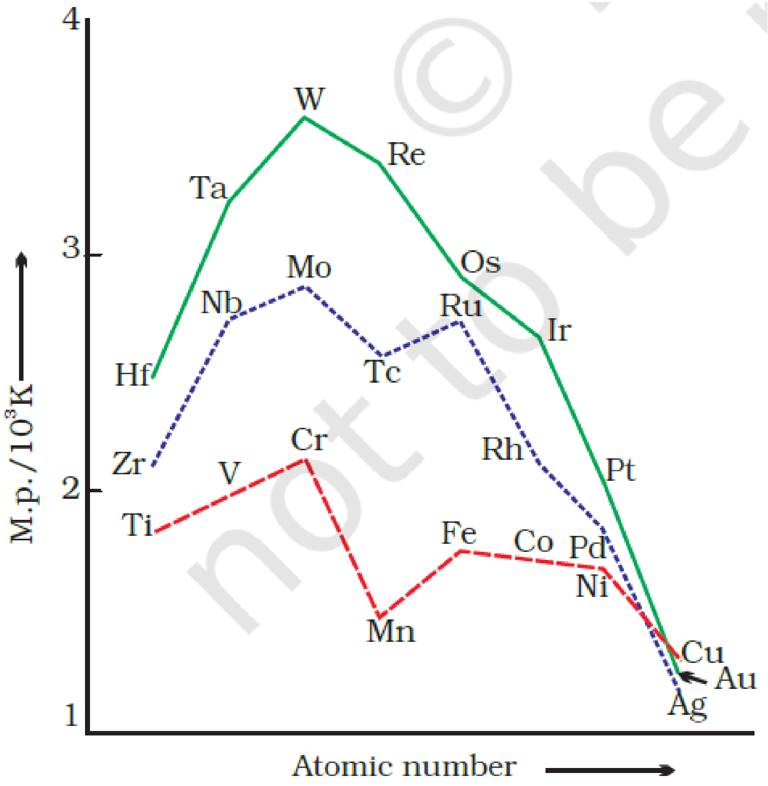

Copper, Cu; 1B(11)


Iron, Fe; 8B(8)


Zinc, Zn; 2B(12)

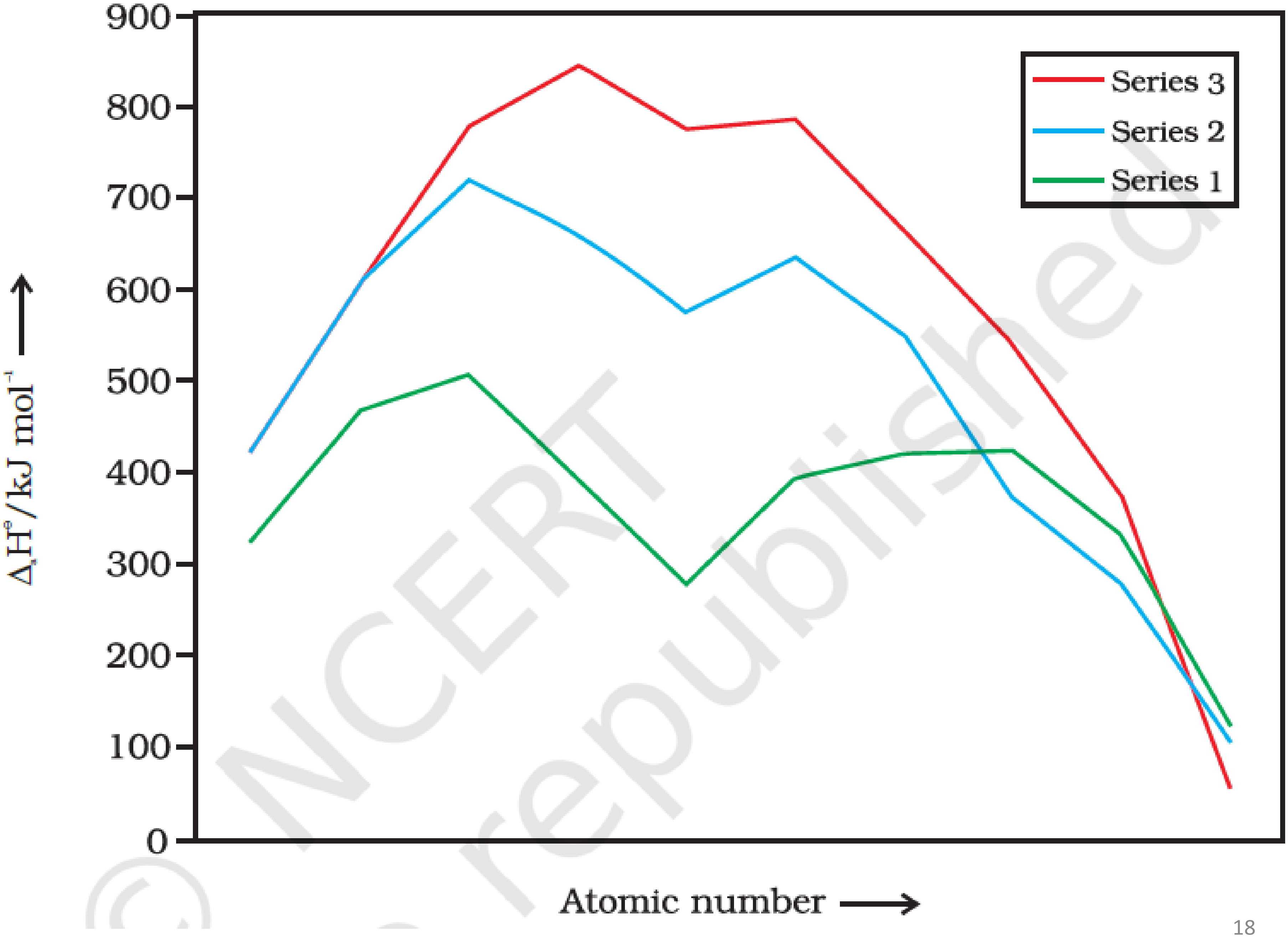

Chromium, Cr; 6B(6)

- The transition metals (with the exception of Zn, Cd and Hg) are very much hard and have low volatility.
- Their melting and boiling points are high.



Trends in melting points of transition elements

- The high melting points of these metals are attributed to the involvement of greater number of electrons from (n-1)d in addition to the ns electrons in the interatomic metallic bonding.
- In any row the melting points of these metals rise to a maximum at d^5 except for anomalous values of Mn and Tc and fall regularly as the atomic number increases.
- They have high enthalpies of atomisation.
- The maxima at about the middle of each series indicate that one unpaired electron per *d orbital is particularly* favourable for strong interatomic interaction.


900
800
700
600
500
400
300
200
100
0
$\Delta_a H^\ominus / \text{kJ mol}^{-1}$
Atomic number
Series 3
Series 2
Series 1

➢In general, greater the number of valence electrons, stronger is the resultant bonding.

➢Since the enthalpy of atomisation is an important factor in determining the standard electrode potential of a metal,

✓metals with very high enthalpy of atomisation (i.e., very high boiling point) tend to be noble in their reactions.

➢Another generalisation that may be drawn from the figure is that the metals of the second and third series have greater enthalpies of atomisation than the corresponding elements of the first series;

- This is an important factor in accounting for the occurrence of much more frequent metal– metal bonding in compounds of the heavy transition metals.

Variation in Atomic and Ionic Sizes of Transition Metals

- In general, ions of the same charge in a given series show progressive decrease in radius with increasing atomic number.
- This is because the new electron enters a *d orbital each time the nuclear charge increases* by unity.
- The same trend is observed in the atomic radii of a given series.

- It may be recalled that the shielding effect of a *d electron is* not that effective, hence the net electrostatic attraction between the nuclear charge and the outermost electron increases and the ionic radius decreases.

- However, the variation within a series is quite small.
- An interesting point emerges when atomic sizes of one series are compared with those of the corresponding elements in the other series.

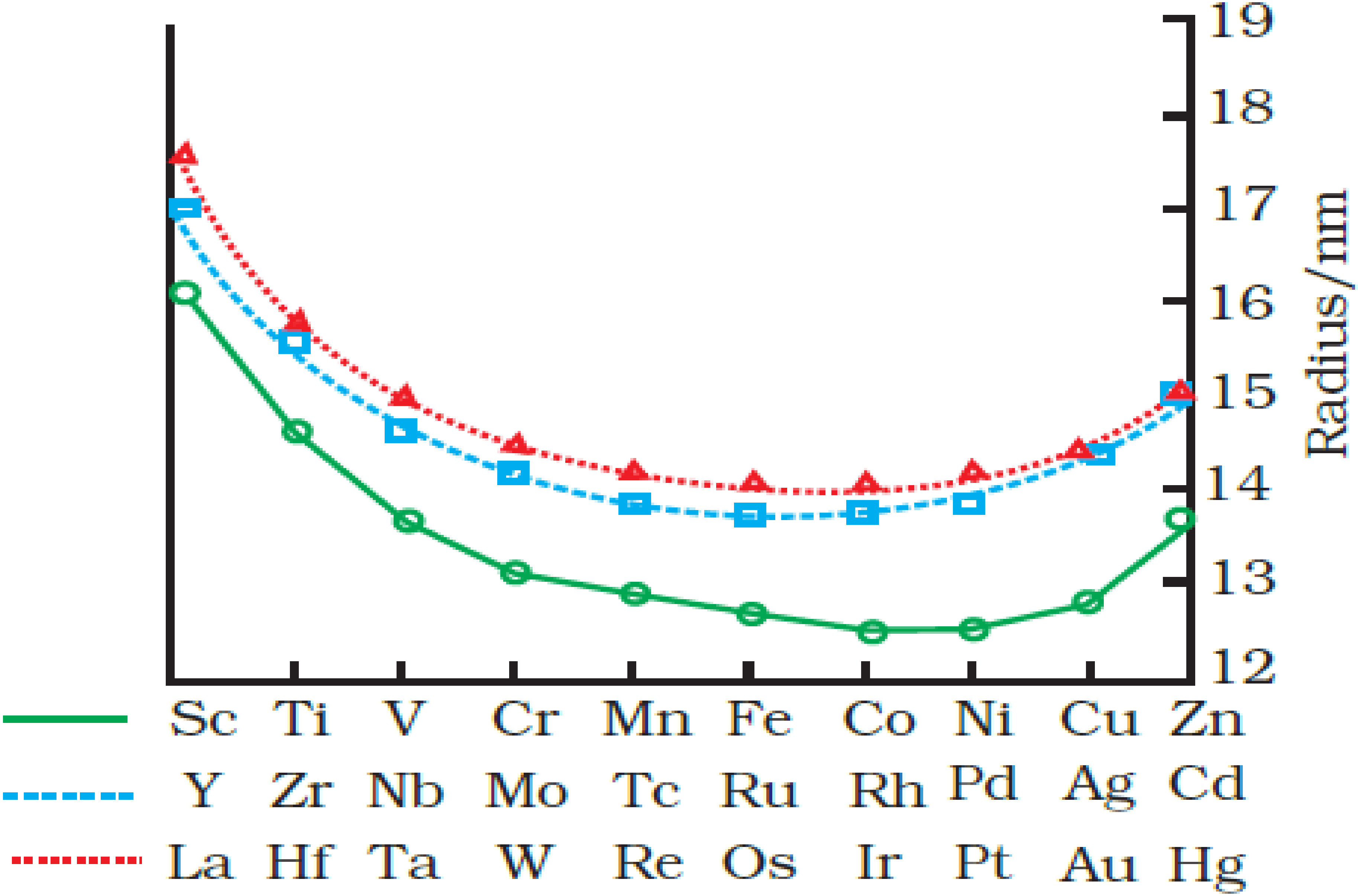


Fig. 8.3: *Trends in atomic radii of transition elements*

- The curves in the above figure show an increase from the first (3d) to the second (4d) series of the elements but the radii of the third (5d) series are virtually the same as those of the corresponding members of the second series.

- This phenomenon is associated with the intervention of the 4*f orbitals which* must be filled before the 5*d series of elements begin*.

- *The filling of 4f* before 5*d orbital results in a regular decrease in atomic radii called* **Lanthanoid contraction which essentially compensates for the expected** increase in atomic size with increasing atomic number.

- ➢The net result of the lanthanoid contraction is that the second and the third *d series* exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm)

- ✓and have very similar physical and chemical properties much more than that expected on the basis of usual family relationship.

- ➢The factor responsible for the lanthanoid contraction is the imperfect shielding of one electron by another in the same set of orbitals.

- The decrease in metallic radius coupled with increase in atomic mass results in a general increase in the density of these elements.

Ionisation Enthalpies

- Due to an increase in nuclear charge which accompanies the filling of the inner *d orbitals*,
- *there is an increase in ionization enthalpy* along each series of the transition elements from left to right.
- However, many small variations occur.

- The magnitude of the increase in the second and third ionisation enthalpies for the successive elements, in general, is much higher.
- The irregular trend in the first ionisation enthalpy of the 3*d* metals can be accounted by considering that the removal of one electron alters the relative energies of 4*s and 3d orbitals*.
- *The successive enthalpies of these elements do not increase as steeply as in the main group elements.*
- So the unipositive ions have d^n configurations with no 4*s* *electrons*.

- There is thus, a reorganization energy accompanying ionization with some gains in exchange energy as the number of electrons increases and from the transference of *s* electrons into *d orbitals.*
- There is the generally expected increasing trend in the values as the effective nuclear charge increases.
- However, the value of Cr is lower because of the absence of any change in the *d configuration and the value for Zn is higher because it represents an* ionization from the 4*s level.*

- The lowest common oxidation state of these metals is +2.

- To form the M^{2+} ions from the gaseous atoms, the sum of the first and second ionization energies is required in addition to the enthalpy of atomization for each element.

- The dominant term is the second ionization enthalpy which shows unusually high values for Cr and Cu where the d^5

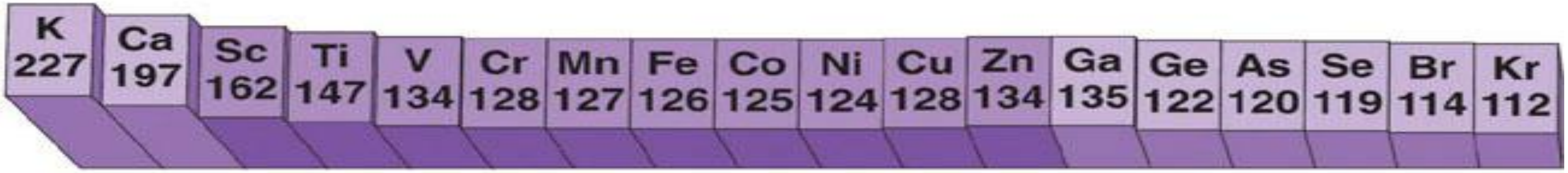
- ✓ *and d^{10} configurations of the M^+ ions are* disrupt with considerable loss of exchange energy.

➢The value for Zn is correspondingly low as the ionization consists of the removal of an electron which allows the production of the stable d^{10} configuration.

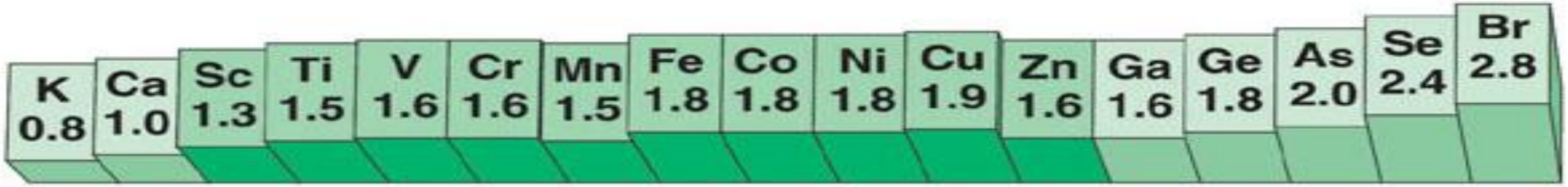
➢The trend in the third ionization enthalpies is not complicated by the 4*s orbital factor and shows the greater difficulty* of removing an electron from the d^5 *(Mn^{2+}) and* d^{10} *(Zn^{2+}) ions* superimposed upon the general increasing trend.

➢In general, the third ionization enthalpies are quite high and there is a marked break between the values for Mn^{2+} and Fe^{2+}.

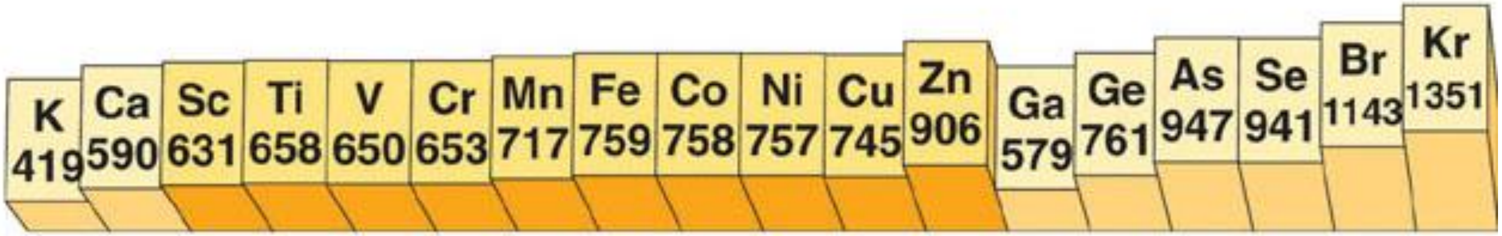
- Also the high values for copper, nickel and zinc indicate why it is difficult to obtain oxidation state greater than two for these elements.
- Electro negativity ***increases*** within a group from Period 4 to 5, then generally remains unchanged from Period 5 to 6.
- The heavier elements often have high EN values.
- Although atomic size increases slightly down the group, nuclear charge increases much more, leading to higher EN values.



A Atomic radius (pm)



B Electronegativity



C First ionization energy (kJ/mol)

- Density increases dramatically down a group since atomic volumes change little while atomic masses increase significantly.

General chemical properties

The inherent variable oxidation states

- One of the key features of transition metal chemistry is the wide range of oxidation states that the metals can show.
- Most transition metals have ***multiple oxidation states***.
- It would be wrong, though, to give the impression that *only* transition metals can have variable oxidation states.

- For example, elements like S or N or Cl have a very wide range of oxidation states in their compounds and these obviously aren't transition metals.
- However, this variability is less common in metals apart from the transition elements.
- Of the familiar metals from the main groups of the Periodic Table, only lead and tin show variable oxidation state to any extent.
- The transtion elements which give the greatest number of oxidation states occur in or near the middle of the series.

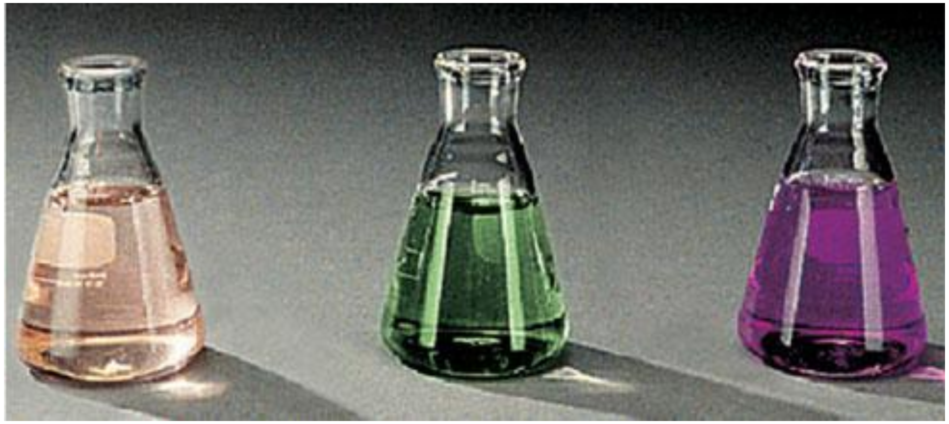
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	**+2**	**+2**	**+2**	**+2**	+1	**+2**
+3	+3	+3	**+3**	+3	**+3**	**+3**	+3	**+2**	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

- The highest oxidation state for elements in Groups 3B(3) through 7B(7) equals the *group number*.
- These states are seen when the elements combine with the highly electronegative oxygen or fluorine.
- Elements in Groups 8B(8), 8B(9) and 8B(10) exhibit fewer oxidation states.
- The higher oxidation state is less common and never equal to the group number.
- **The +2 oxidation state is common because the *ns*^{2} electrons are readily lost.**

+2 Mn^{2+}

+6 MnO_4^{2-}

+7 MnO_4^-



The highest oxidation state for Mn equals its group number.

Transition metal ions are often highly colored.

+5 VO_4^{3-}

+6 $Cr_2O_7^{2-}$

+7 MnO_4^-

- The maximum oxidation states of reasonable stability correspond in value to the sum of the *s and d electrons upto manganese*.
- Although in the *p–block the lower oxidation states are favoured by the heavier members* (due to inert pair effect), the opposite is true in the groups of *d-block*.
- For example, in group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI).
- Thus Cr(VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas MoO_3 and WO_3 are not.

- Low oxidation states are found when a complex compound has ligands capable of π-acceptor character in addition to the σ-bonding.
- For example, in $Ni(CO)_4$ and $Fe(CO)_5$, the oxidation state of nickel and iron is zero.

Explaining the variable oxidation states in the transition metals

- We'll look at the formation of simple ions like Fe^{2+} and Fe^{3+}.
- When a metal forms an ionic compound, the formula of the compound produced depends on the energetics of the process.

- On the whole, the compound formed is the one in which most energy is released.
- The more energy released, the more stable the compound.
- There are several energy terms to think about, but the key ones are:-
- The amount of energy needed to ionise the metal (the sum of the various ionisation energies)
- The amount of energy released when the compound forms.
- This will either be lattice enthalpy if you are thinking about solids, or the hydration enthalpies of the ions if you are thinking about solutions.

- The more highly charged the ion, the more electrons you have to remove and the more ionisation energy you will have to provide.
- But off-setting this, the more highly charged the ion, the more energy is released either as lattice enthalpy or the hydration enthalpy of the metal ion.

Thinking about a typical non-transition metal (calcium)

- If you tried to make CaCl, (containing a Ca^+ ion), the overall process is slightly exothermic.
- By making a Ca^{2+} ion instead, you have to supply more ionisation energy, but you get out lots more lattice energy.

- There is much more attraction between chloride ions and Ca^{2+} ions than there is if you only have a 1+ ion.
- The overall process is very exothermic.
- Because the formation of $CaCl_2$ releases much more energy than making CaCl, then $CaCl_2$ is more stable and so forms instead.
- What about $CaCl_3$?
- This time you have to remove yet another electron from calcium.
- The first two come from the 4s level.

- The third one comes from the 3p.
- That is much closer to the nucleus and therefore much more difficult to remove.
- There is a large jump in ionisation energy between the second and third electron removed.

- Although there will be a gain in lattice enthalpy, it isn't anything like enough to compensate for the extra ionisation energy, and the overall process is very endothermic.
- It definitely isn't energetically sensible to make $CaCl_3$!

Thinking about a typical transition metal (iron)

Here are the changes in the electronic structure of iron to make the 2+ or the 3+ ion.

Fe: [Ar] $3d^6 4s^2$

Fe^{2+}: [Ar] $3d^6$

Fe^{3+}: [Ar] $3d^5$

- ➢The 4s orbital and the 3d orbitals have very similar energies.
- ➢ There isn't a huge jump in the amount of energy you need to remove the third electron compared with the first and second.

The figures for the first three ionisation energies (in kJ mol^{-1}) for iron compared with those of calcium are:

Metal	**1st IE**	**2nd IE**	**3rd IE**
Ca	**590**	**1150**	**4940**
Fe	**762**	**1560**	**2960**

- There is an increase in ionisation energy as you take more electrons off an atom because you have the same number of protons attracting fewer electrons.
- However, there is much less increase when you take the third electron from iron than from calcium.

- In the iron case, the extra ionisation energy is compensated more or less by the extra lattice enthalpy or hydration enthalpy evolved when the 3+ compound is made.
- The net effect of all this is that the overall enthalpy change isn't vastly different whether you make, say, $FeCl_2$ or $FeCl_3$.
- That means that it isn't too difficult to convert between the two compounds.

Metallic Behavior of Transition Metals

- The ***lower*** the oxidation state of the transition metal, the ***more metallic*** its behavior.

- ***Ionic*** bonding is more prevalent for the ***lower*** oxidation states, whereas ***covalent*** bonding occurs more frequently for ***higher*** oxidation states.

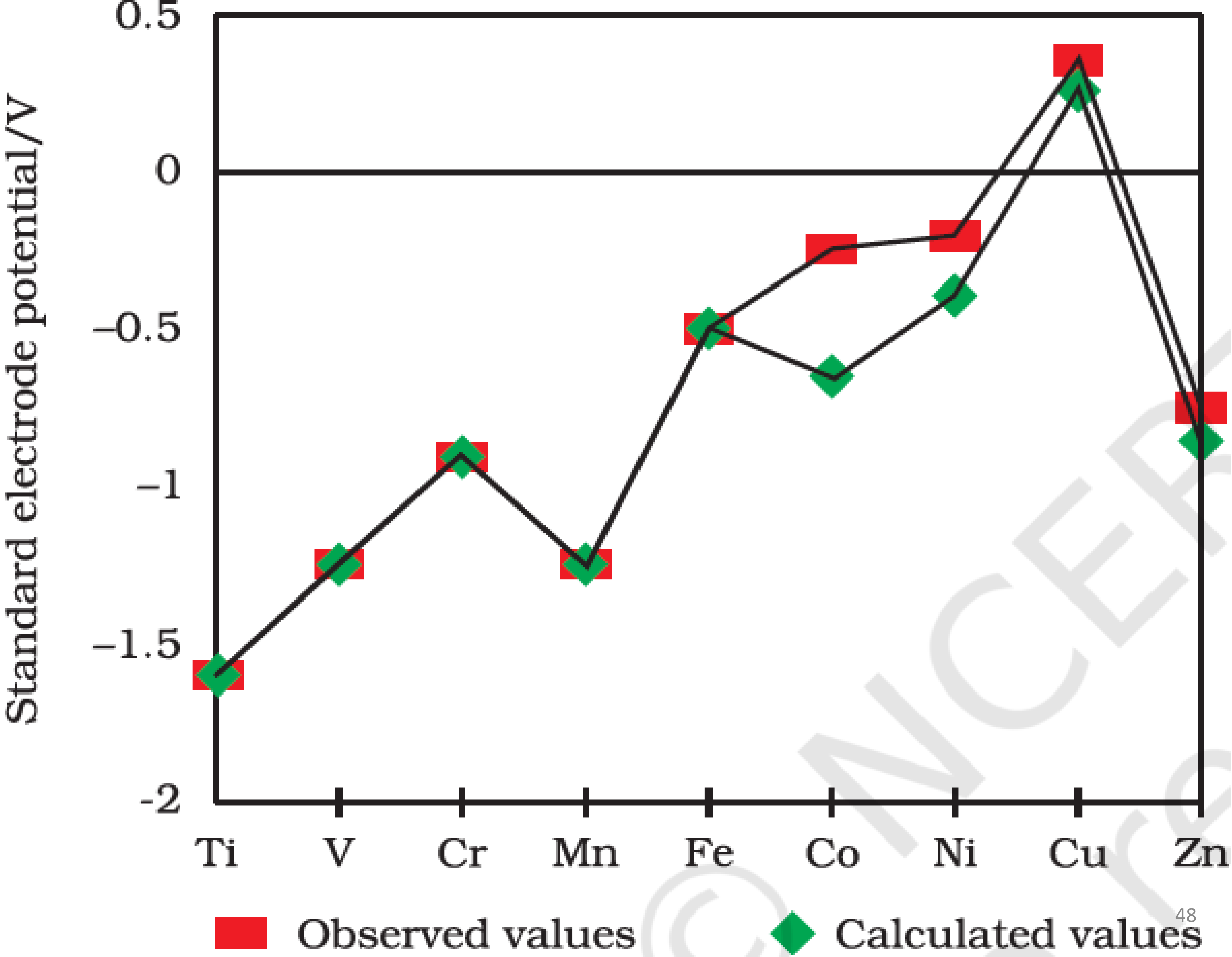
- Metal oxides become ***less basic*** as the oxidation state ***increases***.

- A metal atom in a positive oxidation state has a greater attraction for bonded electrons, and therefore a greater effective electronegativity, or ***valence-state*** electronegativity, than in the zero oxidation state.

- This effect increases as its oxidation state increases.

Trends in the M^{2+}/M Standard Electrode Potentials

Half-Reaction			***E*°(V)**
Ti^{2+}(*aq*) + 2e^{-}	Ti(*s*)	$\rightleftharpoons$	-1.63
V^{2+}(*aq*) + 2e^{-}	V(*s*)	$\rightleftharpoons$	-1.19
Cr^{2+}(*aq*) + 2e^{-}	Cr(*s*)	$\rightleftharpoons$	-0.91
Mn^{2+}(*aq*) + 2e^{-}	Mn(*s*)	$\rightleftharpoons$	-1.18
Fe^{2+}(*aq*) + 2e^{-}	Fe(*s*)	$\rightleftharpoons$	-0.44
Co^{2+}(*aq*) + 2e^{-}	Co(*s*)	$\rightleftharpoons$	-0.28
Ni^{2+}(*aq*) + 2e^{-}	Ni(*s*)	$\rightleftharpoons$	-0.25
Cu^{2+}(*aq*) + 2e^{-}	Cu(*s*)	$\rightleftharpoons$	0.34
Zn^{2+}(*aq*) + 2e^{-}	Zn(*s*)	$\rightleftharpoons$	-0.76


Standard electrode potential/V
0.5
0
–0.5
–1
–1.5
-2
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Observed values
Calculated values

- The unique behaviour of Cu, having a positive $E^\ominus$, accounts for its inability to liberate H_2 from acids.
- Only oxidising acids (nitric and hot concentrated sulphuric) react with Cu, the acids being reduced.
- The high energy to transform Cu(s) to Cu^{2+}(aq) is not balanced by its hydration enthalpy.
- The general trend towards less negative $E^\ominus$ values across the series is related to the general increase in the sum of the first and second ionisation enthalpies.

- It is interesting to note that the value of $E^\ominus$ for Mn, Ni and Zn are more negative than expected from the trend.

- Why is Cr^{2+}reducing and Mn^{3+} oxidising when both have d^4 configuration?
- Cr^{2+} is reducing as its configuration changes from d^4 to d^3, the latter having a half-filled t_{2g} level.

- On the other hand, the change from Mn^{3+} to Mn^{2+} results in the half-filled (d^5) configuration which has extra stability.

Trends in the M^{3+}/M^{2+} Standard Electrode Potentials

- An examination of the $E^{\ominus}$ (M^{3+}/M^{2+}) values shows the varying trends.
- The low value for Sc reflects the stability of Sc^{3+} which has a noble gas configuration.
- The highest value for Zn is due to the removal of an electron from the stable d^{10} configuration of Zn^{2+}.
- The comparatively high value for Mn shows that $Mn^{2+}(d^5)$ is particularly stable, whereas comparatively low value for Fe shows the extra stability of Fe^{3+} (d^5).

- The comparatively low value for V is related to the stability of V^{2+} (half-filled t_{2g} level).

Chemical Reactivityand $E^{\odot}$ Values

- Transition metals vary widely in their chemical reactivity.
- Many of them are sufficiently electropositive to dissolve in mineral acids, although a few are ‘noble’ that is, they are unaffected by single acids.
- The metals of the first series with the exception of copper are relatively more reactive and are oxidised by 1M H^+,
- though the actual rate at which these metals react with oxidising agents like hydrogen ion (H^+) is sometimes slow.

- For example, titanium and vanadium, in practice, are passive to dilute non oxidising acids at room temperature.

- The E^{Θ} *values* for M^{2+}/M indicate a decreasing tendency to form divalent cations across the series.

- This general trend towards less negative E^{Θ} values is related to the increase in the sum of the first and second ionisation enthalpies.

- It is interesting to note that the E^{Θ} values for Mn, Ni and Zn are more negative than expected from the general trend.

- Whereas the stabilities of half-filled d subshell (d^5) in Mn^{2+} and completely filled d subshell (d^{10}) in zinc are related to their $E^\ominus$ values;
- ✓ for nickel, $E^\ominus$ value is related to the highest negative enthalpy of hydration.

Magnetic Properties

- When a magnetic field is applied to substances, mainly two types of magnetic behaviour are observed: diamagnetism and paramagnetism.

- Diamagnetic substances are repelled by the applied field while the paramagnetic substances are attracted.
- Substances which are attracted very strongly are said to be ferromagnetic.
- In fact, ferromagnetism is an extreme form of paramagnetism.
- Many of the transition metal ions are paramagnetic.
- Paramagnetism arises from the presence of unpaired electrons,
- ✓ each such electron having a magnetic moment associated with its spin angular momentum and orbital angular momentum.

- For the compounds of the first series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance.
- For these, the magnetic moment is determined by the number of unpaired electrons and is calculated by using the ‘spin-only’ formula, i.e.,

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

- where n is the number of unpaired electrons and μ is the magnetic moment in units of Bohr magneton (BM).

- A single unpaired electron has a magnetic moment of 1.73 Bohr magnetons (BM).
- The magnetic moment increases with the increasing number of unpaired electrons.
- Thus, the observed magnetic moment gives a useful indication about the number of unpaired electrons present in the atom, molecule or ion.

Ion	Configuration	Unpaired electron(s)	Magnetic moment	
			Calculated	Observed
Sc^{3+}	$3d^0$	0	0	0
Ti^{3+}	$3d^1$	1	1.73	1.75
Ti^{2+}	$3d^2$	2	2.84	2.76
V^{2+}	$3d^3$	3	3.87	3.86
Cr^{2+}	$3d^4$	4	4.90	4.80
Mn^{2+}	$3d^5$	5	5.92	5.96
Fe^{2+}	$3d^6$	4	4.90	5.3 – 5.5
Co^{2+}	$3d^7$	3	3.87	4.4 – 5.2
Ni^{2+}	$3d^8$	2	2.84	2.9 – 3, 4
Cu^{2+}	$3d^9$	1	1.73	1.8 – 2.2
Zn^{2+}	$3d^{10}$	0	0	

- Calculate the magnetic moment of a divalent ion in aqueous solution.

$$\mu = \sqrt{5(5+2)} = 5.92\,\text{BM}$$

Formation of Coloured Ions

- When an electron from a lower energy d orbital is excited to a higher energy d orbital, the energy of excitation corresponds to the frequency of light absorbed.
- This frequency generally lies in the visible region.
- The colour observed corresponds to the complementary colour of the light absorbed.

- The frequency of the light absorbed is determined by the nature of the ligand.

Catalytic Properties

- The transition metals and their compounds are known for their catalytic activity.
- This activity is ascribed to their ability to adopt multiple oxidation states and to form complexes.
- Vanadium(V) oxide (in Contact Process), finely divided iron (in Haber’s Process), and nickel (in Catalytic Hydrogenation) are some of the examples.

- Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst.
- *This has the effect of increasing the* concentration of the reactants at the catalyst surface and also weakening of the bonds in the reacting molecules.
- Also because the transition metal ions can change their oxidation states, they become more effective as catalysts.
- For example, iron(III) catalyses the reaction between iodide and persulphate ions.

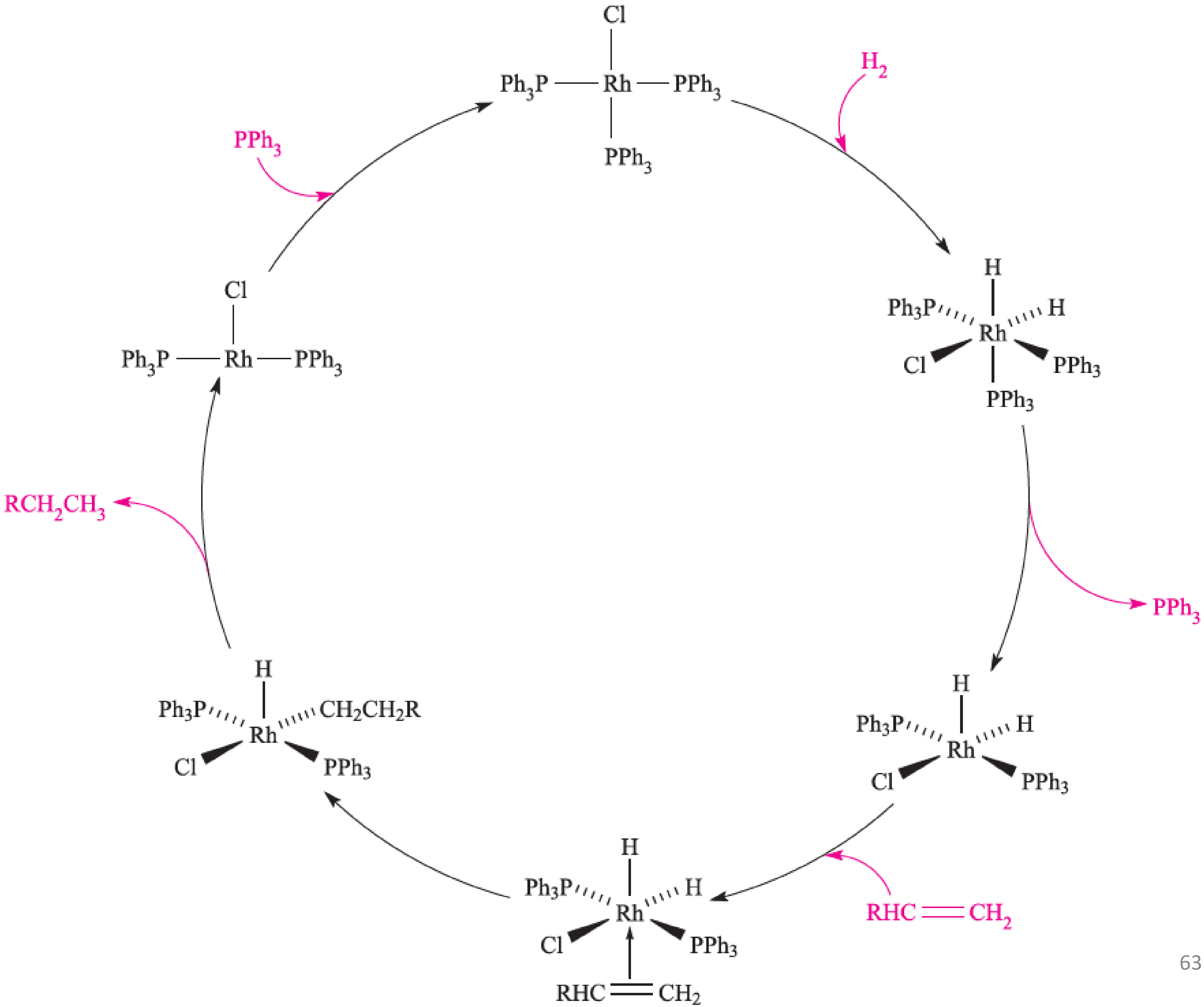
$$2\,I^- + S_2O_8^{2-} \rightarrow I_2 + 2\,SO_4^{2-}$$

- An explanation of this catalytic action can be given as:

$$2\,Fe^{3+} + 2\,I^- \rightarrow 2\,Fe^{2+} + I_2$$

$$2\,Fe^{2+} + S_2O_8^{2-} \rightarrow 2\,Fe^{3+} + 2SO_4^{2-}$$

- Catalytic cycle for the hydrogenation of $RCH{=}CH_2$ using Wilkinson’s catalyst, $RhCl(PPh_3)_3$.


Cl
Ph3P — Rh — PPh3
PPh3
H2
H
Ph3P
H
Rh
Cl
PPh3
PPh3
PPh3
H
Ph3P
H
Rh
Cl
PPh3
RHC=CH2
H
Ph3P
H
Rh
Cl
PPh3
RHC=CH2
H
Ph3P
CH2CH2R
Rh
Cl
PPh3
RCH2CH3
Cl
Ph3P — Rh — PPh3
PPh3

Non-stoichiometric compounds

- Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals.

- They are usually non stoichiometric and are neither typically ionic nor covalent, for example, TiC, Mn_4N, Fe_3H, $VH_{0.56}$ and $TiH_{1.7}$, etc.

- The formulas quoted do not, of course, correspond to any normal oxidation state of the metal.

- Because of the nature of their composition, these compounds are referred to as *interstitial compounds*.
- The principal physical and chemical characteristics of these compounds are as follows:

(i) They have high melting points, higher than those of pure metals.

(ii) They are very hard, some borides approach diamond in hardness.

(iii) They retain metallic conductivity.

(iv) They are chemically inert.

Descriptive Chemistry first series transition metals

Chemistry of Titanium

Properties

- Titanium is Soft, silver-white metal with melting and boiling points of 1814K and 3104K respectively.
- Titanium has the electronic structure [Ar] $4s^2 3d^2$.
- Titanium does not react with alkalis and does not dissolve in mineral acids at room temperature.
- It is attacked by hot HCl, forming Ti(III) and H_2, and hot HNO_3 oxidizes the metal to hydrous TiO_2.
- Titanium reacts with most non-metals at elevated temperatures; with C, O_2, N_2 and halogens.

- The binary hydrides, carbide, nitride and borides are all inert, high-melting, refractory materials.
- Ti exhibits the common oxidation numbers: +2, +3 and +4. +4 is the most stable state and corresponds to the group number.
- This oxidation state is represented by the solid and ionic TiO_2 and the liquid covalent TiC_4.
- The ionic character of the former means that it contains Ti^{4+} ions, of [Ar] configuration.
- This and its high lattice energy account for its stability.
- However, the high polarizing power of Ti^{4+}, makes it energetically more favorable to form the tetrahedral covalent $TiCl_4$**.**

- Ti(II) compounds are the least stable and liberate hydrogen from water.
- On the other hand, Ti(III) compounds in acidified solution can be stored and handled in an inert atmosphere.
- The d^1 configuration of Ti^{3+} give colour, and its visible absorption spectrum, unlike the colourless Ti(IV).

Occurrence and extraction of Titanium

- The main ore of titanium is ilmenite ($FeTiO_3$), and it also occurs as three forms of TiO_2 (anatase, rutile and brookite) and perovskite.

- Production of Ti involves conversion of rutile or ilmenite to $TiCl_4$ (by heating in a stream of Cl_2 at 1200K in the presence of coke) followed by reduction using Mg.
- Titanium(IV) oxide is also purified via $TiCl_4$ in the chloride process.

Importance and compounds of titanium

- Titanium metal is resistant to corrosion at ambient temperatures, and is lightweight and strong, making it valuable as a component in alloys, e.g. in aircraft construction.
- Superconducting magnets (used, for example, in MRI equipment) contain NbTi multicore conductors.

- Titanium(IV) halides can be formed from the elements; industrially, $TiCl_4$ is prepared by reacting TiO_2 with Cl_2 in the presence of carbon.
- Titanium(IV) fluoride is a hygroscopic white solid which forms HF on hydrolysis.
- Both $TiCl_4$ and $TiBr_4$ hydrolyzed more readily than TiF_4.
- At 298K, $TiCl_4$ is a colourless liquid and $TiBr_4$ a yellow solid.
- The tetra-iodide is a red-brown hygroscopic solid which sublimes in vacuo at 473K to a red vapor.
- Tetrahedral molecules are present in the solid and vapor phases of $TiCl_4$, $TiBr_4$ and TiI_4.

- Each tetra-halide acts as a Lewis acid; $TiCl_4$ is the most important, being used with $AlCl_3$ in Ziegler–Natta catalysts for alkenes Polymerization and as a catalyst in a variety of other organic reactions.

- Dissolving dry TiO_2 in acids is difficult, but the hydrous form (precipitated by adding base to solutions of Ti(IV) salts) dissolves in HF, HCl and H_2SO_4 giving fluoro, chloro and sulfato complexes respectively.

- There is no simple aqua ion of Ti^{4+}. The reaction of TiO_2 with CaO at 1620K gives the titanate.

- Titanium(III) fluoride is prepared by passing H_2 and HF over Ti or its hydride at 970 K; it is a blue solid (m.pt 1473 K) with a structure related to ReO_3.
- The trichloride is commercially available; it is used as a catalyst in alkenes polymerization and is a powerful reducing agent.
- In air, $TiCl_3$ is readily oxidized, and disproportionate above 750K.

$$2TiCl_3 \longrightarrow TiCl_4 + TiCl_2$$

- Titanium tribromide is made by heating $TiBr_4$ with Al, or by reaction of BBr_3 with $TiCl_3$

- When aqueous solutions of Ti(IV) are reduced by Zn, the purple aqua ion $[Ti(H_2O)_6]^{3+}$ is obtained.

- This is a powerful reductant and is used in titrimetric analyses of Fe(III) and nitro groups (reduced to NH_2 groups); aqueous solutions of Ti(III) must be protected from aerial oxidation.

Chemistry of Vanadium

Properties

- Ground state electronic configuration of vanadium [Ar]$4s^2 3d^3$.
- Vanadium is Soft, ductile, bright white metal.
- It melts at 2183K and boils at 3650K. In many ways, vanadium metal is similar to Ti.
- Vanadium is a powerful reductant but is passivated by an oxide film.

$$V^{2+} + 2e^- \ V \longrightarrow E^0 = -1.18V$$

- The metal is insoluble in non-oxidizing acids (except HF) and alkalis, but is attacked by HNO_3, aqua-regia and peroxodisulfate solutions.
- On heating, V reacts with halogens and combines with O_2 to give V_2O_5, and with B, C and N_2 to yield solid state materials.
- Vanadium, like the other 3d transition metals, exhibits the common low oxidation state of +2 by the loss of its two s electrons.
- In the highest oxidation state of +5, which corresponds to the group number, all the valence electrons are involved in bonding.

- Vanadium, like the other 3d transition metals, exhibits the common low oxidation state of +2 by the loss of its two s electrons.
- In the highest oxidation state of +5, which corresponds to the group number, all the valence electrons are involved in bonding.
- As usual, O or F stabilizes this state and the oxide V_2O_5 is the most common oxide and is more ionic than the only +5 halide: VF_5.
- Thermodynamically the +3 state is the most stable.
- However, it is susceptible to oxidation in air.

- The +4 state is stable in air. V(II) compounds are strong reductant whereas V(V) compounds are mild oxidants.
- All the oxides representing the four oxidation states are known.
- As the oxidation number and electro negativity increase, the basic character of the oxide decreases and its acidic character increases.
- Thus VO and $V(OH)_2$ are basic whereas V_2O_4 is amphoteric and so is V_2O_5 although it is more acidic than V_2O_4.
- The only binary halide of vanadium(V) is VF_5 (equation 2.2); it is a volatile white solid which is readily hydrolyzed and is a powerful fluorinating agent.

- The oxohalides VOX_3 are made by halogenations of V_2O_5. Reaction of VOF_3 with $(Me_3Si)_2O$ yieldsVO_2F, and treatment of $VOCl_3$ with Cl_2O gives VO_2Cl.
- Vanadium(V) oxide is amphoteric, being sparingly soluble in water but dissolving in alkalis to give a wide range of vanadates, and in strong acids to form complexes of $[VO_2]^+$.

Occurrence and extraction of Vanadium

- Vanadium occurs in several minerals including vanadinite ($Pb_5(VO_4)_3Cl$), carnotite ($K_2(UO_2)_2(VO_4)_2.3H_2O$), roscoelite(a vanadium-containing mica) and the polysulfide patronite (VS_4).

- It also occurs in phosphate rock and in some crude oils. It is not mined directly and extraction of vanadium is associated with that of other metals.
- Roasting vanadium ores with Na_2CO_3 gives water soluble $NaVO_3$ and from solutions of this salt, the sparingly soluble $[NH_4][VO_3]$ can be precipitated.
- This is heated to give V_2O_5, reduction of which with Ca yields V.

Importance and compounds of Vanadium

- The steel industry consumes about 85% of world supplies of V and ferrovanadium (used for toughening steels) is made by reducing a mixture of V_2O_5 and Fe_2O_3 with Al; steel–vanadium alloys are used for spring and high-speed cutting-tool steels.
- Vanadium(V) oxide is used as a catalyst in the oxidations of SO_2 to SO_3 and of naphthalene to phthalic acid.

Chemistry of Chromium

Properties

- Ground state electronic configuration of chromium is [Ar]$4s^1 3d^5$.
- chromium is hard; blue-white metal with melting and boiling points of 2180 K and 2945 K respectively.
- At ordinary temperatures, Cr metal is resistant to chemical attack (although it dissolves in dilute HCl and H_2SO_4).
- Nitric acid renders Cr passive, and Cr is resistant to alkalis.

- At higher temperatures the metal is reactive: it decomposes steam and combines with O_2, halogens, and most other non-metals.

- Borides, carbides and nitrides exist in various phases (e.g. CrN, Cr_2N, Cr_3N, Cr_3N_2) and are inert materials (e.g. CrN is used in wear-resistant coatings).

- The black sulfide Cr_2S_3 is formed by direct combination of the elements on heating; a range of other sulfides are known, but methods of synthesis vary.

- The main oxidation states of chromium are +6, +3 and +2.

- Although the ground state electronic configuration of Cr: $3d^5 4s^1$ suggests the formation of Cr(I) compounds, it is energetically more favorable to form Cr^{2+} ions in solution or in solid compounds.
- However, oxidation states of +1 or lower are stabilized in presence of π-bonding ligands.
- The +2 is the lowest common oxidation state of Cr but Cr(II) compounds are powerful reductants which are readily oxidized to Cr(III): the most stable state.
- A few compounds of Cr(V) and Cr(IV) are known, but are unstable with respect to disproportionation.

Occurrence and extraction of Chromium

- The major ore of chromium is chromite ($FeCr_2O_4$) which has a normal spinel structure.
- Chromite is reduced with carbon to produce ferrochromium for the steel industry; stainless steels contain Cr to increase their corrosion resistance.
- For the production of Cr metal, chromite is fused with Na_2CO_3 in the presence of air to give water-soluble Na_2CrO_4 and insoluble Fe_2O_3.
- Extraction with water followed by acidification with H_2SO_4 gives a solution from which $Na_2Cr_2O_7$ can be crystallized.

Importance and compounds of Chromium

- The corrosion resistance of Cr leads to its widespread use as a protective coating (chromium plating); the metal is deposited by electrolysing aqueous $Cr_2(SO_4)_3$, produced by dissolving Cr_2O_3 in H_2SO_4.

- After the steel industry, the next major consumer of Cr (25%) is the chemical industry; applications include pigments (e.g. chrome yellow), tanning agents, mordants, catalysts and oxidizing agents.
- Chromite is used as a refractory material, e.g. in refractory bricks and furnace linings.
- Chromium compounds are toxic; chromates are corrosive to skin.

- The only halide of chromium(VI) to have been reported is yellow CrF_6, produced by fluorination of the metal at 670K and 200 bar followed by rapid chilling.
- The material so prepared reacts violently in moist air and decomposes at 173K into CrF_5 and F_2.
- The oxohalides CrO_2F_2 and CrO_2Cl_2 are much more stable. Chromium(VI) oxide (‘chromic acid’), CrO_3, separates as a purple-red solid when concentrated H_2SO_4 is added to a solution of a dichromate(VI) salt; it is a powerful oxidant with uses in organic synthesis.

- It melts at 471K and at slightly higher temperatures decomposes to Cr_2O_3 and O_2 with CrO_2 formed as an intermediate.
- Chromium(VI) oxide dissolves in base to give yellow solutions of $[CrO_4]^{2-}$.
- Chromium(VI) is a powerful oxidizing agent in acidic solution.
- Both $Na_2Cr_2O_7$ and $K_2Cr_2O_7$ are manufactured on a large scale; $K_2Cr_2O_7$ is less soluble than $Na_2Cr_2O_7$.
- Both are widely used as oxidants in organic syntheses.

- Chromium(VI) compounds are highly toxic (suspected carcinogens) and must be stored away from combustible materials.
- Unlike CrF_6, CrF_5 is well established.
- It is a red, volatile solid (mp 303 K), formed by direct combination of the elements at around 570K.
- The vapour is yellow and contains distorted trigonal bipyramidal CrF_5 molecules.
- It is a strong oxidizing and fluorinating agent.
- For Cr(V), the fluoride is the only halide known.
- Pure CrF_4 can be made by fluorination of Cr using HF/F_2 under solvothermal conditions.

- The pure material is violet, but the colour of samples prepared by different routes varies (green, green-black, brown) with descriptions being affected by the presence of impurities.
- Chromium(IV) chloride and bromide have been prepared but are unstable. Chromium(IV) oxide, CrO_2, is usually made by controlled decomposition of CrO_3.
- It is a brown-black solid which has the rutile structure and is a metallic conductor.
- The +3 oxidation state is the most stable for chromium in its compounds and octahedral coordination dominates for Cr(III) centres.

- Anhydrous $CrCl_3$ (red-violet solid, mp 1425 K) is made from the metal and Cl_2, and is converted to green CrF_3 by heating with HF at 750 K.
- Solid CrF_3 is isostructural with VF_3, and $CrCl_3$ adopts a BiI_3 structure.
- The dark green tribromide and triiodide can be prepared from Cr and the respective halogen and are isostructural with $CrCl_3$.
- Chromium(III) trifluoride is sparingly soluble and may be precipitated as the hexahydrate.
- Although pure $CrCl_3$ is insoluble in water, addition of a trace of Cr(II) (e.g. $CrCl_2$) results in dissolution.

- Chromium(III) oxide is made by combination of the elements at high temperature, or by reduction of CrO_3.
- Anhydrous CrF_2, $CrCl_2$ and $CrBr_2$ are made by reacting Cr with HX (X=F, Cl, Br) at >850 K; CrI_2 is formed by heating the elements.
- Crystals of $CrCl_2$ are colourless but dissolve in water to give blue solutions of the strongly reducing hexaaqua ion.
- Solutions of $[Cr(H_2O)_6]^{2+}$ are usually obtained by dissolving Cr in acids or by reduction (Zn amalgam or electrolytically) of Cr(III)-containing solutions.
- Hydrated salts such as $Cr(ClO_4)_2.6H_2O$, $CrCl_2.4H_2O$ and $CrSO_4.7H_2O$ may be isolated from solution, but cannot be dehydrated without decomposition.

Chemistry of Manganese

Properties

- Ground state electronic configuration of manganese is [Ar]$4s^2 3d^5$.
- Manganese is Hard; lustrous silver-blue metal with melting and boiling points of 1519 K and 2235K respectively.
- Metallic Mn is slowly attacked by water and dissolves readily in acids.
- The finely divided metal is pyrophoric in air, but the bulk metal is not attacked unless heated.
- At elevated temperatures, it combines with most non-metals, halogens, N_2, C, Si and B.

- Manganese exhibits the widest range of oxidation states of any of the first row d-block metals and more common oxidation numbers than the other 3d transition metals.
- The lowest common oxidation state of +2, represented by Mn^{2+}, is the most stable especially in acidic solution.
- This stability is related to its exactly haif-filled d^{5} sub level. The lowest states are stabilized by -acceptor ligands.
- All oxidation states above Mn(II) are powerful oxidizing agents.

Occurrence and extraction of Manganese

- Several oxides of manganese occur naturally, the most important being pyrolusite (β-MnO_2); South Africa holds 80% of the world's ore reserves but mine production in China, South Africa and Ukraine is currently at similar levels.
- Little recycling of Mn currently takes place.
- Manganese nodules containing up to 24% of the metal have been discovered on the ocean bed.

Importance and compounds of Manganese

- The main use of the element is in the steel industry; pyrolusite is mixed with Fe_2O_3 and reduced with coke to give ferromanganese (80%Mn).
- Almost all steels contain some Mn; those with a high Mn content (up to 12%) possess very high resistance to shock and wear and are suitable for crushing, grinding and excavating machinery.
- Manganese metal is produced by the electrolysis of $MnSO_4$ solutions. Manganese(IV) oxide is used in dry cell batteries.

- The strong oxidizing power of $KMnO_4$ makes this an important chemical; Mn is an essential trace element for plants, and small amounts of $MnSO_4$ are added to fertilizers.
- Binary halides of Mn(VII) have not been isolated.
- The oxohalides MnO_3F and MnO_3Cl may be made by reacting $KMnO_4$ with HSO_3X at low temperature; both are powerful oxidants and decompose explosively at room temperature.
- Manganese(VII) chemistry is dominated by the manganate(VII) ion (permanganate).
- The potassium salt, $KMnO_4$, is a strong oxidizing agent and is corrosive to human tissue; it is manufactured on a large scale by conversion of MnO_2 to K_2MnO_4 followed by electrolytic oxidation.

- Solid $KMnO_4$ forms dark purple-black crystals and is isostructural with $KClO_4$.
- Aqueous solutions of $KMnO_4$ deposit MnO_2 on standing.
- Potassium permanganate is intensely coloured owing to charge transfer from O to Mn.
- No binary halides of Mn(VI) have been isolated, and the only oxohalide is MnO_2Cl_2.
- It is prepared by reducing $KMnO_4$ with SO_2 at low temperature in HSO_3Cl, and is a brown liquid which readily hydrolyses and decomposes at 240 K.
- Salts of dark green $[MnO_4]^{2-}$ are made by fusing MnO_2 with group one metal hydroxides in the presence of air.

- Manganate(VI) is unstable with respect to disproportionation in the presence of even weak acids such as H_2CO_3 and is therefore not formed in the reduction of acidified $[MnO_4]^-$.

$$3[MnO_4]^{2-} + 4H^+ \longrightarrow 2[MnO_4]^- + MnO_2 + 2H_2O$$

- The only binary halide of Mn(IV) is MnF_4, prepared from the elements.
- It is an unstable blue solid which decomposes at ambient temperatures.

- Manganese(IV) oxide is polymorphic and often markedly non-stoichiometric.
- It acts as an oxidizing agent when heated with concentrated acids.
- The only binary halide of Mn(III) is the red-purple MnF_3 which is made by the action of F_2 on Mn(II) halides at 520 K.
- It is thermally stable but is immediately hydrolysed by water.
- The solid state structure of MnF_3 is related to those of TiF_3, VF_3, CrF_3, FeF_3 and CoF_3.
- The red aqua ion $[Mn(H_2O)_6]^{3+}$ can be obtained by electrolytic oxidation of aqueous Mn^{2+} and is present in the alum $CsMn(SO_4)_2.12H_2O$.

Chemistry of Iron

Properties

- Ground state electronic configuration of iron is $[Ar]4s^2 3d^6$.
- Iron is Hard; lustrous silver-blue metal with melting and boiling points of 1811K and 3023K respectively.
- Finely divided Fe is pyrophoric in air, but the bulk metal oxidizes in dry air only when heated.
- In moist air, Fe rusts, forming a hydrated oxide $Fe_2O_3.xH_2O$.
- Iron reacts with halogens at 470–570K to give FeF_3, $FeCl_3$, $FeBr_3$ and FeI_2, respectively.

- The metal dissolves in dilute mineral acids to yield Fe(II) salts, but concentrated HNO_3 and other powerful oxidizing agents make it passive; it is unaffected by alkalis.
- When powdered iron and sulfur are heated together, FeS is produced.
- The chemistry of iron is less extensive than that of manganese. After group 7, transition metals become reluctant to achieve high oxidation states.
- The common oxidation states of iron are +2, +3 and +6.
- The latter is only stable as the tetrahedral $[FeO_4]^{2-}$ in alkaline solution and quickly liberate O_2 at lower pH values.

- Iron (II) is represented by the non-stoichiometric oxide and numerous salts and complexes.
- Although it has a d^6 configuration, most of its complexes are high spin.
- Most of the chemistry of Fe involves Fe(II) or Fe(III), with Fe(IV) and Fe(VI) known in a small number of compounds; Fe(V) is rare.
- Ligands capable of π bonding stabilize oxidation states lower than 2.

Occurrence and extraction of Iron

- Iron is the most important of all metals and is the fourth most abundant element in the Earth's crust.
- The Earth's core is believed to consist mainly of iron and it is the main constituent of metallic meteorites.
- The chief ores are haematite (α-Fe_2O_3), magnetite (Fe_3O_4), siderite ($FeCO_3$), goethite (α-$Fe(O)OH$) and lepidocrocite (γ-$Fe(O)OH$).
- While iron pyrites (FeS_2) and chalcopyrite ($CuFeS_2$) are common, their high sulfur contents render them unsuitable for Fe production.

- Pure Fe (made by reduction of the oxides with H_2) is reactive and rapidly corrodes; finely divided iron is pyrophoric.

Importance and compounds of Iron

- Although pure iron is not of commercial importance, steel production is carried out on a huge scale.
- α-Iron(III) oxide is used as a polishing and grinding agent and in the formation of ferrites; iron oxides are important commercial pigments: α-Fe_2O_3 (red), ɣ-Fe_2O_3 (red-brown), Fe_3O_4 (black) and Fe(O)OH (yellow).

- Iron is of immense biological importance, and is present in, for example, haemoglobin and myoglobin (O_2 carriers), ferredoxins and cytochromes (redox processes), ferritin (iron storage), acid phosphatase (hydrolysis of phosphates), superoxide dismutases (O_2 dismutation) and nitrogenase (nitrogen fixation).
- A deficiency of iron in the body causes anaemia, while an excess causes haemochromatosis

Chemistry of Cobalt

- Ground state electronic configuration of cobalt is [Ar]$4s^2 3d^7$.
- Cobalt is Hard; brittle; lustrous blue-white metal with melting and boiling points of 1768 K and 3143 K respectively.
- Cobalt is less reactive than Fe and its chemistry is simpler than that of iron ; Co does not react with O_2 unless heated, and in very finely divided form it is pyrophoric.
- It dissolves slowly in dilute mineral acids, but concentrated HNO_3 makes it passive; alkalis have no effect on the metal.

- Cobalt reacts at 520K with F_2 to give CoF_3, but with Cl_2, Br_2 and I_2, CoX_2 is formed.
- Even when heated, cobalt does not react with H_2 or N_2, but it does combine with B, C, P, As and S.
- The trend in decreasing stability of high oxidation states on going from Mn to Fe continues along the row.
- The +6 state is the highest oxidation state but it is of far less importance than Co(III) and Co(II).
- Although the two common oxidation states of +2 and +3 are known, Co^{3+} is not stable in aqueous solution, liberating oxygen from water.

- Cobalt (I) and lower oxidation states are stabilized in organometallic species by-acceptor ligands.

Occurrence and extraction of Cobalt

- Cobalt occurs as a number of sulfide and arsenide ores including cobaltite (CoAsS) and skutterudite ((Co,Ni)As_3 which contains planar As4-units).
- Production of the metal generally relies on the fact that it often occurs in ores of other metals (e.g. Ni, Cu and Ag) and the final processes involve reduction of Co_3O_4 with Al or C followed by electrolytic refining.

Importance and compounds of Cobalt

- Pure Co is brittle but it is commercially important in special steels, alloyed with Al, Fe and Ni(Alnico is a group of carbon-free alloys) in permanent magnets, and in the form of hard, strong, corrosion-resistant non-ferrous alloys (e.g. with Cr and W) which are important in the manufacture of jet engines and aerospace components.
- Cobalt compounds are widely used as pigments (blue hues in porcelain, enamels and glass, catalysts and as additives to animal feeds.

- Vitamin B_{12} is a cobalt complex, and a range of enzymes require B_{12} coenzymes.
- The artificial isotope ^{60}Co is used as a tracer.
- Few Co(IV) species have been established.
- Yellow $Cs_2[CoF_6]$ is obtained by fluorination of a mixture of CsCl and $CoCl_2$ at 570 K.
- Cobalt(IV) oxide is prepared by oxidizing Co(II) using alkaline hypochlorite and it is poorly defined.
- Several mixed oxides are known: Ba_2CoO_4 and M_2CoO_3 (M=K, Rb, Cs).

- There are few binary compounds of Co(III) and only a limited number of Co(III) compounds are commercially available.
- The only binary halide is brown CoF_3 which is isostructural with FeF_3.
- It is used as a fluorinating agent, e.g. for preparing perfluorinated organics, and is corrosive and an oxidant.
- The reaction of N_2O_5 with CoF_3 at 200K gives the dark green, anhydrous $Co(NO_3)_3$.
- Although reports of Co_2O_3 are found in the literature, the anhydrous compound probably does not exist.

- In contrast to Co(III), Co(II) forms a variety of simple compounds and all four Co(II) halides are known.
- Reaction of anhydrous $CoCl_2$ with HF at 570K gives sparingly soluble pink CoF_2 which crystallizes with the rutile structure.
- Blue $CoCl_2$ is made by combination of the elements and has a $CdCl_2$ lattice.
- It turns pink on exposure to moisture and readily forms hydrates.
- The dark pink hexahydrate is commercially available and is a common starting material in Co(II) chemistry.
- In aqueous solutions of $CoCl_2$, the major species are $[Co(H_2O)_6]^{2+}$, $[CoCl(H_2O)_5]^{+}$ and $[CoCl_4]^{2-}$, and the minor species are $[CoCl_2(H_2O)_4]$ and $[CoCl_3(H_2O)]^{-}$.

Chemistry of Nickel

Properties

- Ground state electronic configuration of nickel is $[Ar]4s^2 3d^8$.
- Nickel is Hard; malleable and ductile; grey-white metal with melting and boiling points of 1728 K and 3005 K respectively.
- It is attacked by dilute mineral acids, made passive by concentrated HNO_3, and is resistant to aqueous alkalis.
- The bulk metal is oxidized by air or steam only at high temperatures, but Raney nickel is pyrophoric.

- Nickel reacts with F_2 to give a coherent coating of NiF_2 which prevents further attack; hence the use of nickel and its alloy Monel metal in apparatus for handling F_2 or xenon fluorides.
- With Cl_2, Br_2 and I_2, Ni(II) halides are formed.
- At elevated temperatures, Ni reacts with P, S and B and a range of different phosphide, sulfide and boride phases are known.
- Nickel(II) is far the most important oxidation state for the metal.

- The +2oxidation state dominates the chemistry of nickel.

- Low oxidation states are most common in organometallic species, but other Ni(0) species include $[Ni(PF_3)_4]$ and $[Ni(CN)_4]^{4-}$.

- Yellow $K_4[Ni(CN)_4]$ is made by reduction of $K_2[Ni(CN)_4]$ in liquid NH_3 using excess K, but oxidizes immediately on exposure to air.

Occurrence and extraction of Nickel

- Like cobalt, nickel occurs as sulfide and arsenide minerals, e.g. pentlandite, $(Ni,Fe)_9S_8$.

- Roasting such ores in air gives nickel oxide which is then reduced to the metal using carbon.

- The metal is refined electrolytically or by conversion to $Ni(CO)_4$ followed by thermal decomposition.

- This is the Mond process which is based on the fact that Ni forms a carbonyl derivative more readily than any other metal.

Importance and compounds of Nickel

- Nickel is used extensively in alloys, notably in stainless steel, other corrosion-resistant alloys such as Monel metal, and coinage metals.

- Electroplated Ni provides a protective coat for other metals.
- Nickel has widespread use in batteries; recently, this has included the production of ‘environmentally friendly’ nickel–metal hydride batteries which out-perform NiCd cells as rechargeable sources of power in portable appliances.
- Nickel is an important catalyst, e.g. for the hydrogenation of unsaturated organic compounds and in the water–gas shift reaction

Chemistry of Copper

Properties

- Its ground state electronic configuration is $[Ar]4s^1 3d^{10}$.
- Copper is Malleable and ductile; reddish metal with melting and boiling points of 1358 K and 2840 K respectively.
- Copper is the least reactive of the first row metals.
- It is not attacked by non-oxidizing acids in the absence of air, but it reacts with hot concentrated sulfuric acid and with HNO_3 of all concentrations.
- In the presence of air, Cu reacts with many dilute acids and also dissolves in aqueous NH_3 to give $[Cu(NH_3)_4]^{2+}$.
- When heated strongly, Cu combines with O_2.

- Heating Cu with F_2, Cl_2 or Br_2 produces the corresponding dihalide.
- Copper is the only first row d-block metal to exhibit a stable +1 oxidation state.
- In aqueous solution, Cu(I) is unstable by a relatively small margin with respect to Cu(II) and the metal.
- Copper(I) can be stabilized by the formation of an insoluble compound like CuCl or a complex $Cu(CN)_4]^{3-}$.
- Copper(0) is rarely stabilized; the unstable $Cu_2(CO)_6$ has been isolated in a matrix at low temperature.
- The highest oxidation state attained for copper is +4.

Occurrence and extraction of Copper

- Copper is, by a considerable margin, the most noble of the first row metals and occurs native in small deposits in several countries.
- The chief ore is chalcopyrite ($CuFeS_2$) (80% of world copper production); others include chalcanthite ($CuSO_4.5H_2O$), atacamite ($Cu_2Cl(OH)_3$), cuprite (Cu_2O) and malachite ($Cu_2(OH)_2CO_3$).
- Polished malachite is widely used for decorative purposes.
- The first step in Cu production is to roast chalcopyrite in a limited air supply to give Cu_2S and FeO; the latter is removed by combination with silica to form a slag, and Cu_2S is converted to Cu by reaction with oxygen.

Importance and compounds of Copper

- Being corrosion-resistant, Cu is in demand for water and steam piping and is used on the exterior of buildings, e.g. roofing and flashing, where long-term exposure results in a green patina of basic copper sulfate or carbonate.
- Alloys of Cu such as brass (Cu/Zn), bronze (Cu/Sn), nickel silver (Cu/Zn/Ni) and
- coinage metal (Cu/Ni) are commercially important.
- Copper(II) sulfate is used extensively as a fungicide.
- Copper has a vital biochemical role, e.g. in cytochrome oxidase (involved in reduction of O_2 to H_2O) and haemocyanin (an O_2-carrying copper protein in arthropods).

- Copper compounds have numerous catalytic uses, and analytical applications include the biuret test and use of Fehling’s solution.

Chemistry of Zinc

Properties

- Its ground state electronic configuration is [Ar]$4s^2 3d^{10}$.
- Zinc is Brittle at 298K; malleable 373–423K; Lustrous blue-white metal with melting and boiling points of 693 K and 1180 K respectively.
- Zinc is not attacked by air or water at room temperature, but the hot metal burns in air and decomposes steam, forming ZnO.

- Zinc is much more reactive than Cu, liberating H_2 from dilute mineral acids and from alkalis.
- On heating, Zn reacts with all the halogens to give ZnX_2, and combines with elemental S and P.
- The first (Sc) and last (Zn) members of the first row of the d-block exhibit a more restricted range of oxidation states than the other metals.
- The zinc group metals: Zn, Cd and Hg form the M^{2+} ions by losing the two s electrons, the elements which have a completed sub-shell.

- This stable configuration explains the prominence of the +2 oxidation state in binary and complex compounds.
- This configuration also accounts for the diamagnetism of the compounds and the absence of d-d bands in their electronic spectra.
- The +1 oxidation state is significant for Hg but becomes much less significant in Cd and is hardly observed in Zn.
- The chemistry of Zn is confined to that of Zn(II).

Occurrence and extraction of Zinc

- The principal ores of zinc are sphalerite (zinc blende, ZnS), calamine (hemimorphite, $Zn_4Si_2O_7(OH)_2H_2O$) and smithsonite ($ZnCO_3$).
- Extraction from ZnS involves roasting in air to give ZnO followed by reduction with carbon.
- Zinc is more volatile (bp 1180 K) than most metals and can be separated by rapid chilling (to prevent reversing the reaction) and purified by distillation or electrolysis.
- Recycling of Zn has grown in importance, providing a secondary source of the metal.

Importance and compounds of Zinc

- Zinc is used to galvanize steel and Zn alloys are commercially important, e.g. brass (Cu/Zn) and nickel silver (Cu/Zn/Ni).
- Dry cell batteries use zinc as the anode.
- A recent development is that of the zinc–air battery for use in electrically powered vehicles.
- Binary halides are best made by action of HF, HCl, Br_2 or I_2 on hot Zn; ZnF_2 is also prepared by thermal decomposition of $Zn(BF_4)_2$.
- Solid ZnF_2 adopts a rutile structure and has a high lattice energy and melting point.

- Evidence for significant covalent character is apparent in the structures and properties of $ZnCl_2$, $ZnBr_2$ and ZnI_2 which possess layer lattices, have lower melting points than ZnF_2 and are soluble in a range of organic solvents.
- The water solubility of ZnF_2 is low, but $ZnCl_2$, $ZnBr_2$ and ZnI_2 are highly soluble.
- ZnO is its most important compound.
- It is a white solid with the wurtzite structure at 298 K.
- It turns yellow on heating and in this form is a semiconductor owing to loss of oxygen and production of some interstitial Zn atoms.

- Zinc oxide is amphoteric, dissolving in acids to give solutions containing $[Zn(H_2O)_6]^{2+}$ or derivatives there of (some anions coordinate to Zn^{2+}), but hydrolysis of $[Zn(H_2O)_6]^{2+}$ occurs to give various solution species resulting from H^+ loss.
- In alkalis, ZnO forms zincates such as $[Zn(OH)_{4]}{}^{2-}$.
- This ion also forms when $Zn(OH)_2$ dissolves in aqueous alkalis.
- Zinc hydroxide is water-insoluble and thermodynamically the most stable.
- Zinc sulfide occurs naturally as the minerals zinc blend and, more rarely, wurtzite; these are structural prototypes.

- The conversion of ZnS to ZnO by roasting in air is the commercial method of producing the oxide.
- Other Zn(II) compounds that are commercially available include the carbonate, sulfate and nitrate.
- The sulfate is very soluble in water; crystals of $ZnSO_4.7H_2O$ form on evaporating solutions from reactions of Zn, ZnO, $Zn(OH)_2$ or $ZnCO_3$ with aqueous H_2SO_4.
- Zinc nitrate can be obtained as one of several hydrates, of which $Zn(NO_3)_2.6H_2O$ is the most common.
- Anhydrous $Zn(NO_3)_2$ is made from Zn and N_2O_4 since heating the hydrates yields hydroxy salts.

CHAPTER TWO

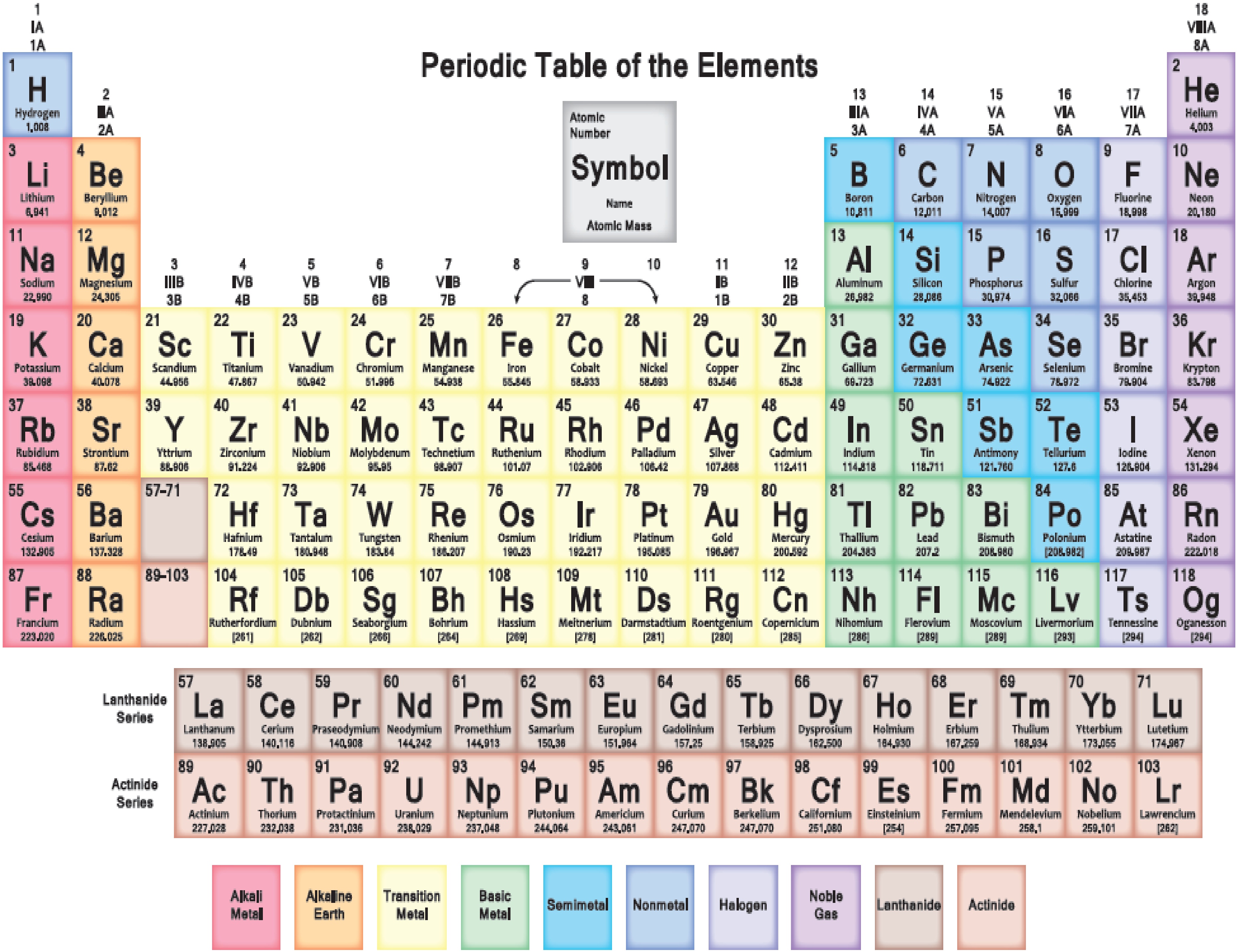
Chemistry of f-block elements

- ➢ The elements constituting the f -block are those in which the 4f and 5f orbitals are progressively filled in the latter two long periods;

- ✓ these elements are formal members of group 3 from which they have been taken out to form a separate f-block of the periodic table.

- ➢ The f-block consists of the two series, lanthanoids (the fourteen elements following lanthanum) and actinoids (the fourteen elements following actinium).

Periodic Table of the Elements



Atomic Number
Symbol
Name
Atomic Mass

1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 **H** Hydrogen 1.008																	2 **He** Helium 4.003
3 **Li** Lithium 6.941	4 **Be** Beryllium 9.012											5 **B** Boron 10.811	6 **C** Carbon 12.011	7 **N** Nitrogen 14.007	8 **O** Oxygen 15.999	9 **F** Fluorine 18.998	10 **Ne** Neon 20.180
11 **Na** Sodium 22.990	12 **Mg** Magnesium 24.305											13 **Al** Aluminum 26.982	14 **Si** Silicon 28.086	15 **P** Phosphorus 30.974	16 **S** Sulfur 32.066	17 **Cl** Chlorine 35.453	18 **Ar** Argon 39.948
19 **K** Potassium 39.098	20 **Ca** Calcium 40.078	21 **Sc** Scandium 44.956	22 **Ti** Titanium 47.867	23 **V** Vanadium 50.942	24 **Cr** Chromium 51.996	25 **Mn** Manganese 54.938	26 **Fe** Iron 55.845	27 **Co** Cobalt 58.933	28 **Ni** Nickel 58.693	29 **Cu** Copper 63.546	30 **Zn** Zinc 65.38	31 **Ga** Gallium 69.723	32 **Ge** Germanium 72.631	33 **As** Arsenic 74.922	34 **Se** Selenium 78.972	35 **Br** Bromine 79.904	36 **Kr** Krypton 83.798
37 **Rb** Rubidium 85.468	38 **Sr** Strontium 87.62	39 **Y** Yttrium 88.906	40 **Zr** Zirconium 91.224	41 **Nb** Niobium 92.906	42 **Mo** Molybdenum 95.95	43 **Tc** Technetium 98.907	44 **Ru** Ruthenium 101.07	45 **Rh** Rhodium 102.906	46 **Pd** Palladium 106.42	47 **Ag** Silver 107.868	48 **Cd** Cadmium 112.411	49 **In** Indium 114.818	50 **Sn** Tin 118.711	51 **Sb** Antimony 121.760	52 **Te** Tellurium 127.6	53 **I** Iodine 126.904	54 **Xe** Xenon 131.294
55 **Cs** Cesium 132.905	56 **Ba** Barium 137.328	57-71	72 **Hf** Hafnium 178.49	73 **Ta** Tantalum 180.948	74 **W** Tungsten 183.84	75 **Re** Rhenium 186.207	76 **Os** Osmium 190.23	77 **Ir** Iridium 192.217	78 **Pt** Platinum 195.085	79 **Au** Gold 196.967	80 **Hg** Mercury 200.592	81 **Tl** Thallium 204.383	82 **Pb** Lead 207.2	83 **Bi** Bismuth 208.980	84 **Po** Polonium [208.982]	85 **At** Astatine 209.987	86 **Rn** Radon 222.018
87 **Fr** Francium 223.020	88 **Ra** Radium 226.025	89-103	104 **Rf** Rutherfordium [261]	105 **Db** Dubnium [262]	106 **Sg** Seaborgium [266]	107 **Bh** Bohrium [264]	108 **Hs** Hassium [269]	109 **Mt** Meitnerium [278]	110 **Ds** Darmstadtium [281]	111 **Rg** Roentgenium [280]	112 **Cn** Copernicium [285]	113 **Nh** Nihonium [286]	114 **Fl** Flerovium [289]	115 **Mc** Moscovium [289]	116 **Lv** Livermorium [293]	117 **Ts** Tennessine [294]	118 **Og** Oganesson [294]

Lanthanide Series	57 **La** Lanthanum 138.905	58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.908	60 **Nd** Neodymium 144.242	61 **Pm** Promethium 144.913	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.925	66 **Dy** Dysprosium 162.500	67 **Ho** Holmium 164.930	68 **Er** Erbium 167.259	69 **Tm** Thulium 168.934	70 **Yb** Ytterbium 173.055	71 **Lu** Lutetium 174.967
Actinide Series	89 **Ac** Actinium 227.028	90 **Th** Thorium 232.038	91 **Pa** Protactinium 231.036	92 **U** Uranium 238.029	93 **Np** Neptunium 237.048	94 **Pu** Plutonium 244.064	95 **Am** Americium 243.061	96 **Cm** Curium 247.070	97 **Bk** Berkelium 247.070	98 **Cf** Californium 251.080	99 **Es** Einsteinium [254]	100 **Fm** Fermium 257.095	101 **Md** Mendelevium 258.1	102 **No** Nobelium 259.101	103 **Lr** Lawrencium [262]

Alkali Metal	Alkaline Earth	Transition Metal	Basic Metal	Semimetal	Nonmetal	Halogen	Noble Gas	Lanthanide	Actinide

- Because lanthanum closely resembles the lanthanoids,
- ✓ it is usually included in any discussion of the lanthanoids for which the general symbol Ln is often used.

- Similarly, a discussion of the actinoids includes actinium besides the fourteen elements constituting the series.

- The lanthanoids resemble one another more closely than do the members of ordinary transition elements in any series.

- They have only one stable oxidation state and their chemistry provides an excellent opportunity to examine the effect of small changes in size and nuclear charge along a series of otherwise similar elements.
- The chemistry of the actinoids is, on the other hand, much more complicated.
- The complication arises partly owing to the occurrence of a wide range of oxidation states in these elements and partly because their radioactivity creates special problems in their study.

The Lanthanoids

Electronic Configurations

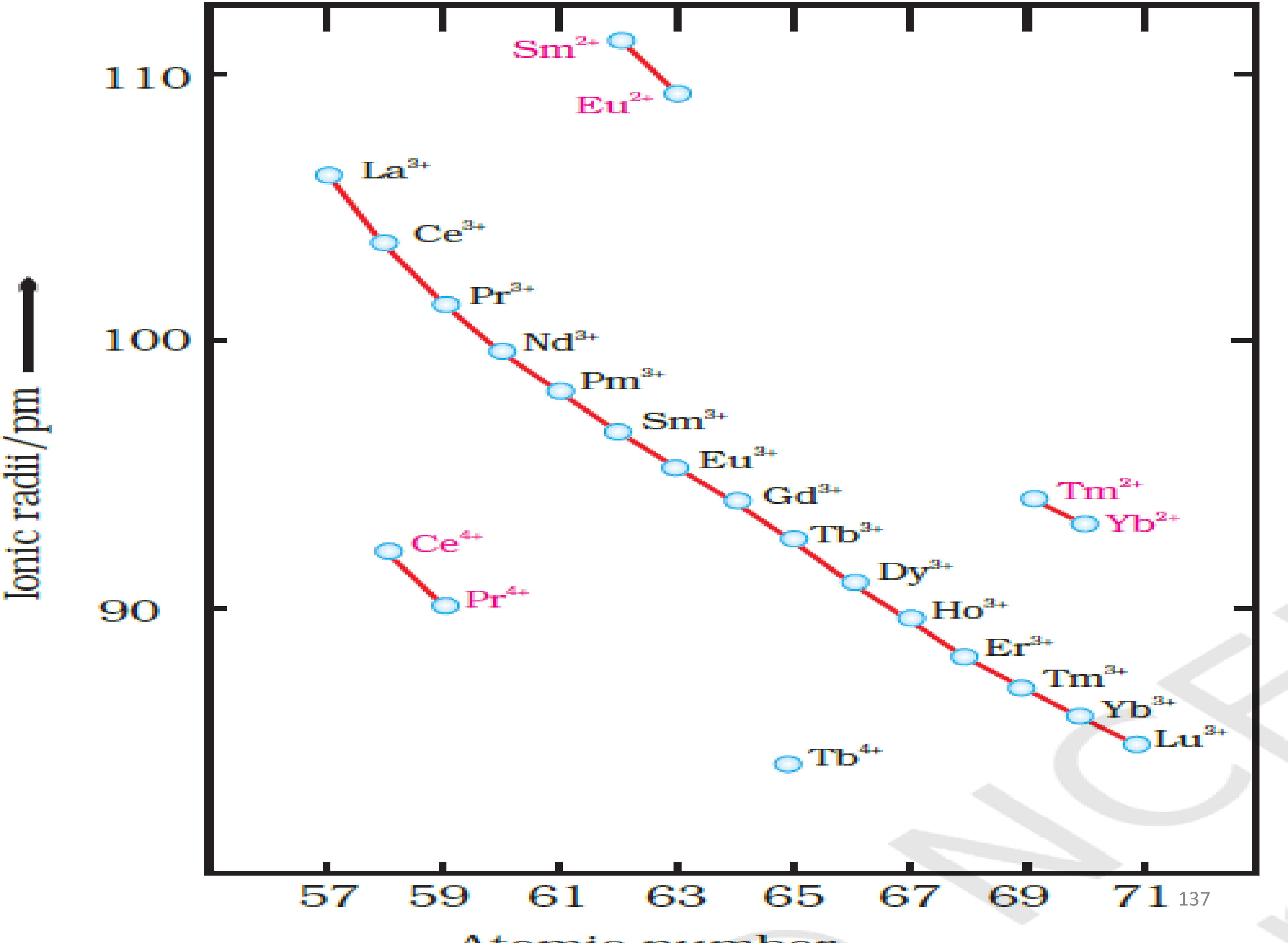
- It may be noted that atoms of these elements have electronic configuration with $6s^2$ common but with variable occupancy of 4f level.
- However, the electronic configurations of all the tripositive ions (the most stable oxidation state of all the lanthanoids) are of the form $4f^n$ ($n = 1$ to 14 with increasing atomic number).

Element name	Symbol	Z	Ground state electronic configuration				Radius / pm	
			Ln	Ln^{2+}	Ln^{3+}	Ln^{4+}	Ln	Ln^{3+} ‡
Lanthanum	La	57	$[Xe]6s^2 5d^1$	$[Xe]5d^1$	$[Xe]4f^0$		188	116
Cerium	Ce	58	$[Xe]4f^1 6s^2 5d^1$	$[Xe]4f^2$	$[Xe]4f^1$	$[Xe]4f^0$	183	114
Praseodymium	Pr	59	$[Xe]4f^3 6s^2$	$[Xe]4f^3$	$[Xe]4f^2$	$[Xe]4f^1$	182	113
Neodymium	Nd	60	$[Xe]4f^4 6s^2$	$[Xe]4f^4$	$[Xe]4f^3$		181	111
Promethium	Pm	61	$[Xe]4f^5 6s^2$	$[Xe]4f^5$	$[Xe]4f^4$		181	109
Samarium	Sm	62	$[Xe]4f^6 6s^2$	$[Xe]4f^6$	$[Xe]4f^5$		180	108
Europium	Eu	63	$[Xe]4f^7 6s^2$	$[Xe]4f^7$	$[Xe]4f^6$		199	107
Gadolinium	Gd	64	$[Xe]4f^7 6s^2 5d^1$	$[Xe]4f^7 5d^1$	$[Xe]4f^7$		180	105
Terbium	Tb	65	$[Xe]4f^9 6s^2$	$[Xe]4f^9$	$[Xe]4f^8$	$[Xe]4f^7$	178	104
Dysprosium	Dy	66	$[Xe]4f^{10} 6s^2$	$[Xe]4f^{10}$	$[Xe]4f^9$	$[Xe]4f^8$	177	103
Holmium	Ho	67	$[Xe]4f^{11} 6s^2$	$[Xe]4f^{11}$	$[Xe]4f^{10}$		176	102
Erbium	Er	68	$[Xe]4f^{12} 6s^2$	$[Xe]4f^{12}$	$[Xe]4f^{11}$		175	100
Thulium	Tm	69	$[Xe]4f^{13} 6s^2$	$[Xe]4f^{13}$	$[Xe]4f^{12}$		174	99
Ytterbium	Yb	70	$[Xe]4f^{14} 6s^2$	$[Xe]4f^{14}$	$[Xe]4f^{13}$		194	99
Lutetium	Lu	71	$[Xe]4f^{14} 6s^2 5d^1$	$[Xe]4f^{14} 5d^1$	$[Xe]4f^{14}$		173	98

Atomic and Ionic Sizes

- The overall decrease in atomic and ionic radii from lanthanum to lutetium (the **lanthanoid contraction) is a unique feature in the** chemistry of the lanthanoids.
- The decrease in atomic radii (derived from the structures of

metals) is not quite regular as it is regular in M^{3+} ions.


Ionic radii /pm
110
100
90
Sm²⁺
Eu²⁺
La³⁺
Ce³⁺
Pr³⁺
Nd³⁺
Pm³⁺
Sm³⁺
Eu³⁺
Gd³⁺
Tb³⁺
Dy³⁺
Ho³⁺
Er³⁺
Tm³⁺
Yb³⁺
Lu³⁺
Tm²⁺
Yb²⁺
Ce⁴⁺
Pr⁴⁺
Tb⁴⁺
57
59
61
63
65
67
69
71

Oxidation States

- In the lanthanoids, La(II) and Ln(III) compounds are predominant species.
- However, occasionally +2 and +4 ions in solution or in solid compounds are also obtained.
- This irregularity arises mainly from the extra stability of empty, half-filled or filled f subshell.
- Thus, the formation of Ce^{IV} is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state.

- The E^o value for Ce^{4+}/ Ce^{3+} is +1.74 V which suggests that it can oxidise water.
- However, the reaction rate is very slow and hence Ce(IV) is a good analytical reagent.
- Pr, Nd, Tb and Dy also exhibit +4 state but only in oxides, MO_2.
- Eu^{2+} is formed by losing the two s electrons and its f^7 configuration accounts for the formation of this ion.
- However, Eu^{2+} is a strong reducing agent changing to the common +3 state.
- Similarly Yb^{2+} which has f^{14} configuration is a reductant.

- The behaviour of samarium is very much like europium, exhibiting both +2 and +3 oxidation states.

General physical and chemical properties

- All the lanthanoids are silvery white soft metals and tarnish rapidly in air.
- The hardness increases with increasing atomic number, samarium being steel hard.
- Their melting points range between 1000 to 1200 K but samarium melts at 1623 K.

- They have typical metallic structure and are good conductors of heat and electricity.
- Density and other properties change smoothly except for Eu and Yb and occasionally for Sm and Tm.
- Many trivalent lanthanoid ions are coloured both in the solid state
- and in aqueous solutions.
- Colour of these ions may be attributed to the presence of *f electrons*.

- *Neither La^{3+} nor Lu^{3+} ion shows any colour* but the rest do so.
- However, absorption bands are narrow, probably because of the excitation within *f level*.
- The lanthanoid ions other than the f^0 type (La^{3+} and Ce^{4+}) and the f^{14} type (Yb^{2+} and Lu^{3+}) are all paramagnetic.
- The paramagnetism rises to maximum in neodymium.

- The first ionisation enthalpies of the lanthanoids are around 600 kJ mol^{-1}, the second about 1200 kJ mol^{-1} comparable with those of calcium.
- In general, the earlier members of the series are quite reactive similar to calcium but, with increasing atomic number, they behave more like aluminium.
- The metals combine with hydrogen when gently heated in the gas.
- The carbides, Ln_3C, Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon.

- They liberate hydrogen from dilute acids and burn in halogens to form halides.
- They form oxides M_2O_3 and hydroxides $M(OH_{)3}$.
- The hydroxides are definite compounds, not just hydrated oxides.
- They are basic like alkaline earth metal oxides and hydroxides.

The Actinoids

- ➢ The actinoids include the fourteen elements from Th to Lr.
- ➢ The actinoids are radioactive elements and the earlier members have relatively long half-lives,
- ✓ the latter ones have half-life values ranging from a day to 3 minutes for lawrencium (Z =103).
- ➢ The latter members could be prepared only in nanogram quantities.
- ➢ These facts render their study more difficult.

Electronic Configurations

- ➢ All the actinoids are believed to have the electronic configuration of $7s^2$ and variable occupancy of the 5f and 6d subshells.

- ➢ The fourteen electrons are formally added to 5f, though not in thorium (Z = 90) but from Pa onwards the 5f orbitals are complete at element 103.

- ➢ The irregularities in the electronic configurations of the actinoids,

- ✓ like those in the lanthanoids are related to the stabilities of the f^0, f^7 and f^{14} occupancies of the 5f orbitals.

- Thus, the configurations of Am and Cm are [Rn] $5f^{7}7s^{2}$ and [Rn] $5f^{7}6d^{1}7s^{2}$.

- Although the 5f orbitals resemble the 4f orbitals in their angular part of the wave-function,

- ✓ they are not as buried as 4f orbitals and hence 5f electrons can participate in bonding to a far greater extent.

Ionic Sizes

- The general trend in lanthanoids is observable in the actinoids as well.

- There is a gradual decrease in the size of atoms or M^{3+} ions across the series.
- This may be referred to as the actinoid contraction (like lanthanoid contraction).
- The contraction is, however, greater from element to element in this series resulting from poor shielding by 5f electrons.

Oxidation States

- There is a greater range of oxidation states, which is in part attributed to the fact that the 5f, 6d and 7s levels are of comparable energies.

- The actinoids show in general +3 oxidation state.
- The elements, in the first half of the series frequently exhibit higher oxidation states.
- For example, the maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements .
- The actinoids resemble the lanthanoids in having more compounds in +3 state than in the +4 state.
- However, +3 and +4 ions tend to hydrolyse.

- Because the distribution of oxidation states among the actinoids is so uneven and so different for the former and later elements,

✓ it is unsatisfactory to review their chemistry in terms of oxidation states.

General Properties and Comparison with Lanthanoids

- The actinoid metals are all silvery in appearance but display a variety of structures.

- The structural variability is obtained due to irregularities in metallic radii which are far greater than in lanthanoids.
- The actinoids are highly reactive metals, especially when finely divided.
- The action of boiling water on them, for example,
- ✓ gives a mixture of oxide and hydride and combination with most non metals takes place at moderate temperatures.
- HCl attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers; alkalies have no action.

- The magnetic properties of the actinoids are more complex than those of the lanthanoids.
- Although the variation in the magnetic susceptibility of the actinoids with the number of unpaired 5f electrons is roughly parallel to the corresponding results for the lanthanoids,
- ✓ the latter have higher values.
- It is evident from the behaviour of the actinoids that the ionisation enthalpies of the early actinoids, though not accurately known,
- ✓ but are lower than for the early lanthanoids.

- This is quite reasonable since it is to be expected that when 5f orbitals are beginning to be occupied, they will penetrate less into the inner core of electrons.
- The 5f electrons, will therefore, be more effectively shielded from the nuclear charge than the 4f electrons of the corresponding lanthanoids.
- Because the outer electrons are less firmly held, they are available for bonding in the actinoids.

- A comparison of the actinoids with the lanthanoids,
  - ✓ with respect to different characteristics as discussed above,
  - ✓ reveals that behaviour similar to that of the lanthanoids is not evident until the second half of the actinoid series.
- However, even the early actinoids resemble the lanthanoids in showing close similarities with each other and in gradual variation in properties which do not entail change in oxidation state.

- The lanthanoid and actinoid contractions, have extended effects on the sizes, and therefore, the properties of the elements succeeding them in their respective periods.
- The lanthanoid contraction is more important because the chemistry of elements succeeding the actinoids are much less known at the present time.

Properties of Lanthanoids

- Lanthanum and the lanthanoids, except Eu, crystallize in one or both of the close-packed structures; Eu has a bcc lattice.

- All the lanthanoids are soft white metals.
- The later metals are passivated by an oxide coating and are kinetically more inert than the earlier metals.
- All the metals liberate H_2 from dilute acids or steam.
- They burn in air to give Ln_2O_3 with the exception of Ce which
- forms CeO_2.
- When heated, lanthanoids react with H_2 to give a range of compounds between metallic (i.e. conducting) hydrides LnH_2 (best formulated as $Ln^{3+}(H^-)_2(e^-)$) and saline hydrides LnH_3.

- Non-stoichiometric hydrides are typified by ‘GdH_3’ which actually has compositions in the range $GdH_{2.85-3}$.
- Europium forms only EuH_2.
- The alloy $LaNi_5$ is a potential ‘hydrogen storage vessel’ since it reversibly absorbs $H_{2.}$
- The carbides Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon.
- The LnC_2 carbides adopt the same structure as CaC_2, but the CC bonds (128 pm) are significantly lengthened (119pm in CaC_2).

Occurrence and separation of the lanthanoides

- All the lanthanoides except Pm occur naturally.
- The most stable isotope of promethium, 147Pm (β-emitter) is formed as a product of the fission of heavy nuclei and is obtained in mg amounts from products of nuclear reactors.
- Bastnasite and monazite are the main ores for La and the lanthanoids.
- All the metals (excluding Pm) can be obtained from monazite, a mixed phosphate (Ce, La, Nd, Pr,Th,Y . . .)PO_4.

- Bastnasite, (Ce, La . . .)CO_3F, is a source of the lighter lanthanoids.
- The first step in extraction of the metals from monazite is removal of phosphate and thorium.
- The ore is heated with caustic soda, and, after cooling, Na_3PO_4 is dissolved in water.
- The residual hydrated Th(IV) and Ln(III) oxides are treated with hot, aqueous HCl; ThO_2 is not dissolved, but the Ln(III) oxides give a solution of MCl_3 (M = La, Ce. . .) which is then purified.

- Starting from bastnasite, the ore is treated with dilute HCl to remove $CaCO_3$, and then converted to anaqueous solution of MCl_3 (M = La, Ce . . .).
- The similarity in ion size and properties of the lanthanoids makes separation difficult.

The actinoid metals

- The artificial nature of all but two of the actinoid metals affects the extent of knowledge of their properties, and this is reflected in the varying amounts of information that we give for each metal.
- The instability of the actinoids with respect to radioactive decay has already been mentioned

- All the actinoids are highly toxic, the ingestion of long-lived a-emitters such as ^{231}Pa being extremely hazardous; lethal doses are extremely small.

Properties

- Actinium is a soft metal which glows in the dark.
- It is readily oxidized to Ac_2O_3 in moist air, and liberates H_2 from H_2O.
- Thorium is relatively stable in air, but is attacked slowly by H_2O and rapidly by steam or dilute HCl.

- On heating, Th reacts with H_2 to give ThH_2, halogens to give ThX_4, and N_2 and C to give nitrides and carbides; it forms alloys with a range of metals (e.g. Th_2Zn, $CuTh_2$).
- Protactinium is ductile and malleable, is not corroded by air, but reacts with O_2, H_2 and halogens when heated, and with concentrated HF, HCl and H_2SO_4.
- Uranium corrodes in air; it is attacked by water and dilute acids but not alkali.
- With O_2, UO_2 is produced, but on heating, U_3O_8 forms.

- Neptunium is a reactive metal which quickly tarnishes in air.

- It reacts with dilute acids liberating H_2, but is not attacked by alkali.

- Despite the fact that the critical mass of plutonium is <0.5 kg and it is extremely toxic, its uses as a nuclear fuel and explosive make it a much-studied element.

- It reacts with O_2, steam and acids, but is inert towards alkali; on heating, Pu combines with many non-metals to give, for example, PuH_2, PuH_3, $PuCl_3$, PuO_2 and Pu_3C_2.

- Americium is a very intense α- and ɣ-emitter.
- It tarnishes slowly in dry air, reacts with steam and acids, and on heating forms binary compounds with a range of non-metals.
- Curium corrodes rapidly in air; only minute quantities can be handled (<20mg in controlled conditions).
- Berkelium and californium behave similarly to Cm, being attacked by air and acids, but not by alkali.
- Curium and the later elements are handled only in specialized research laboratories.

Occurrence and separation of actinoids

- With the exception of Th and U, the actinoids are manmade, produced by nuclear reactions .
- Radiation hazards of all but Th and U lead to technical difficulties in studying actinoid compounds, and conventional experimental techniques are not generally applicable.
- Uranium and thorium are isolated from natural sources.
- Thorium is extracted from monazite as ThO_2, and the most important source of uranium is pitchblende (U_3O_8).

- The uranium ore is heated with H_2SO_4 in the presence of an oxidizing agent to give the sulfate salt of the uranyl cation, $[UO_2]^{2+}$, which is separated on an anionexchange resin, eluting with HNO_3 to give $[UO_2][NO_3]_2$.
- After further work-up, the uranium is precipitated as the oxo-peroxo complex $UO_2(O_2).2H_2O$ or as ‘yellow cake’ (approximate composition $[NH_4]_2[U_2O_7]$).
- Thermal decomposition gives yellow UO_3 which is converted to UF_4; reduction with Mg yields U metal.
- The isotopes ^{227}Ac and ^{231}Pa can be isolated from the decay products of ^{235}U in pitchblende, but are better synthesized by nuclear reactions.

CHAPTER THREE

COORDINATION CHEMISTRY OF TRANSITION METALS

- Coordination chemistry concerns compounds in which a small number of molecules or ions called **ligands** surround a **central metal** atom or ion.

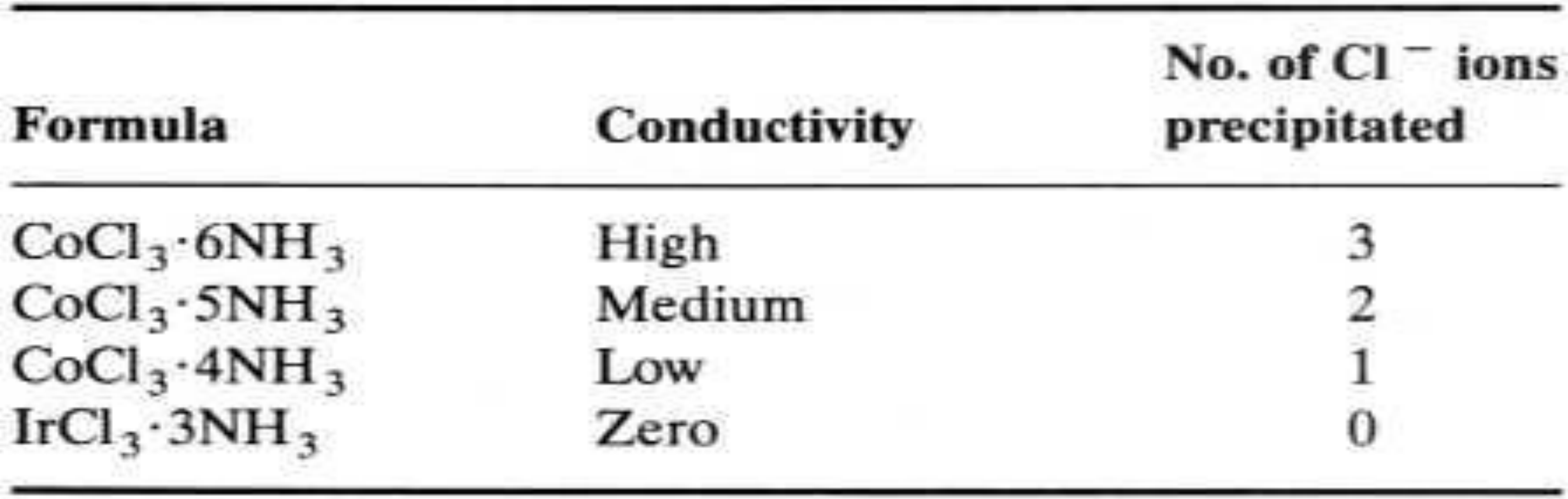
- Each ligand (from the Latin ligare, meaning “to bind”) shares a pair of its electrons with the metal.

- The metal ligand bond, often represented as M ⟵ :L, is an example of a coordinate-covalent bond in which both the electrons come from one atom.

The History of Coordination Compounds

- At the very end of the eighteenth century, **Tassaert**-a French chemist observed that ammonia combined with a cobalt ore to yield a reddish-brown product.
- This was most likely the first known coordination compound.
- Throughout the first half of the nineteenth century, many other, often beautifully crystalline examples of various cobalt ammonates were prepared.

- These compounds were strikingly colored, and the names given to them, for example, roseo-, luteo- (from the Latin luteus, meaning “deep yellow”), and purpureocobaltic chlorides reflected these colors.



Formula	Conductivity	No. of Cl^- ions precipitated
$CoCl_3 \cdot 6NH_3$	High	3
$CoCl_3 \cdot 5NH_3$	Medium	2
$CoCl_3 \cdot 4NH_3$	Low	1
$IrCl_3 \cdot 3NH_3$	Zero	0

The Cobalt Ammonate Chlorides

- In the second half of the century, other ammonates, particularly those of **chromium** and **platinum**, were prepared.
- Despite various attempts, however, no **theoretical basis** was developed to account satisfactorily for these wondrous compounds.
- Given the success of organic chemists in describing the **structural units** and fixed atomic valences found in carbon-based compounds, it was natural that these ideas be applied to the ammonates.

- The formulas used in the last few decades of the nineteenth century indicated the **ammonia-to-cobalt** mole ratio but left the **nature** of the **bonding** between them to the imagination.
- This uncertainty (or lack of knowledge about the bonding) was reflected in the dot used in the formula to connect, for example, $CoCl_3$ to the appropriate number of ammonias.
- The compound with a 3:1 ammonia-to-cobalt ratio proved difficult to prepare.
- The corresponding iridium compound was used instead.

- Conductivities measured when these compounds were dissolved in water are given qualitatively.
- Conductivity was just then starting to be taken as a measure of the number of ions produced in solution.
- The “number of chloride ions precipitated” was determined by the addition of aqueous silver nitrate.

$$\mathrm{AgNO_3}(aq) + \mathrm{Cl^-}(aq) \longrightarrow \mathrm{AgCl}(s) + \mathrm{NO_3^-}(aq)$$

- Now how might you explain such data?

- ➢ More important, from a historical point of view, how did the chemists of the late 1860s,
- ✓ who had been schooled in the relatively new but extraordinarily successful ideas of organic chemistry, explain such data?
- ➢ It seemed to have been fairly well established by then that each element has a valence, sometimes called a *combining capacity*, *which is a* single fixed value.

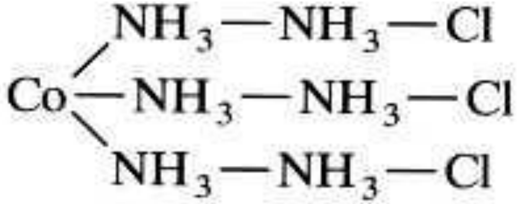
- Furthermore, many workers had found that organic compounds could be pictured as **vast chains** of carbon atoms composed of **radicals** and groups of various types that also appeared to have fixed valences.

- For example, hexane, $CH_3–CH_2–CH_2–CH_2–CH_2–CH_3$, with its chain of six carbon atoms,
- could be pictured as containing monovalent methyl ($CH_3–$) groups on the ends with four divalent methylene ($–CH_2–$) groups in the middle.

The Blomstrand–Jørgensen Chain Theory

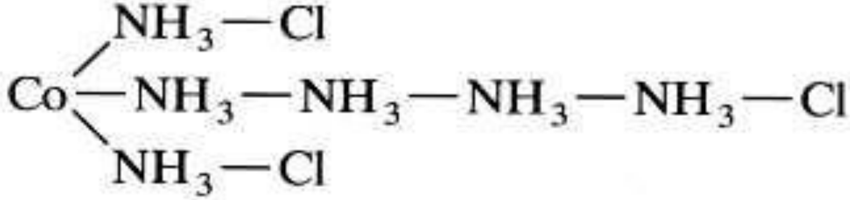
- In 1869 **Christian Wilhelm Blomstrand** first formulated his chain theory to account for the cobalt ammonate chlorides and other series of ammonates.
- Blomstrand, knowing that the fixed valence of cobalt was established at 3, chained together cobalt atoms,
- ✓ divalent ammonia groups, and monovalent chlorides to produce a picture of $CoCl_3 \cdot 6NH_3$, something like that shown in Figure below.

(*a*) $CoCl_3 \cdot 6NH_3$

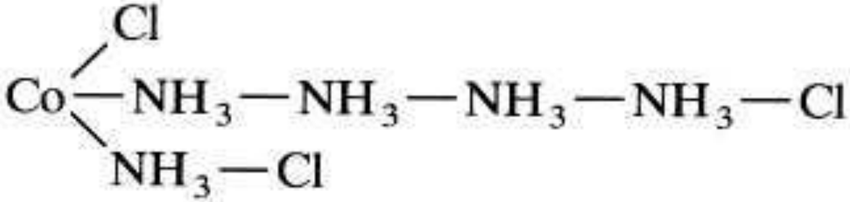


(*b*)

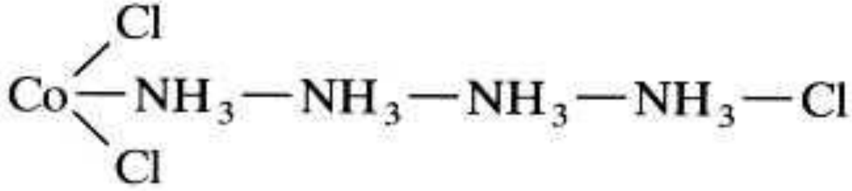
(1) $CoCl_3 \cdot 6NH_3$



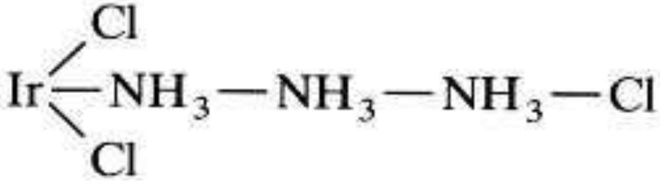
(2) $CoCl_3 \cdot 5NH_3$



(3) $CoCl_3 \cdot 4NH_3$



(4) $IrCl_3 \cdot 3NH_3$



- Based on the prevailing ideas of the time, this was a perfectly reasonable structure.
- The divalent ammonia he proposed was consistent with a view of ammonium chloride written as $H–NH_3–Cl$.
- The valence of 3 for cobalt was **satisfied**, nitrogen atoms were chained together much like carbon was in organic compounds,
- ✓ and the three monovalent chlorides were **far enough** removed from the cobalt atom to be available to be precipitated by aqueous silver nitrate.

- In 1884 Sophus Mads Jørgensen, a student of Blomstrand’s, proposed some **amendments** to his mentor’s picture.
- First, he had new evidence that correctly indicated that these compounds were monomeric.
- Second, he **adjusted** the **distance** of the chloride groups from the cobalt to account for the **rates** at which various chlorides were precipitated.
- The first chloride is precipitated much more **rapidly** than the others and so was put farther away and therefore less under the influence of the cobalt atom.

- Note that, in the second compound, one chloride is now **directly** attached to the cobalt and therefore, Jørgensen assumed, **unavailable** to be precipitated by silver nitrate.

- In the third compound, two chlorides are similarly pictured.

- These changes significantly improved the chain theory, but a number of unanswered questions remained.

- For example, why are there only 6 ammonia molecules? Why not 8 or 10?

- Why do we not see ammonia molecules that are chemically different depending on their positions in the chain?
- On balance, however, it appeared that the Blomstrand-Jørgensen theory of the cobalt ammonates was on the right track.
- But was there a compound with only three ammonias?
- The chain theory predicted that it should exist and, furthermore, should have one ionizable chloride.
- But this critical compound was not available.

- **Jørgensen** set out to prepare it to test his version of the chain theory.
- Try as he might, this excellent synthetic chemist could not come up with the desired cobalt compound.
- He did, however, manage to prepare, after considerable time and effort, the analogous iridium ammonate chloride.
- Alas, it was found to be a neutral compound with no ionizable chlorides.
- With no small amount of irony, the chain theory was in trouble-thanks to the considerable efforts of one of its principal proponents.

The Werner Coordination Theory

- Alfred Werner, a German-Swiss chemist, was torn between organic and inorganic chemistry.

- His first contributions (the stereochemistry, or spatial arrangements, of atoms in nitrogen compounds) were in the organic field, but so many intriguing inorganic questions were being raised in those days that he decided that this was the area in which he would work.

- He observed the difficulties that inorganic chemists were having in explaining coordination compounds,
- ✓ and he was aware that the established ideas of organic chemistry seemed to lead only into blind alleys and dead ends.
- In 1892, when Werner was only 26 years old, his coordination theory came to him in a dream.
- He woke up and started to write it down, and by five o’clock in the morning it was essentially complete.

- But his new theory broke with the earlier traditions, and he had essentially no experimental proof to support his ideas.
- Jørgensen, Blomstrand, and others considered Werner to be an impulsive young man and his theory to be audacious fiction.
- Werner spent the rest of his life directing a systematic and thorough research program to prove that his intuition was correct.
- Werner decided that the idea of a single fixed valence could not apply to cobalt and other similar metals.

- Working with the cobalt ammonates and other related series involving chromium and platinum,

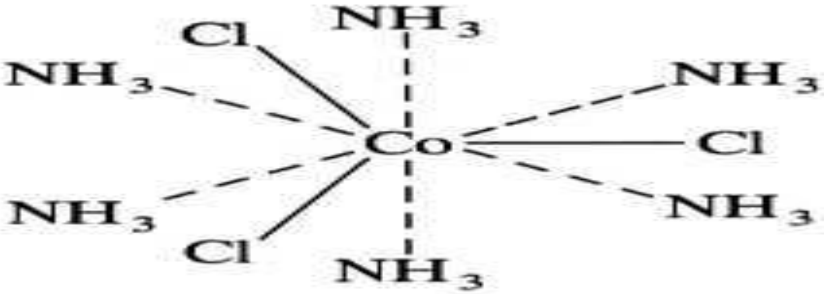
- ✓ he proposed instead that these metals have two types of valence, a **primary valence** and a secondary valence.

- The primary, or ionizable, valence corresponded to what we call today the oxidation state; for cobalt, it is the 3+ state.

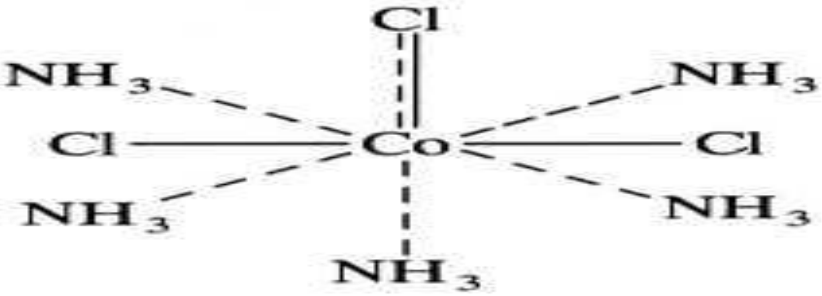
- The secondary valence is more commonly called the coordination number ; for cobalt, it is **6**.

- Werner maintained that this secondary valence was directed toward fixed geometric positions in space.

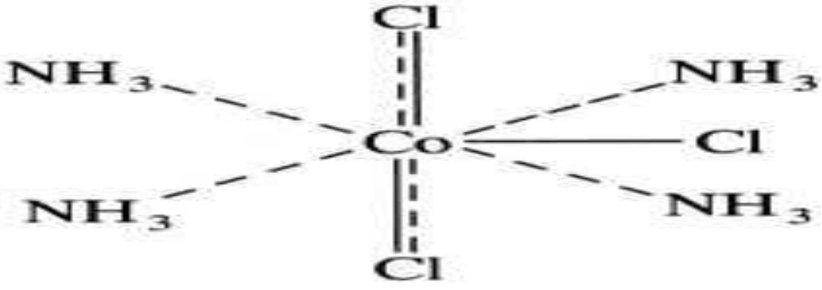
(1) $CoCl_3 \cdot 6NH_3$



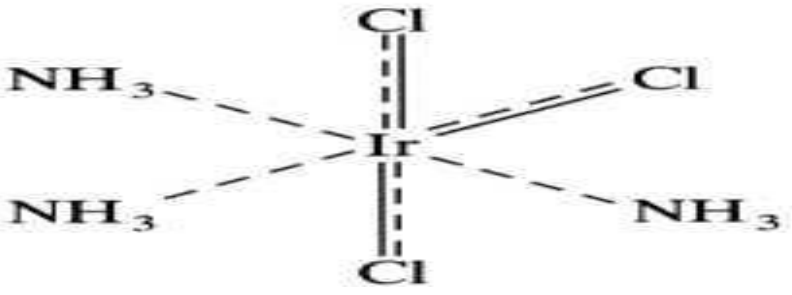
(2) $CoCl_3 \cdot 5NH_3$



(3) $CoCl_3 \cdot 4NH_3$



(4) $IrCl_3 \cdot 3NH_3$

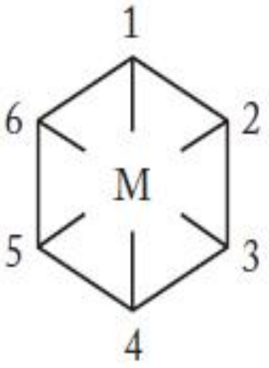
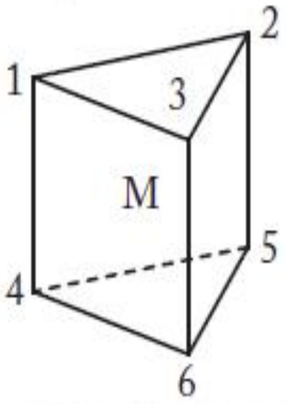
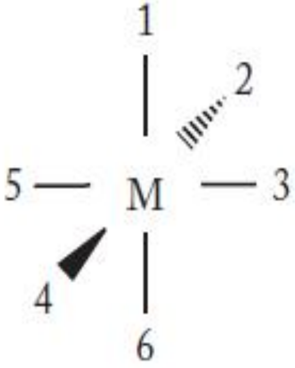


- **Werner** said that the cobalt must simultaneously satisfy both its primary and secondary valences.
- The solid lines show the groups that satisfy the primary valence, and the dashed lines,
- ✓ always directed toward the same fixed positions in space, show how the secondary valence was satisfied.
- In compound (1), all three chlorides satisfy only the primary valence, and the six ammonias satisfy only the secondary.

- In **compound (2)**, one chloride must do double duty and help satisfy both valences.
- The chloride that satisfies the secondary valence (and is directly bound to the Co^{3+} ion) was concluded to be unavailable for precipitation by silver nitrate.
- **Compound (3)** has two chlorides doing double duty and only one available for precipitation.
- **Compound (4)**, according to Werner, should be a neutral compound with no ionizable chlorides.
- This was exactly what Jørgensen had found with the iridium compound.

- Werner next turned to the geometry of the secondary valence (or coordination number).
- As shown in Table 2.2, six ammonias about a central metal atom or ion might assume one of several different common geometries, including hexagonal planar, trigonal prismatic, and octahedral.
- The table compares some information about the predicted and actual number of isomers for a variety of substituted coordination compounds.
- *Isomers are* defined here as compounds that have the same numbers and types of chemical bonds but differ in the spatial arrangements of those bonds.

- The number of predicted isomers refers to the number of theoretically possible geometric arrangements in space.
- For example, for the octahedral MA_5B case, there is only one possible geometry, even though there are numerous ways to draw it.
- In each case, the same configuration has simply been oriented differently in space so that the one B ligand is either up in the axial position or in a different equatorial position.
- In other words, all six octahedral positions are equivalent, and it does not matter which position is occupied by the one B ligand.

	Hexagonal planar  	Trigonal prism  	Octahedral  	
Formula	**No. of predicted isomers (numbers in parentheses indicate position of the B ligands)**			**No. of actual isomers**
MA_5B	One	One	One	One
MA_4B_2	Three	Three	Two	Two
	(1, 2)	(1, 2)	(1, 2)	
	(1, 3)	(1, 4)	(1, 6)	
	(1, 4)	(1, 6)		
MA_3B_3	Three	Three	Two	Two
	(1, 2, 3)	(1, 2, 3)	(1, 2, 3)	
	(1, 2, 4)	(1, 2, 4)	(1, 2, 6)	
	(1, 3, 5)	(1, 2, 6)		

- Given these results (obtained by analyzing a large number of series of coordination compounds),

- ✓ Werner could predict that two isomers would be found for the $CoCl_3.4NH_3$ case.

- These proved somewhat difficult to prepare, but in 1907 Werner was finally successful.
- He found two isomers, one a bright green and the other a vivid violet.

- Now although all this would be considered “negative” evidence by a philosopher of science (it was the *absence* of an isomer that constituted the evidence), the case for the coordination theory was growing stronger.

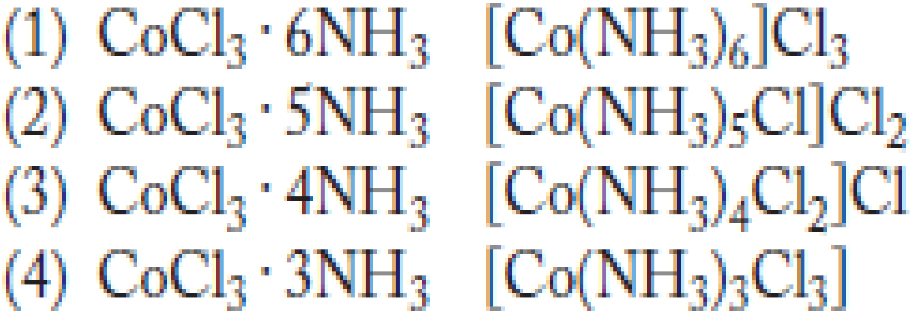
- The “negative” proof, however, was enough for Jørgensen.
- In 1907 he dropped his opposition to Werner’s “audacious” coordination theory.
- Blomstrand and Jørgensen tried to extend the established ideas of organic chemistry to account for the newer coordination compounds.
- In doing so, one could argue, they actually impaired progress in the understanding of this branch of chemistry.
- The trick, of course, is to know when to stick to the established ideas and when to break away from them.

- Werner chose the latter course and, 20 years later in 1913, received the **Nobel Prize** in chemistry.

THE MODERN VIEW OF COORDINATION COMPOUNDS

- Today, the molecular formulas of coordination compounds are represented in a manner that makes it clearer which groups are part of the coordination sphere and which are not.
- As indicated in the introduction to this chapter, the metal atom or ion and the ligands coordinated to it are enclosed in brackets.

- It follows that the cobalt ammonate chlorides can be represented as



(1)	$CoCl_3 \cdot 6NH_3$	$[Co(NH_3)_6]Cl_3$
(2)	$CoCl_3 \cdot 5NH_3$	$[Co(NH_3)_5Cl]Cl_2$
(3)	$CoCl_3 \cdot 4NH_3$	$[Co(NH_3)_4Cl_2]Cl$
(4)	$CoCl_3 \cdot 3NH_3$	$[Co(NH_3)_3Cl_3]$

- The ammonia molecules and chloride ions inside the brackets satisfy the coordination number of cobalt.
- The chlorides in the coordination sphere do double duty, also helping to satisfy the 3+ oxidation state of the cobalt.

- The chlorides outside the brackets, sometimes called *counter ions*, *help satisfy only the* oxidation state.
- They are the only ionic chlorides available to be precipitated by silver nitrate.
- For example, if compound (2) is placed in water and treated with aqueous silver ions, the resulting reaction would be that represented by Equation below:

$$[Co(NH_3)_5Cl]Cl_2(s) + 2Ag^+(aq) \longrightarrow 2AgCl(s) + [Co(NH_3)_5Cl]^{2+}(aq)$$

- Although cobalt compounds were the most prevalent subject of his research program, Werner and his collaborators worked with other metals as well.

(1) $[Pt(NH_3)_6]Cl_4$

(2) $[Pt(NH_3)_5Cl]Cl_3$

(3) $[Pt(NH_3)_4Cl_2]Cl_2$

(4) $[Pt(NH_3)_3Cl_3]Cl$

(5) $[Pt(NH_3)_2Cl_4]$

(6) $K[Pt(NH_3)Cl_5]$

(7) $K_2[PtCl_6]$

Coordination compounds

- **Coordination compounds** are molecules that possess a metal center that is bound to ligands.
- They are also known as complex ions or coordination complexes because they are Lewis acid-base complexes.
- These complexes can be neutral or charged.
- When the complex is charged, it is stabilized by neighboring counter-ions.
- They are distinct chemical species.

- Their properties and behavior are different from the metal atom/ion and ligands from which they are composed.
- They retain their identity in solid state as well as in dissolved state.
- Each ligand shares a pair of its electrons with the metal.
- The metal ligand bond, often represented as $M \longleftarrow :L$, is an example of a *coordinate covalent bond* in which both the electrons come from one atom.
- A typical formula might be $[ML_6]X_n$ or $M'_n[ML_4]$, where the M’ is a simple metal cation and X might be any of a variety of anions.

- Note that in the first formula, the coordination sphere and the metal M constitute a cation, whereas in the second they make an anion.
- Such coordinated metal ions are sometimes referred to as complex cations or anions.

- **Ligands** are the neutral molecule or ions which are directly attached to the central metal ion or atom through coordinate bonds in the complex ion.

- Almost all anions such as F^-, Cl^-, CN^-, OH^-, SCN^-, NO_2^-, etc can act as ligands.
- A large number of neutral molecules such as H_2O, NH_3, CO, amines, phosphines, sulfides, ethers, etc. can also function as ligands.
- A few cations (e.g., $H_2N–NH_3^+$) also have sites that can bind to metal ions by electron pair donation.
- Ligands should have lone pair of electrons.
- The Ligand is Lewis base and central metal ion is a Lewis acid.

- Ligands donate the lone pair to the central metal atom or ion forming coordinate covalent bond.

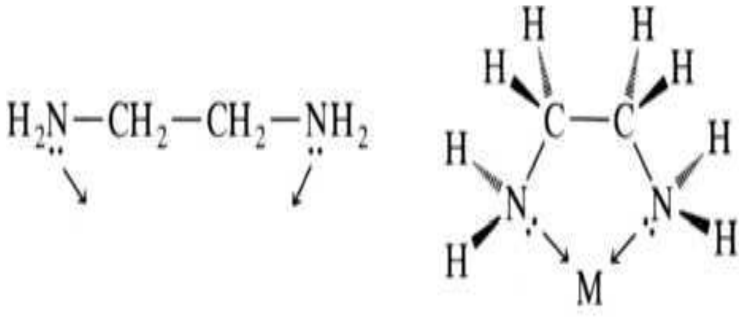
Types of ligands

1. **Monodentate ligands:** defined as one that shares only a single pair of electrons with a metal atom or ion.

- The word *monodentate* comes from the Greek *monos* and the Latin *dentis* and, not unexpectedly, literally means "one tooth."
- A monodentate ligand, then, has only one pair of electrons with which to "bite" the metal.

2. **Bidentate ligand:** ligand having two donor atoms. Ethylenediamine is a bidentate ligand.

- Notice that both of the nitrogen atoms in this compound have a lone pair of electrons that can be shared with a metal.
- Notice also that when both electron pairs interact with the same metal, the resulting configuration rather resembles a crab clutching at its prey.



(a) (b)

3. Polydentate ligands: these are ligands having more than two donor atoms(tridentate, tetradentate, pentadentate, hexadentate, etc).

- Multidentate ligands that form one or more rings with a metal atom in this manner are called *chelates* or *chelating agents*, terms derived from the Greek *chele*, meaning “claw.”
- Chelating ligands generally forms a ring structure around the central metal ion.
- **Denticity** of a ligand: the number of pairs of electrons it shares with a metal atom or ion.

4.Ambident ligands: A monodendate ligand which binds with the metal ion through more than one site.

- If we represent this type of ligand as :AB:, then it can form one of two possible coordinate-covalent bonds, either

$M \leftarrow :AB:$ or $:AB: \rightarrow M$, with a metal atom.

- Common ambidentate ligands include cyanide, thiocyanate, and nitrite.

Bridging ligands: those containing *two* pairs of electrons shared with two metal atoms simultaneously.

- The interaction of such ligands with metal atoms can be represented as $M \longleftarrow :L: \longrightarrow M$.
- Ligands of the bridging type include amide (NH_2^-), carbonyl (CO), chloride (Cl^-), cyanide (CN^-), hydroxide (OH^-), nitrite (NO_2^-), oxide (O^{2-}), peroxide (O_2^{2-}), sulfate (SO_4^{2-}) and thiocyanate (SCN^-).

TABLE 2.3
Common Monodentate, Multidentate, Bridging, and Ambidentate Ligands

	Usually monodentate ligands		
F^-	fluoro		
Br^-	bromo		
I^-	iodo		
CO_3^{2-}	carbonato		
NO_3^-	nitrato		
SO_3^{2-}	sulfito		
$S_2O_3^{2-}$	thiosulfato		
SO_4^{2-}	sulfato	Common bridging ligands	
CO	carbonyl		
Cl^-	chloro		
O^{2-}	oxo		
O_2^{2-}	peroxo		
OH^-	hydroxo		
NH_2^-	amido		
CN^-	cyano/isocyano		Ambidentate ligands
SCN^-	thiocyanato/isothiocyanato		
NO_2^-	nitro/nitrito		
H_2O	aqua		
NH_3	ammine		
CH_3NH_2	methylamine		
$P(C_6H_5)_3$	triphenylphosphine		
$As(C_6H_5)_3$	triphenylarsine		
N_2	dinitrogen		
O_2	dioxygen		
NO	nitrosyl		
C_2H_4	ethylene		
C_5H_5N	pyridine		
	Multidentate ligands		
$NH_2CH_2CH_2NH_2$	ethylenediamine (en)	(2)	
 $CH_3\underset{\|\|}{\overset{}{C}}\overset{(-)}{CH}\underset{\|\|}{C}CH_3$ with O below each marked C	acetylacetonato (acac)	(2)	
$C_2O_4^{2-}$	oxalato (ox)	(2)	
$NH_2CH_2COO^-$	glycinato (gly)	(2)	
$NH_2CH_2CH_2NHCH_2CH_2NH_2$	diethylenetriamine (dien)	(3)	
$N(CH_2COO)_3^{3-}$	nitrilotriacetato (NTA)	(4)	
$(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2^{4-}$	ethylenediamine-tetraacetato (EDTA)	(6)	

- **Coordination number**: the total number of coordinate bonds formed between a central metal ion and its ligands.
- **Inner coordination sphere** or the **first sphere** refers to ligands that are directly bound to the central metal.
- **Outer coordination sphere** or the **second sphere** refers to other ions that are attached to the complex ion.
- In $[Pt(NH_3)_6]Cl_4$, NH_3 is the inner sphere ligand, Cl is the outer sphere ligand.
- **Charge of a complex**
- In the formula of the complex ion: square brackets group together the species making up the complex ion.

- ✓ the overall charge is shown outside the brackets.
- ✓ The overall charge is the sum of the individual charges of the transition metal ion and those of the ligands present in the complex.

Worked examples

1. State the formula and charge of the complex ion made from one titanium(III) ion and six water molecules. $[Ti(H_2O)_6]^{3+}$

- ➢ The formula shows that six H_2O ligands are bonded to one titanium(III) ion.

- As water is a neutral ligand, the overall charge on the ion is the same as the transition metal ion, which is +3.

2. What is the oxidation number of the transition metal in the complex ion $[Co(H_2O)_5Cl]^+$?

- This complex ion has five neutral water ligands with no charge, and one chloride ligand with a charge of –1.
- Overall the complex ion has a 1+ positive charge.
- In $[Co(H_2O)_5Cl]^+$, cobalt must have the oxidation state +2 to give the overall charge of +1.

COORDINATION NUMBER AND SHAPE

- ➢ Coordination complexes adopt a limited number of basic shapes.
- ➢ Previously you have developed a predictive set of molecular shapes evolving from an electrostatic model of the distributions predicted for from two to six point charges dispersed on a spherical surface.
- ➢ These shapes, evolving from a modification of the VSEPR model that was itself developed initially for main group compounds,
- ✓ are satisfactory as models for many of the basic shapes met experimentally for complexes throughout the Periodic Table.

- The original VSEPR model and its electron counting rules have limited predictive value for shape in complexes of d-block elements compared with its application for p-block elements.
- This relates to the defined directional properties of lone pairs in p-block elements, whereas in transition elements nonbonding electrons play a much reduced role in defining shape.
- Rather, it is simply the number of donor groups bound about the metal that is the key to shape in transition metal complexes.

- ➢ This is recognized in the Kepert model,
- ✓ which is a variation of the VSEPR concept developed for transition elements that ignores nonbonding electrons and considers only the set of donor groups represented as point charges on a surface.
- ➢ This essentially electrostatic model has limitations,
- ✓ as shape is influenced by other factors such as inherent ligand shape and steric interactions between ligands,
- ✓ as well as the size and valence electron set of the central metal ion.

- There are in fact several effects that contribute to the outcome of metal–ligand assembly.
- Overall, stereochemistry and coordination number in complexes appear to depend on four key factors:

1. Central metal–ligand electronic interactions, particularly influenced by the number of d(or f) electrons of the metal ion;
2. Metal ion size and preferred metal–ligand donor bond lengths;
3. ligand–ligand repulsion forces;
4. Inherent ligand geometry and rigidity.

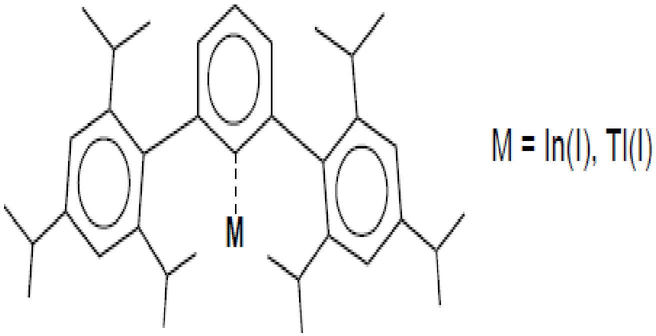
One Coordination (ML)

- ➢ This unlikely coordination number suffers from the fact that a single donor bound to the metal would still leave the metal highly exposed,
- ✓ a situation that would most likely lead to additional ligands adding and thus increasing the coordination number.
- ➢ It is nevertheless prudent to describe it as extremely rare,
- ➢ because there is a small possibility that a suitably bulky and appropriately shaped ligand may achieve one-coordination.

- It may be more practicable in the gas phase under high dilution conditions, where metal–ligand encounters are limited.

- As a consequence, it is not surprising that there appears to be only one isolated structure claimed.

- This is of the indium(I) and thallium(I) complexes with a single M-C bond from a δ-bonded benzene anion that carries two bulky tri-substituted benzene substituents in *ortho* positions.



An extremely rare one-coordinate complex

Two Coordination (ML_2)

- Two coordination is the lowest stable coordination number that is well reported.
- We expect a ML_2 molecule to be linear, with the two donor groups disposed as far away from each other as possible on opposite ends of a line joining them and passing through the metal centre.

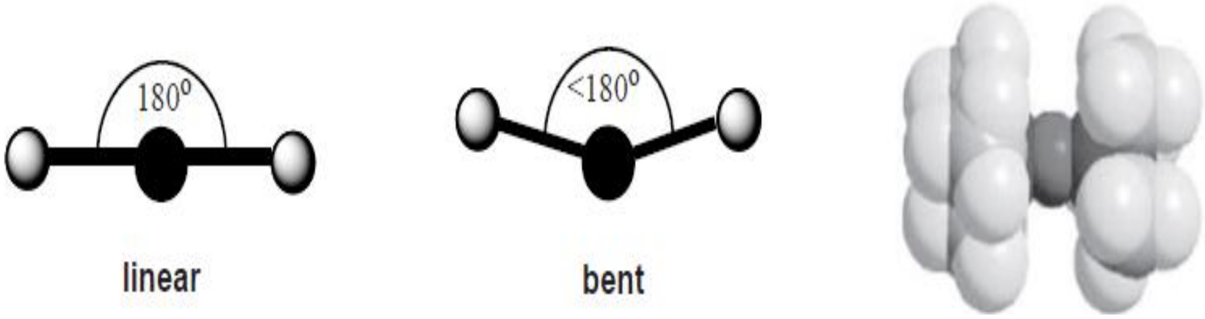
- Deviation from prediction may arise in this case simply by *bond angle deformation*, with the usual 180◦ L-M-L bond angle reduced to <180◦ through bending.
- Experimentally, ML_2 complexes are overwhelmingly linear.
- Both electron pair repulsion and simple steric arguments favour this shape.
- If bending occurs, it brings the two ligands closer towards each other,
- providing greater opportunity for repulsive interaction between the ligands; this would seem both unreasonable and unlikely, yet bent molecules do occur.

➢ ‘Bent’ geometries are well known in p-block chemistry, of course,

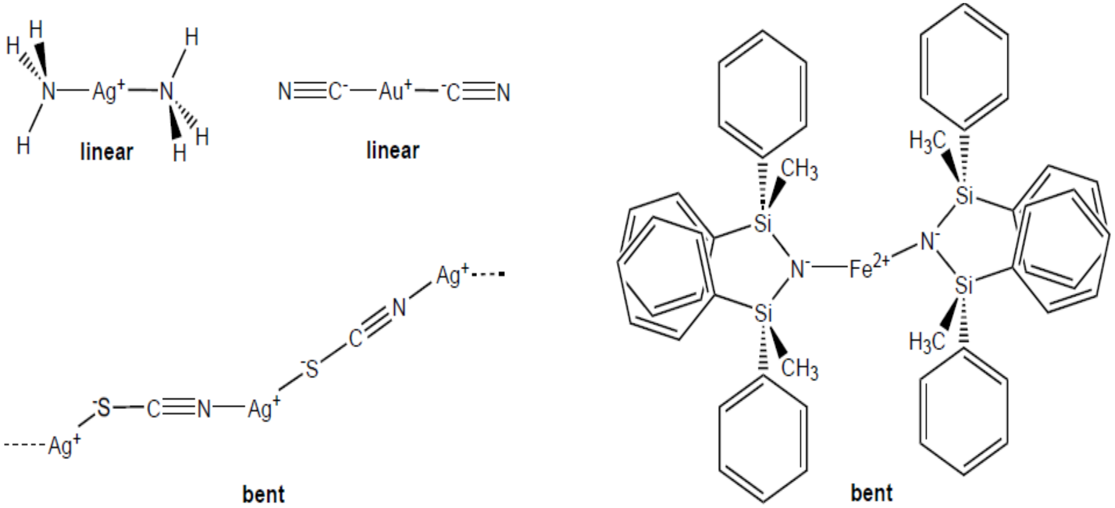
✓ where lone pairs play an important directional role.

➢ Water is the classical example, with its two lone pairs and two bond pairs around the oxygen centre leading to a bent H—O H as a result of its inherently tetrahedral shape (on including lone pairs) as well as additional effects due to differing repulsions between the lone pairs and bond pairs.

- ➢ Where such bending is seen in metal complexes,
- ✓ it can often be assigned to a higher pseudo-coordination number shape with nonbonding orbitals present contributing and occupying some region of space.
- ➢ X-ray crystallography defines atomic centres but cannot readily detect regions of electron density that do not involve atoms.
- ➢ Lone pairs are effectively not observable directly; the presence of directed nonbonding electron density can only be inferred,
- ✓ as a result of an influence on structure through repulsive terms, seen experimentally as changes in bond angles.



Possible shapes for two-coordination, and (at right) an example of a linear complex cation, $[Au(PR_3)_2]^+$ (where R = CH_3).



Examples of complexes with two-coordination, including both linear and bent species.

- The ML_2 geometry is rare for all but metal ions rich in d electrons, particularly d^{10} and d^9 metal ions.
- This is a recurring theme in coordination number for transition metal complexes – as a very rough rule,

✓ the more electrons in the valence shell, the lower the coordination number.

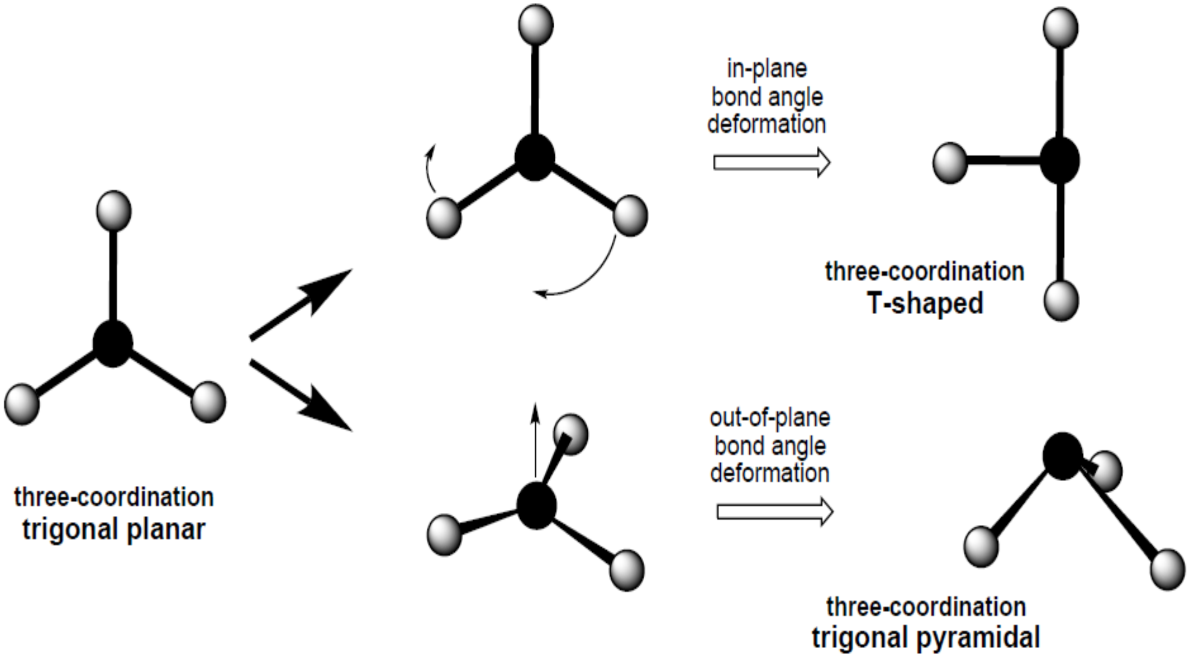
- Complexes which are two-coordinate include those of the d^{10} cations Ag(I) and Au(I), for example the $[Ag(NH_3)_2]^+$ and $[Au(CN)_2]^-$ complexes, which have linear N-Ag-N and C-Au-C cores respectively.

Three Coordination (ML_3)

- The VSEPR-predicted shape, *trigonal planar*, is well represented amongst this relatively rare coordination number.
- ML_3 is (like ML_2) favoured by transition metal ions with lots of d electrons (d^8, d^9, d^{10}).
- Two other shapes are known, however; one is called *T-shape* (for obvious reasons), and the other called *trigonal pyramidal*.
- These latter two can be seen to arise from distortions of the 'parent' trigonal planar shape.

➢ It is usual for different shapes for a particular coordination number to be able to interconvert without any bond breaking,

✓ simply through rearrangements such as those exemplified below.



- molecules may adopt a shape that is intermediate or part-way along the process of changing from one basic shape to another.

Four Coordination (ML_4)

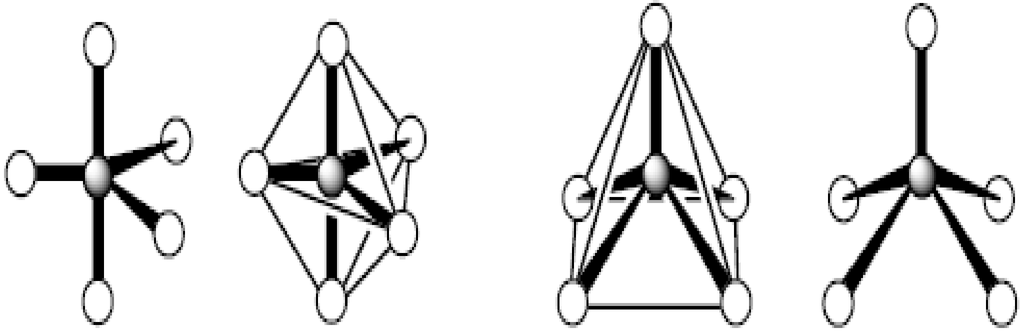
- Coordination number four (ML_4) is common and has two major forms, *tetrahedral* and *square planar*.
- The former is the shape predicted by the electron pair repulsion model;
- ✓ the latter is a different shape observed experimentally, with many examples known.

- These are ideal or limiting structures, in the sense that they represent the perfect shapes which lie at the structural limits for this coordination number.
- ideal structures are relatively rare in coordination chemistry, and distorted or *intermediate* geometries are more likely met.
- The two limiting geometries can be converted one into the other by displacement of groups without any bond breaking being involved.

Five Coordination(ML_5)

- Although once considered rare, growth in coordination chemistry has led to five-coordination becoming met almost as frequently as four-coordination.
- Examples of ML_5 are found for all of the first row transition metal ions, as well as some other metal ions.
- Five-coordination is commonly met in complexes of the lighter, smaller transition metals ions.
- The amended VSEPR model predicts two forms of five-coordination, and experimental chemistry has clearly identified many examples of both forms.

- These limiting structures are square-based pyramidal (or, simply, square pyramidal) and trigonal bipyramidal.



trigonal bipyramidal

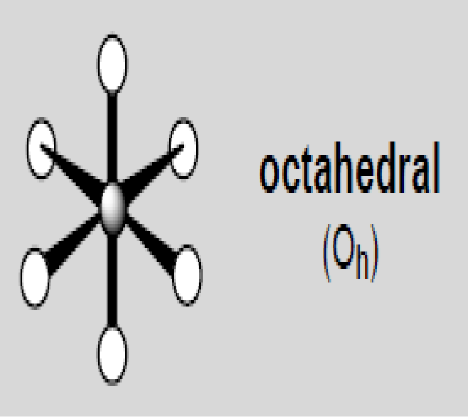
square pyramidal

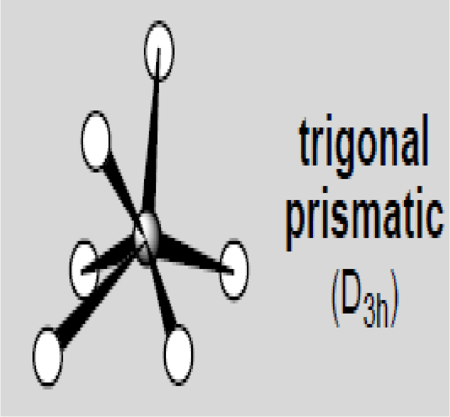
- In reality, almost no complexes exhibit this classical square-based pyramidal shape, but rather adopt a distorted square pyramidal shape.

- Considering electron pair repulsion alone, this distorted shape is actually more stable than the form created by simply truncating an octahedron,
- ✓ and is only slightly less stable than the trigonal bipyramidal geometry.
- it is possible to convert from one form to the other through bond angle changes without any bond-breaking.
- Both geometries are common, but in practice there are many structures that are intermediate between these two.
- The two limiting structures are of similar energy and as predicted, some complexes display an equilibrium between the two.

Six Coordination (ML_6)

- ➢ ML_6 is the most common coordination type by far that is met for transition metal elements (seen for all configurations from d^0 to d^{10}),
- ✓ and also is often met for complexes of metal ions from s and p blocks of the Periodic Table.
- ➢ Of the two limiting shapes, the *octahedral* geometry is by far the most common, though a few examples of the other limiting shape, *trigonal prismatic*, exist.





- Because the six donor atoms come into closer contact in the trigonal prismatic than in the octahedral geometry, trigonal prismatic is predicted to be less stable.
- However, many structures show distortion that places them as intermediate between ideal octahedral and the ideal trigonal prismatic form.

Factors Influencing Shape

Metallic Genetics – Metal Ion Influences

- ➢ If we focus first on the central atom or ion, there are two of the four key factors mentioned earlier that we can consider metal-centric. These are:
- ✓ the number of d electrons on the metal ion; and
- ✓ metal ion size and preferred metal ion–ligand donor group bond length.
- ➢ Each metal in a particular oxidation state brings a unique character, almost like a gene, to play in its complexes.

- Examples of the way the size and bond distances vary across the d block are given below

Metal ion	d-Electron configuration	Free ion radius (pm)	Typical M—O (pm)	Typical M—N (pm)	Typical M—Cl (pm)
Sc(III)	d^0	74.5	210	—	245
Ti(IV)	d^0	60.5	195	210	230
Ti(III)	d^1	67	185	215	235
V(IV)	d^1	58	185	205	215
V(III)	d^2	64	215	225	235
Cr(III)	d^3	61.5	195	210	235
Mn(IV)	d^3	53	185	210	230
Cr(II)	d^4	80	200	215	245
Mn(III)	d^4	64.5	195	205	230
Mn(II)	d^5	83	215	240	250
Fe(III)	d^5	64.5	190	205	230
Fe(II)	d^6	78	205	215	240
Co(III)	d^6	61	185	195	225
Rh(III)	d^6	*66.5*	*195*	*205*	*235*
Ir(III)	d^6	*68*	*210*	*215*	*240*
Co(II)	d^7	74.5	205	220	240
Ni(II)	d^8	69	205	210	235
Cu(II)	d^9	73	200	200	225
Zn(II)	d^{10}	74	205	210	230

- ➢ The M-L distances are averages only, as distances vary over a range of at least 20 pm,
- ✓ influenced by the specific type of donor group for a particular type of donor atom, the ligand shape and associated strain energy,
- ✓ as well as influences of other donors in the coordination sphere.
- ➢ Moreover, the spin state of the central metal plays a role (e.g. M-O distances for high spin Mn(III) are typically 20 pm longer than for low-spin compounds).

- ➢ As mentioned above, distances vary for any particular metal ion depending on the character of the donor, influences from the ligand framework itself, and influences of other ligands bound to the same complex.
- ➢ there is a modest relationship between bond distances and the size of the metal ion.
- ✓ The increase in metal cation size from the first to the second and third row of the Periodic Table is accompanied by usually longer M-L distances.

- ➢ Overall, metal–donor distances fall within a range of ≈160–260 pm,
- ✓ with the smaller distances found where highly charged metal ions, small anionic ligands and/or multiple bonding operate.

Ligand Influences

- ➢ there are also two of the four key factors mentioned earlier that we can consider ligand-centric.
- ➢ These are:
- ligand–ligand repulsion forces; and
- ligand rigidity or geometry.

- Obviously, each ligand is unique in its shape and size.

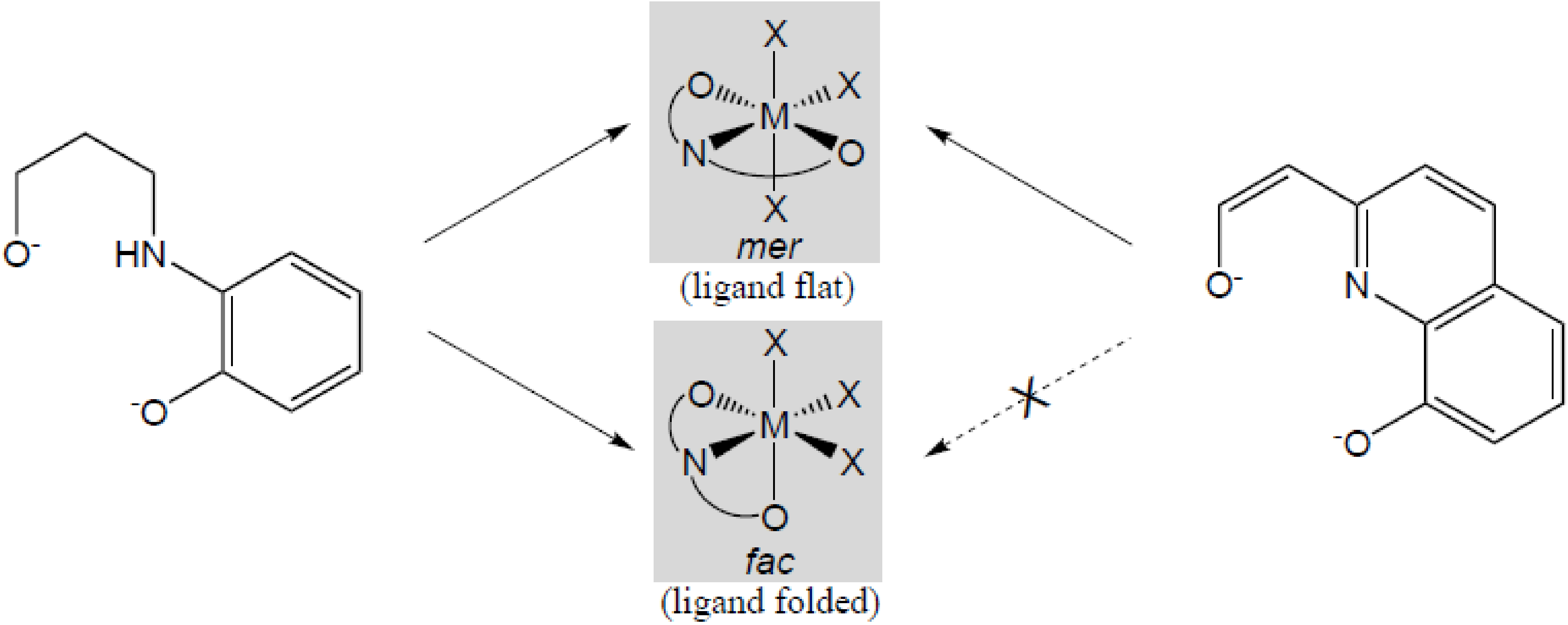
- The effect of repulsion between ligands can be termed as *nonbonding interactions*.

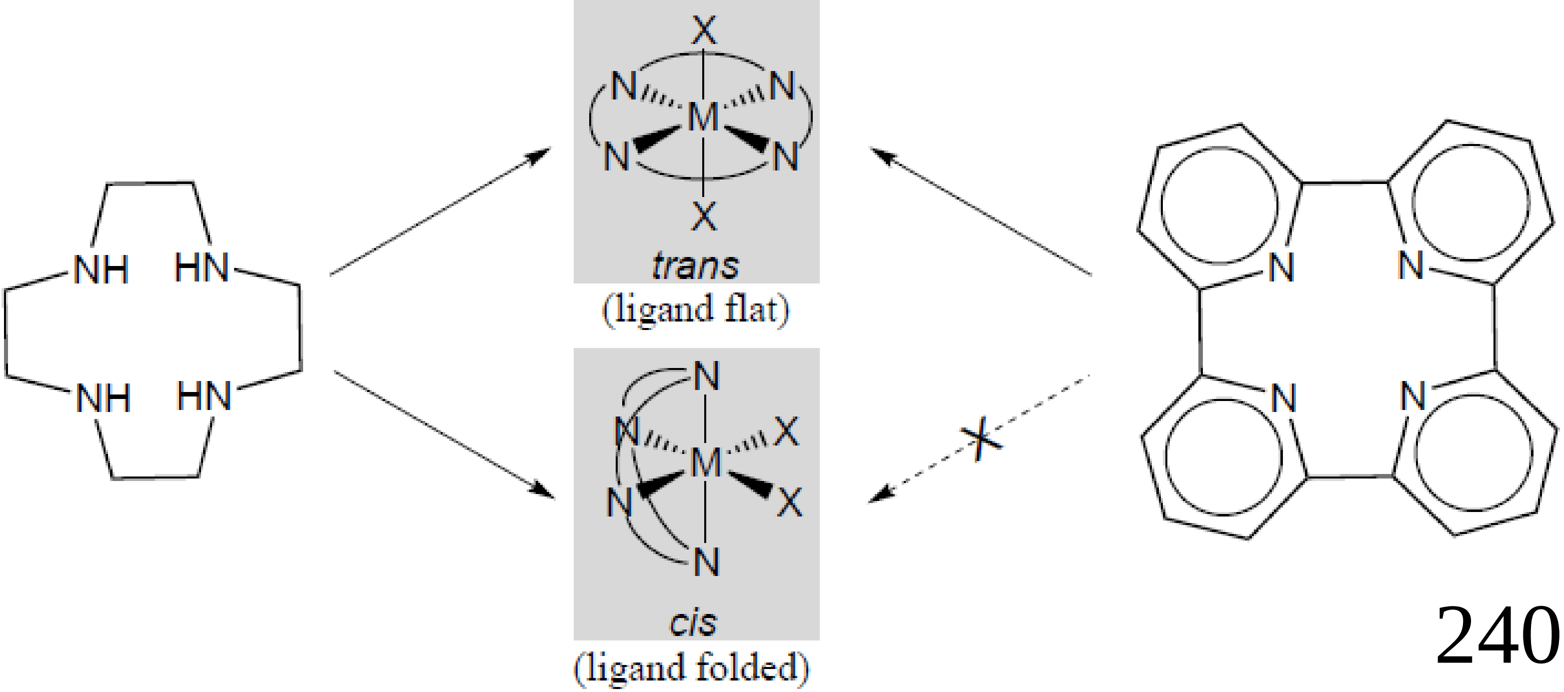
- Two PH_3 molecules may bind in a square planar shaped complex with little preference for *trans* over *cis* geometry,

- ✓ whereas two very bulky $P(C_6H_5)_3$ molecules may exhibit strong preference for coordination in a *trans* geometry, where they are much further apart.

- ➢ Another way that two *cis*-disposed bulky ligands can relieve ligand–ligand repulsion is for the complex to undergo distortion from square planar towards tetrahedral,
- ✓ which leads to the two ligands moving further apart in space.
- ➢ Some ligands are structurally so rigid that they can bind to a metal ion in only one manner.
- ➢ The aromatic porphyrin molecule is completely flat, and large amounts of energy are required to distort it.

- Therefore, when it binds to a metal, it seeks to retain this shape, and will simply use the square-shaped array of four N-donors to wrap around a metal ion in a planar manner.
- Not only aromatic ligands are rigid; some polycyclic fused-ring aliphatic molecules may be sufficiently rigid and require a particular shape.
- An example of a cyclic rigid four nitrogen donor ligand that can bind effectively only with the square-shaped array of four N-donors in the plane about the metal ion contrasts with the flexible aliphatic ligand also shown, which can bind in a flat or ‘bent’ arrangement.


mer
(ligand flat)
fac
(ligand folded)


trans
(ligand flat)
cis
(ligand folded)

- ➢ The more rigid ligands on the right do not permit folding,
- ✓ whereas the more flexible ones on the left can accommodate folding and thus offer options when coordinating to an octahedral metal ion.

NOMENCLATURE OF COORDINATION COMPOUNDS

- ➢ Here we consider the basics of naming ligands (including multidentate, ambidentate, and bridging) that occur in simple neutral as well as ionic coordination compounds.
- ➢ Note that the name of anionic ligands is modified by removing the –*ide* suffix of halides, oxides, hydroxides,
- ✓ and so forth, or the last -*e* of an -*ate* or –*ite* ending and replacing these with -*o*.
- ➢ Accordingly, fluoride becomes fluoro, nitrate becomes nitrato, sulfite becomes sulfito, and so forth.

- As usual in nomenclature, there are a few exceptions; for example, amide becomes amido and the N-bonding form of the ambidentate nitrite becomes nitro.
- The very few positive ligands are modified by adding an -*ium* suffix to the root name.
- The names of neutral ligands are usually not modified, but a few common neutral ligands have special names.
- For example, water becomes aqua, ammonia is called ammine, carbon monoxide is carbonyl, and nitrogen oxide is nitrosyl.

- Molecular oxygen and nitrogen are referred to as dioxygen and dinitrogen, respectively.
- In naming a coordination compound, the cation is named first and then the anion (just as for ordinary salts—for example, sodium chloride or ammonium nitrate).
- For a given complex, the ligands are always named first in alphabetical order, followed by the name of the metal.
- The oxidation state of the metal is indicated by Roman numerals in parentheses after the name.
- An oxidation state of zero is indicated by a numeral zero, 0, in the parentheses.

- If the complex is an anion, the -*ate* suffix is added to the name of the metal.
- Occasionally, the -*ium* or other suffix has to be removed from the name of the metal before the -*ate* is added.
- For example, chromium becomes chromate, manganese becomes manganate, and molybdenum becomes molybdenate.
- Some metals, such as copper, iron, gold, and silver, retain the Latin stem for the metal and become cuprate, ferrate, aurate, and argentate, respectively, in an anionic setting.

- Note that there are two sets of prefixes,
- one (*di*-, *tri*-, *tetra*-, etc.) for monoatomic ions, polyatomic ions with short names, or the special neutral ligands noted previously,
- and a second (*bis*-, *tris*-, *tetrakis*-, etc.) for ligands that already contain a prefix from the first list-for example, ethylenediamine or triphenylphosphine- or for ligands whose names commonly appear in parentheses.
- Generally, neutral ligands without special names and ionic ligands with particularly long names are enclosed in parentheses.

- So, for example, acetylacetonato is generally enclosed in parentheses, whereas oxalato is not.
- There are two ways to handle ambidentate ligands.
- One is to use a slightly different form of the name, depending on the atom that is donating the electron pair to the metal.
- The second is to put the symbol of the donating atom before the name of the ligand.
- So –SCN might be called thiocyanato or *S*-thiocyanato, whereas –NCS would be isothiocyanato or *N*-thiocyanato.
- $-NO_2$ and –ONO, however, are most always referred to as nitro and nitrito, respectively.

- Bridging ligands are designated by placing the Greek letter m before the name of the ligand.

- So a bridging hydroxide (OH^{-}), amide (NH_2^{-}), or peroxide (O_2^{2-}) ligand becomes μ-hydroxo, μ -amido, or μ -peroxo, respectively.

- If there is more than one of a given bridging ligand, the prefix indicating the number of ligands is placed after them.

- For example, if there are two bridging chloride ligands, they are indicated as μ-dichloro.

- If there are two or more different bridging ligands, they are given in alphabetical order.

Example 1: **$[Pt(NH_3)_4]Cl_2$**

- There are two negative chloride ions outside of the complex, so the complex itself must have the formula $[Pt(NH_3)_4]^{2+}$.
- The ammonia ligands are neutral; thus, the platinum must have an oxidation state of +2. As a result, we start with the stem name platinum(II).
- The ligand is ammonia, which has the name ammine.

- But there are four ammonia ligands, so the prefix is added to give tetraammine.
- Finally, the chloride anions must be included.
- They are free, uncoordinated chloride ions, so they are called chloride, not chloro.
- We do not identify the number of chloride ions because the oxidation state of the metal ion enables us to deduce it.

- Hence, the full name is tetraammineplatinum(II)chloride.

Example 2: **$[PtCl_2(NH_3)_2]$**

- This is a non-ionic species, so it will have a one word name.
- Again, to balance the two chloride ions, the platinum is in the 12 oxidation state, so we start with platinum(II).
- The ligands are named ammine for ammonia and chloro for chloride.
- Alphabetically, ammine comes before chloro; thus, we have the prefix diamminedichloro.
- The whole name is diamminedichloroplatinum(II).

Example 3: $K_2[PtCl_4]$

- Again, two words are needed , but in this case, the platinum is in the anion, $[PtCl4]^{2-}$.
- The metal is in the +2 oxidation state, so the anionic name will be platinate(II) .
- There are four chloride ligands, giving the prefix tetrachloride and the separate potassium cations.
- The complete name is potassium tetrachloroplatinate(II).

Example 4: $[Co(en)_3]Cl_3$

- The complex ion is $[Co(en)_3]^{3+}$.

- Because (en), $H_2NCH_2CH_2NH_2$, is a neutral ligand, the cobalt must be in a +3 oxidation state.
- The metal, then, will be cobalt(III).

The full name of the ligand is 1,2-diaminoethane and contains a numerical prefix, so we use the alternate prefix set to give tris(1,2-diaminoethane) parentheses are used to separate the ligand name from the other parts of the name.

- Finally, we add the chloride anions.
- The full name is tris(1,2-diaminoethane)cobalt(III) chloride.

Example 5: $[Co(NH_3)_4Cl_2]Cl$.

- We start by naming the complex cation.
- The ligands are named alphabetically with ammine first and then chloro.
- There are four ammonias and two chlorides, so the prefixes *tetra*- and *di*- are used.
- The cobalt oxidation state is determined by tracing the charges back as follows:
- The net charge on the complex cation must be 1+ to balance the one 1- chloride anion.

- Since there are two chlorides in the coordination sphere, the cobalt must be 3+ in order for the net charge on the cation to come out as 1+.
- **Example 6: $(NH_4)_2[Pt(NCS)_6]$**
- Here we have a platinum-containing complex anion and the common ammonium ion, NH_4^+, as the cation.
- Given that the ligand is written with the N symbol first, we know that it is the isothiocyanato (or, alternatively, *N*-thiocyanato) form of the ambidentate ligand.
- There are six of these ligands, so we use the *hexa*- prefix.

- The anion must have a net charge of 2- to balance the two 1+ ammonium cations.
- Since the thiocyanate ion is also 1-, the platinum oxidation state must be 4+ to give a net 2- charge on the anion.
- Because the platinum is contained in a complex anion, its-*um* suffix is removed and replaced with -*ate*.
- Accordingly, the full name of the compound is ammonium hexaisothiocyanatoplatinate(IV).
- **Example 7:** Write the formula for the compound triamminechloro(ethylene)nitroplatinum(IV) phosphate.

- This compound has four different types of ligands in the coordination sphere: NH_3, Cl_2, C_2H_4, and NO_2^-(bonded through the nitrogen).

- The only real difficulty in constructing this formula is figuring out how many cations and anions there must be.

- The cation has a net charge of 2+, and the anion is 3-.

- Therefore, there must be three cations and two anions to ensure electrical neutrality.

- The formula for this compound is $[Pt(NH_3)_3Cl(C_2H_4)NO_2]_3(PO_4)_2$

- **Example 8:** Write the formula for the compound (acetylacetonato)tetraaquacobalt(II) chloride.
- The acac and four waters constitute the coordination sphere that with the cobalt(II) cation are set apart in brackets.
- The net charge on the complex cation is 1+ (because the acac is 1-), so one chloride counteranion is needed.
- The e formula of the compound is $[Co(acac)(H_2O)_4]Cl$.

Exercise

(i) Name the following coordination complexes.

(a) $[Cr(NH_3)_5(H_2O)](NO_3)_3$

(b) $[Cr(NH_3)_4Cl_2]Cl$

(c) $[Ag(NH_3)(CH_3NH_2)]_2[PtCl_2(ONO)_2]$

(d) $[Pt(NH_3)_4Cl_2]SO_4$

(e) $K_3[Mo(CN)_6F_2]$

(f) $[Ni(acac)\{P(C_6H_5)_3\}_4]NO_3$

(ii) Determine the formulas of the following compounds.

(a) potassium hexacyanoferrate(II)

(b) tris(ethylenediamine)chromium(III) chloride

(c) Aquabis(ethylenediamine)thiocyanatocobalt(III) nitrate

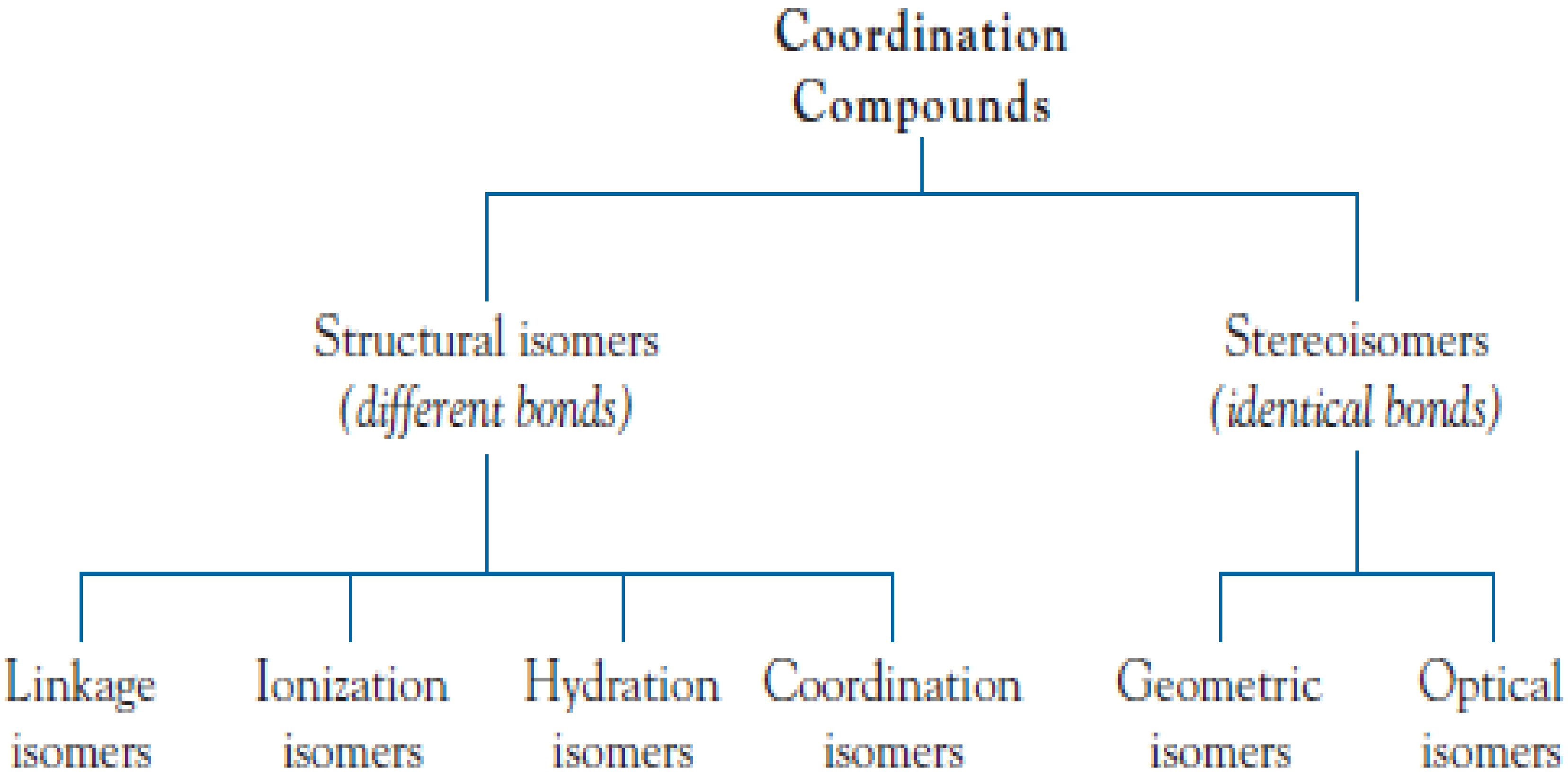
(d) Tetrakis(pyridine)bis(triphenylarsine)cobalt(III) chloride

(e)Diamminebis(triphenylphosphine)palladium(II) bis(oxalato)aurate(III)

ISOMERISM IN TRANSITION METAL COMPLEXES

- ➢ In the early history of coordination chemistry,
- ✓ the existence of pairs of compounds with the same formula yet different properties proved to be very perplexing to inorganic chemists.
- ➢ Werner was among the first to realize that the different properties represented different structural arrangements (isomers).
- ➢ Isomers can be categorized as *structural isomers* and *stereoisomers*.

- For stereoisomers, the bonds to the metal ion are identical, whereas the bonds of structural isomers are different.
- These categories can be further subdivided, as shown below.



Coordination Compounds

Structural isomers
(different bonds)

Stereoisomers
(identical bonds)

Linkage isomers
Ionization isomers
Hydration isomers
Coordination isomers
Geometric isomers
Optical isomers

- Stereoisomers are species with the same structural formula but with a different arrangement of the atoms in space.
- In transition element chemistry, it is possible to have stereoisomers from complexes containing all types of ligands.

Structural Isomerism

- Structural isomerism has four common types:
- ✓ linkage isomerism, ionization isomerism, hydration isomerism, and coordination isomerism.

- Ionization and hydration isomerism are sometimes categorized together as coordination-sphere isomerism because in both cases it is the identity of the ligands that differs.

1. **Linkage isomerism:-** Some ligands can form bonds through more than one atom.

- For example, the thiocyanate ion, NCS^-, can bond through either the nitrogen or the sulfur.
- This particular ambidentate ligand is a borderline base, since the choice of ligating atom depends in part on the hard-soft acid nature of the metal ion.

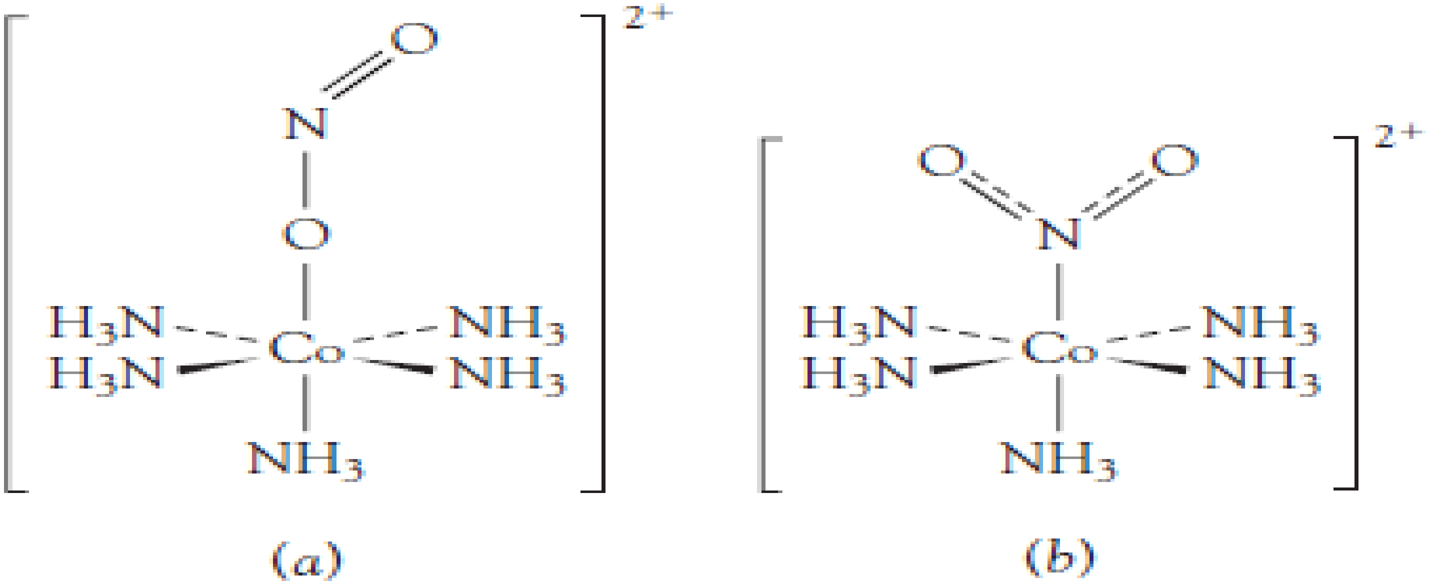
➢ A classic example of linkage isomerism involves the nitrite ion,

✓ which can form bonds through the nitrogen atom, $^-NO_2$, referred to as *nitro*, or through one of the oxygen atoms, -ONO, referred to as *nitrito*.

➢ A pentamminecobalt(III) complex, $Co(NH_3)_5Cl_2(NO_2)$, conveniently illustrates this isomerism since the two isomers have different colors.

➢ One of these, the red form, contains the $[Co(ONO)(NH_3)_5]^{2+}$ ion, in which one of the oxygen atoms of the nitrite ion is bonded to the cobalt(III) ion.

- The other isomer, the yellow form, contains the $[Co(NO_2)(NH_3)_5]^{2+}$ ion, in which the nitrogen atom is bonded to the cobalt(III) ion.



- The two linkage isomers of the pentamminecobalt(III) nitrite complex: (*a*) the nitrito form, (*b*) the nitro form.

2. Ionization isomerism:- Ionization isomers give different ions when dissolved in solution.

- Again, there is a classic example: $Co(NH_3)_5Br(SO_4)$.
- If barium ion is added to a solution of the red-violet form, a white precipitate of barium sulfate forms.
- Addition of silver ion has no effect.
- Hence, the complex ion must have the formula $[CoBr(NH_3)_5]^{2+}$, with an ionic sulfate ion.

- A solution of the red form, however, does not give a precipitate with barium ion; instead, a cream-colored precipitate is formed with silver ion.

- Hence, this complex ion must have the structure of $[CoSO_4(NH_3)_5]^+$, with an ionic bromide ion.

3. **Hydration isomerism:-** Hydration isomerism is very similar to ionization isomerism in that the identity of the ligand species is different for the two isomers.

- In this case, rather than different types of ions, it is the proportion of coordinated water molecules that differs between isomers.

- The three structural isomers of formula $CrCl_3.6H_2O$ provide the best example.
- In the violet form, the six water molecules are coordinated; hence, the formula for this compound is more correctly written as $[Cr(OH_2)_6]Cl_3$.
- As evidence, all three chloride ions are precipitated from solution by silver ion.
- In the light green form, one of the chloride ions is not precipitated by silver ion; hence, the complex is assigned the structure $[CrCl(OH_2)_5]Cl_2.H_2O$.

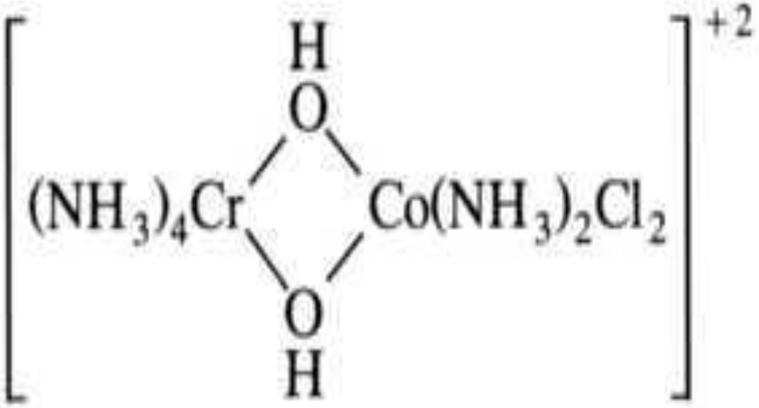
- Finally, only one chloride ion can be precipitated by silver ion from a solution of the dark green form;

- ✓ hence, this compound must have the structure $[CrCl_2(OH_2)_4]Cl.2H_2O$.

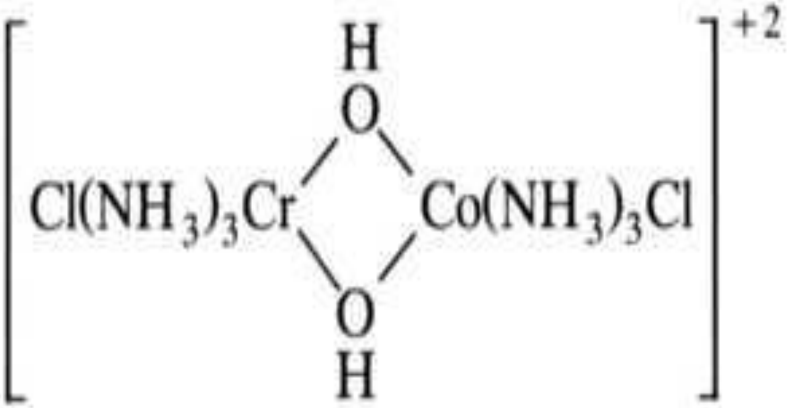
4. Coordination isomerism:-*Coordination isomerism* occurs when both the cation and the anion are complex ions.

- The ligands interchange between the cation and anion, leading to different coordinated ligands.

- For example, $[Cr(NH_3)_6][Co(CN)_6]$ and $[Co(NH_3)_5CN][Co(CN)_5(NH_3)]$ are coordination isomers.



tetraamminechromium(III)-μ-dihydroxodiamminedichlorocobalt(III)



triamminechlorochromium(III)-μ-dihydroxotriamminechlorocobalt(III)

Two coordination isomers of a bridged cation.

Stereoisomerism

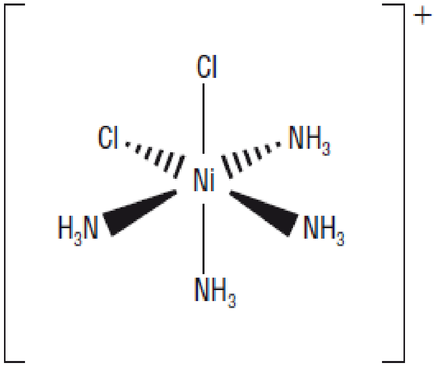
- ➢ The two types of inorganic stereoisomers, *geometric isomers* and *optical isomers*,
- ✓ are parallel to those found in organic chemistry except that in inorganic chemistry,
- ✓ optical isomerism is most common for a metal ion in an octahedral environment rather than for the tetrahedral environment of organic carbon compounds.

1. **Geometric isomerism:-** Inorganic geometric isomers are analogous to organic geometric isomers that contain carbon-carbon double bonds.

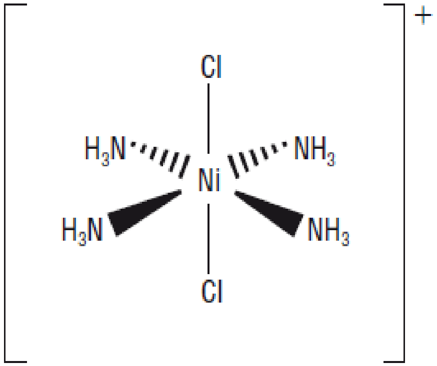
- Geometric isomers must have two different ligands, A and B, attached to the same metal, M.
- For square planar compounds, geometric isomerism occurs in compounds of the form MA_2B_2, such as $[PtCl_2(NH_3)_2]$.
- The term ***cis*** is used for the isomer in which ligands of one kind are neighbors, and ***trans*** is used to identify the isomer in which ligands of one kind are opposite each other.
- Geometric isomers also exist for square planar complexes of the form MA_2BC,

✓ where *cis* refers to ligands A being neighbors and *trans* to ligands A being opposite each other.

- There are two formulas of octahedral compounds having only two kinds of ligands for which geometric isomers are possible.
- Compounds with the formula MA_4B_2 can have the two B ligands on opposite sides or as neighbors.
- Hence, these, too, are known as *trans* and *cis* isomers.

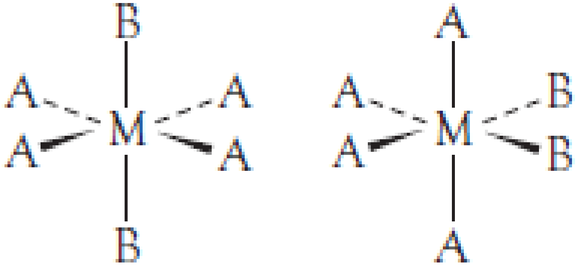


Cis



Trans

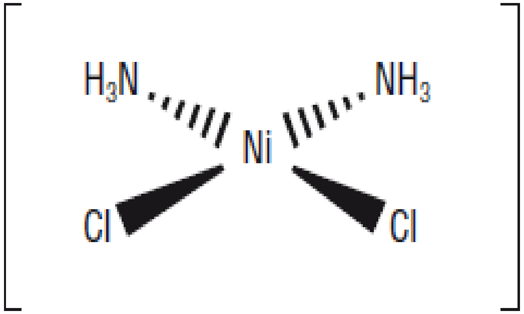
- *Cis–trans* isomerism in $[Co(NH_3)_4Cl_2]^+$



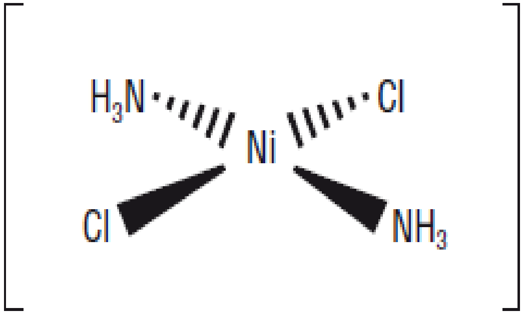
trans *cis*

The geometric isomers of an octahedral MA_4B_2 arrangement.

- Octahedral compounds with the formula MA_3B_3 also can have geometric isomers.
- *Cis–trans* isomerism is also possible in some four-coordinate complexes with a square planar shape



Cis



Trans

Optical isomerism:- Again, inorganic optical isomerism is analogous to that of organic chemistry.

- ➢ Optical isomers are pairs of compounds in which one isomer is a non superimposable mirror image of the other.
- ➢ One of the characteristics of optical isomers is that they rotate the plane of polarized light,
- ✓ one isomer rotating the light in one direction and the other isomer in the opposite direction.
- ➢ Compounds that exist as optical isomers are called *chiral compounds*.

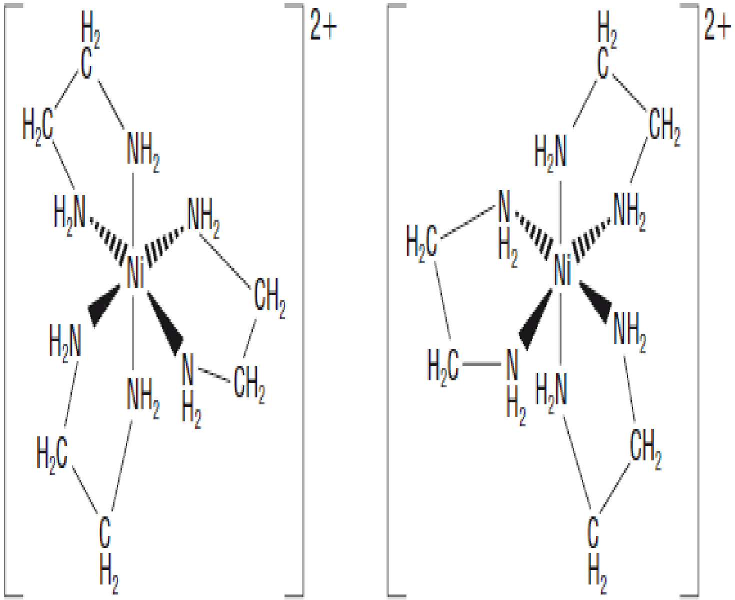
- Such molecules are known as optical isomers or enantiomers.

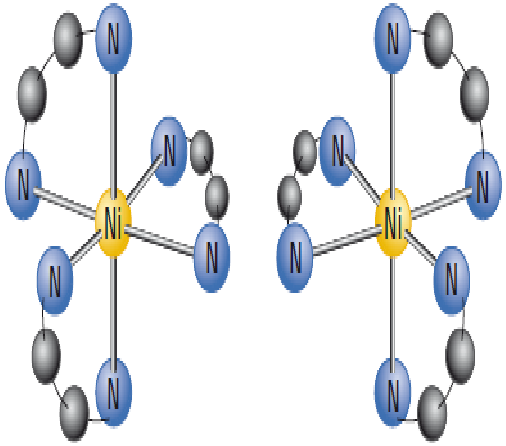
- The word *enantiomer* comes from the Greek words *enantios*, meaning “opposite,” and *meros*, meaning “part,”

- ✓ so that *enantiomers* are the matched left and right-handed forms of a given chiral molecule.

- These enantiomers always have identical melting points, boiling points, dipole moments, solvent capabilities, and so forth, but one property that distinguishes them is the ability to rotate the plane of polarized light in opposite directions.

- Optical isomerism can be seen in the structures of the two isomers of $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$.





- Optical isomers of $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$**Exercise**

1. Draw diagrams showing the structures of and name all the stereoisomers of $[CoCl_2(en)_2]Cl$.

2. The complex $[Pt(NH_3)_2(SCN)_2]$ forms two stereoisomers, whereas the complex $[Pt(en)(SCN)_2]$ forms only one.

- ✓ What, if anything, does this prove about the geometry of these complexes? Explain.
- ✓ As part of your answer, sketch and name these three isomers.

3. Draw the two linkage isomers of pentamminethiocyanatocobalt(III) chloride.

- ✓ One of these is orange, the other violet. Speculate on the color of each isomer. Provide a brief rationalization of your answer.

4. *Trans*-bis(ethylenediamine)dithiocyanatocopper(II) forms three linkage isomers.

- ✓ Write structural formulas and name each isomer.

5. How many coordination isomers could be formed starting with $[Cu(NH_3)_4][PtBr_4]$?

- ✓ Write the formula for and name each isomer.

Bonding in d-block Metal Complexes:

Valence bond theory

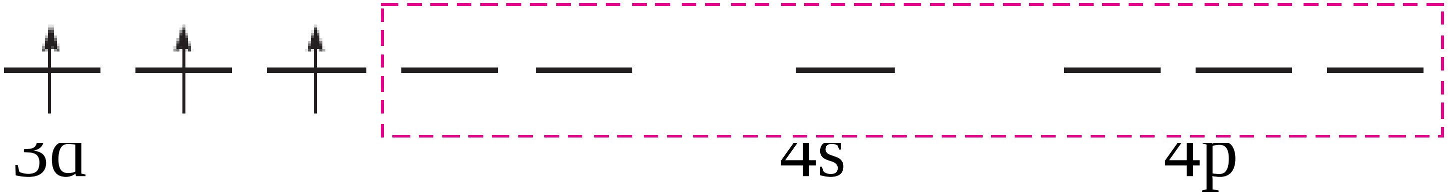
- VBT was developed by Pauling in the 1930s

- It uses hybridization schemes to describe the bonding in d-block metal complexes;

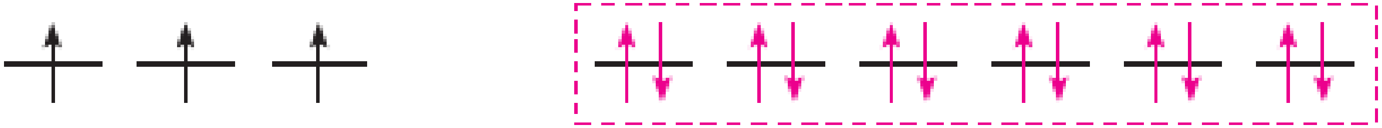
- an empty hybrid orbital on the metal centre can accept a pair of electrons from a ligand to form a σ-bond.

Applying VB theory

- consider an octahedral complexes of Cr(III) (d^3) and Fe(III) (d^5) and octahedral, tetrahedral and square planar complexes of Ni(II) (d^8)
- The Cr^{3+} ion has:-

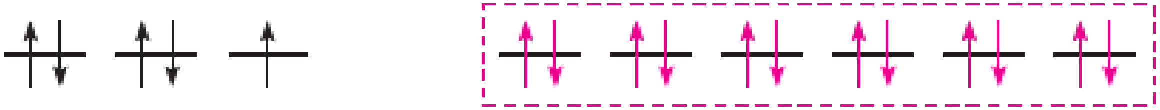


- With the electrons from the ligands included, the diagram becomes:

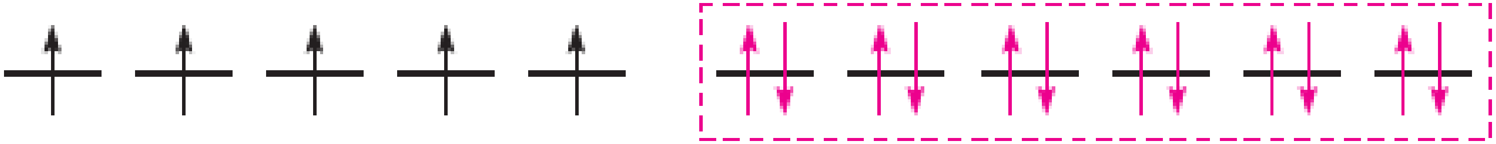


- For octahedral Fe(III) complexes, we must account for the existence of both high- and low-spin complexes. Fe^{3+} ion has:

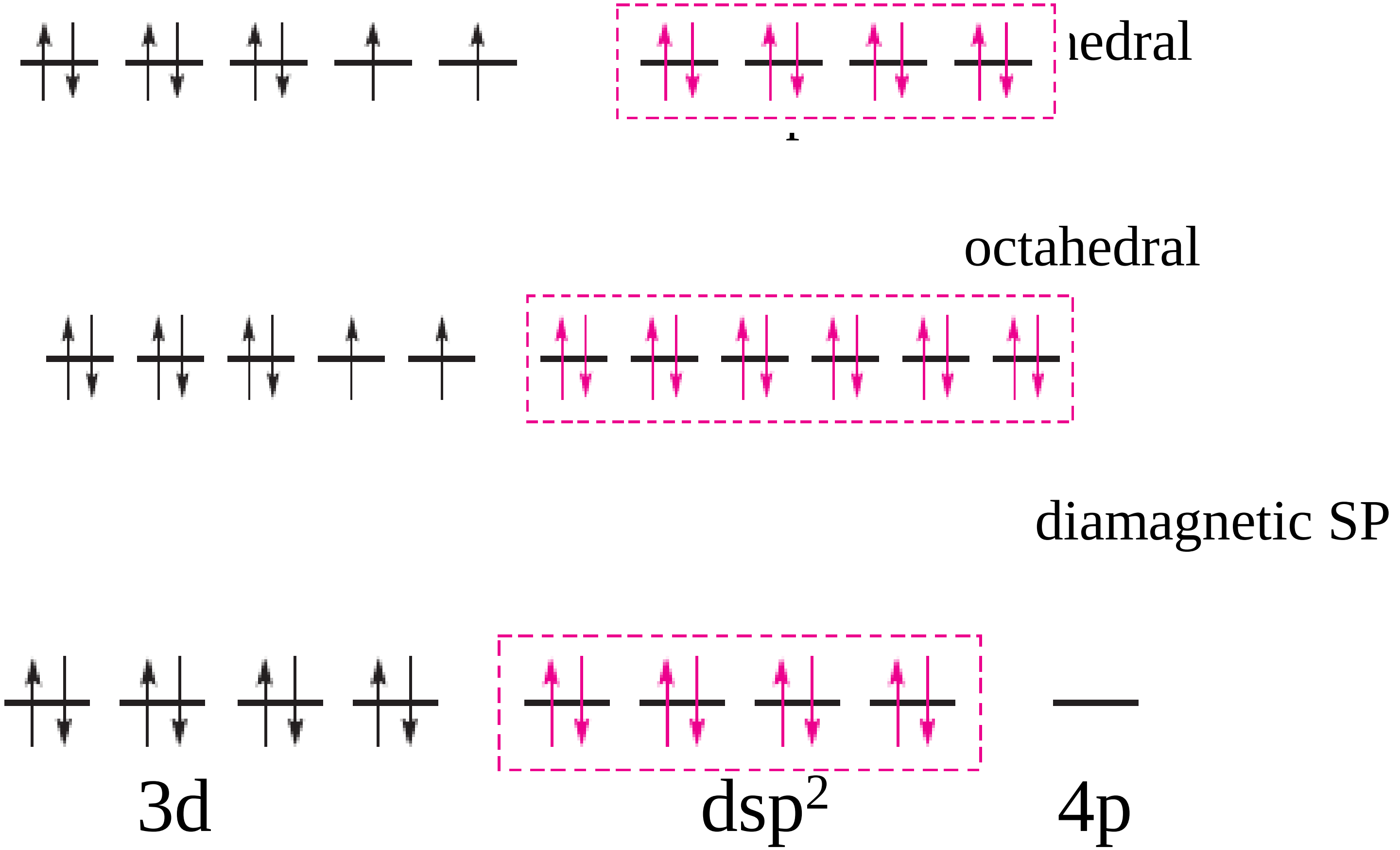
- For a low-spin octahedral complexes; the diagram becomes:



  - For a high-spin octahedral complex such as $[FeF_6]^{3-}$; the diagram becomes:



- This scheme, however, is **unrealistic** b/c the 4d orbitals are at a significantly higher energy than the 3d atomic orbitals.
- Nickel(II) (d^8) forms paramagnetic tetrahedral and octahedral complexes, and diamagnetic square planar complexes.

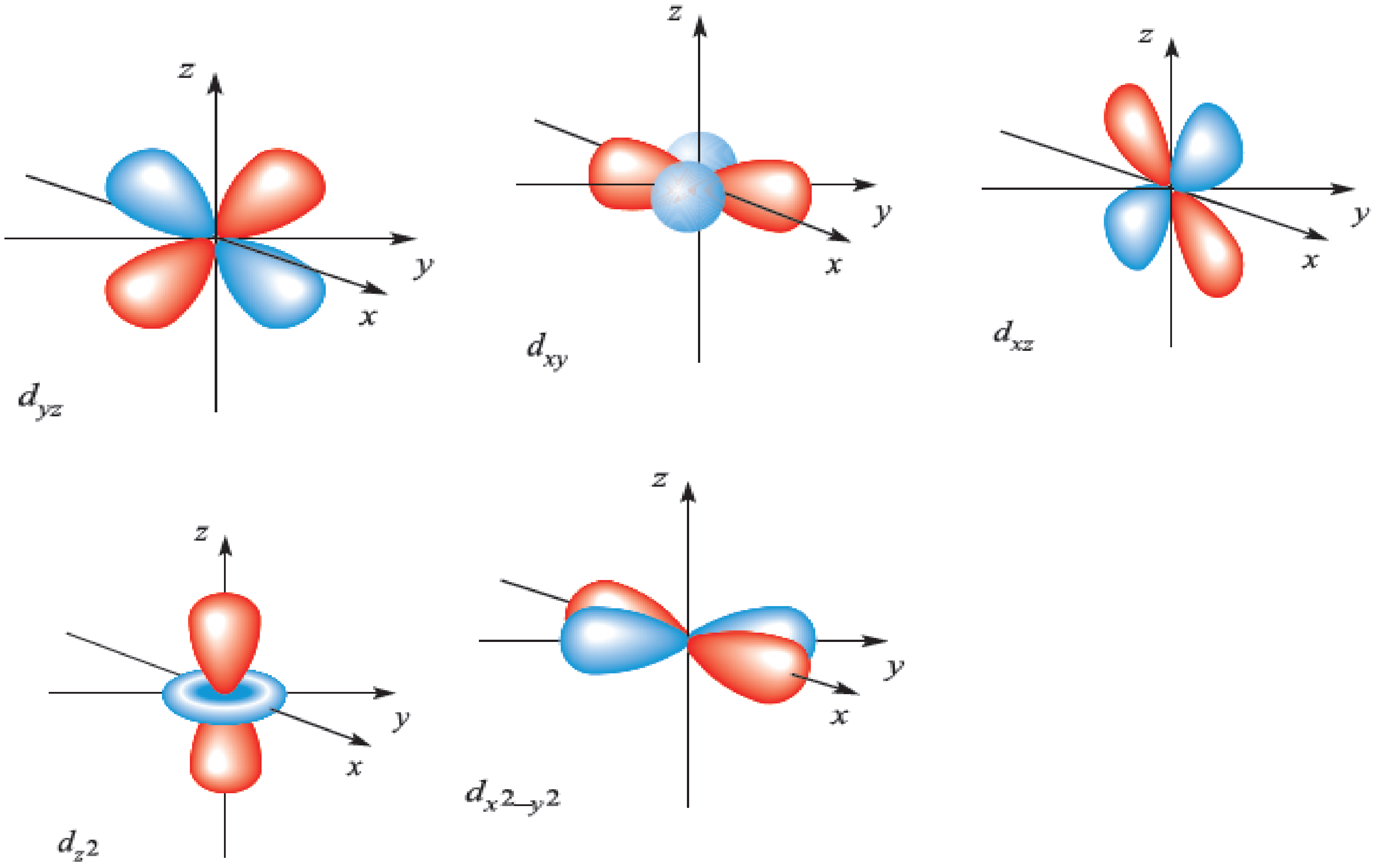


- VBT rationalizes stereochemical and magnetic properties at only a simplistic level.
- the use of the very high energy *4d* orbitals seems unlikely, and the results do not lend themselves to a good explanation of the electronic spectra of complexes (serious shortcoming).

- The model implies a misleading distinction between high- and low-spin complexes.
- Finally, it can’t tell us why certain ligands are associated with the formation of high- (or low-)spin complexes.

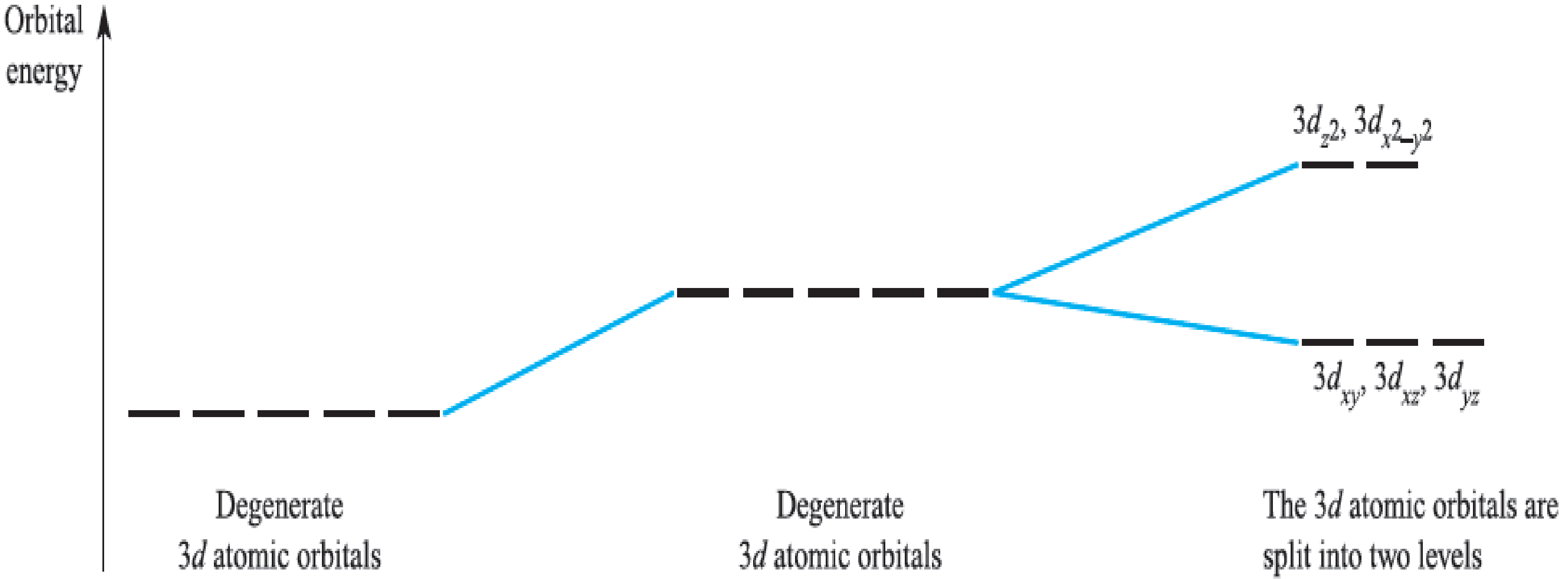
Crystal Field Theory(CFT)

- CFT was first proposed in 1929 by **Hans Bethe.**
- It assumes that the only interaction between the metal ion and the ligands is an **electrostatic** one.
- Ligands are considered as point charges and there are no metal–ligand covalent interactions.
- ✓ In order to understand clearly the interactions that are responsible for crystal or ligand field effects in transition metal complexes, it is necessary to have a firm grasp of the geometrical relationships of the *d* orbitals.



The five *d* orbitals in an isolated, gaseous metal ion are **degenerate**.

- If a spherically symmetric field of negative charges is placed around the metal, the orbitals will remain degenerate, but all of them will be raised in energy as a result of the repulsion between the negative field and the negative electrons in the orbitals.
- But, under the influence of ligands, the **degeneracy** of the *d* orbitals will be removed.
- It is this splitting of *d* orbital energies and its consequences that are at the **heart** of CFT.



Metal ion M^{n+} and six ligands L at an infinite distance away

→

If the electrostatic field created by the point charge ligands is *spherical*, the energies of the electrons in the 3*d* orbitals are raised uniformly

→

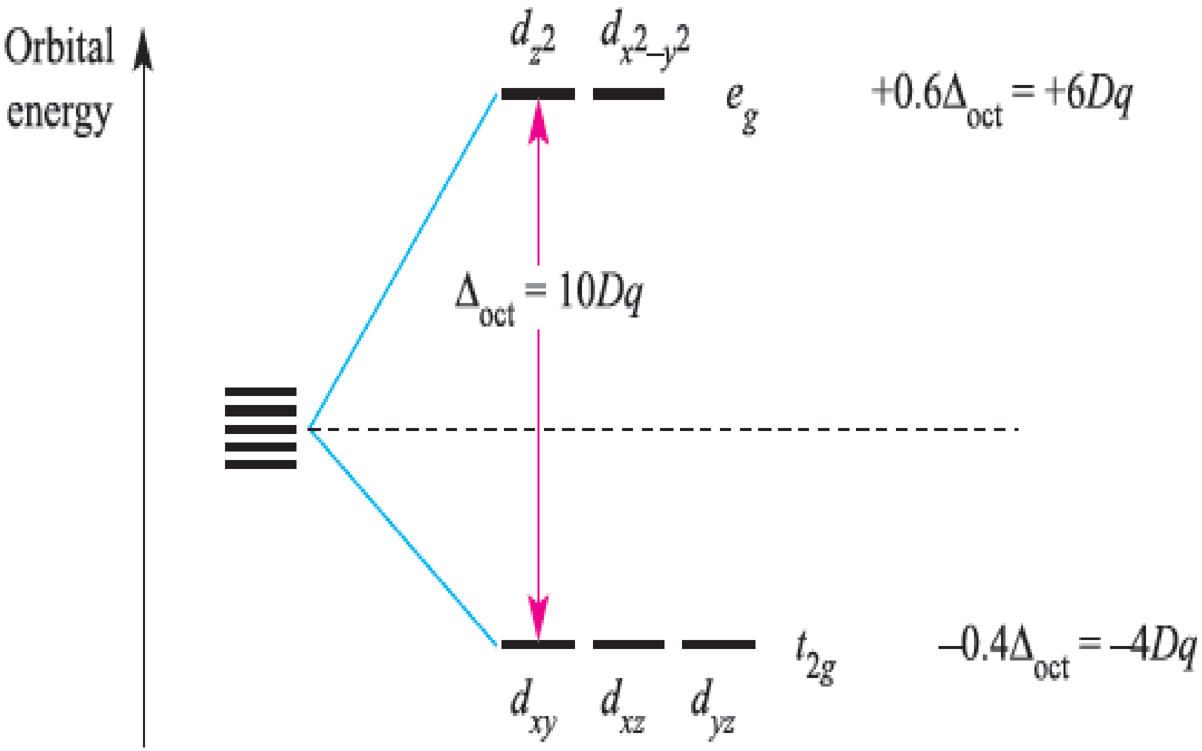
If the electrostatic field created by the point charge ligands is *octahedral*, the energy of the electrons in the 3*d* orbitals that point *directly* at the ligands is raised with respect to that in the spherical field, while the energy of the electrons in the orbitals that point *between* the ligands is lowered with respect to the spherical field

The octahedral crystal field

- There is an electrostatic attraction between the metal ion and ligands.
- However, there is also a repulsive interaction between electrons in the d orbitals and the ligand point charges.
- If the electrostatic field (CF) were spherical, then the energies of the five 3d orbitals would be raised(destabilized) by the same amount.

- However, the d_z2 and $d_{x^2-y^2}$ atomic orbitals point directly at the ligands(destabilized) while the d_{xy}, d_{yz} and d_{xz} atomic orbitals point between them(stablized).
- dz^2 and dx^2-y^2 orbitals have e_g symmetry, while the d_{xy}, d_{yz} and d_{xz} orbitals possess t_{2g} symmetry.
- The energy separation between them is Δ_{oct} ('delta oct') or 10Dq.
- The overall stabilization of the t_{2g} orbitals equals the overall destabilization of the e_g set.

- Thus, orbitals in the e_g set are raised by $0.6\Delta_{oct}$ with respect to the barycentre while those in the t_{2g} set are lowered by $0.4\Delta_{oct}$.



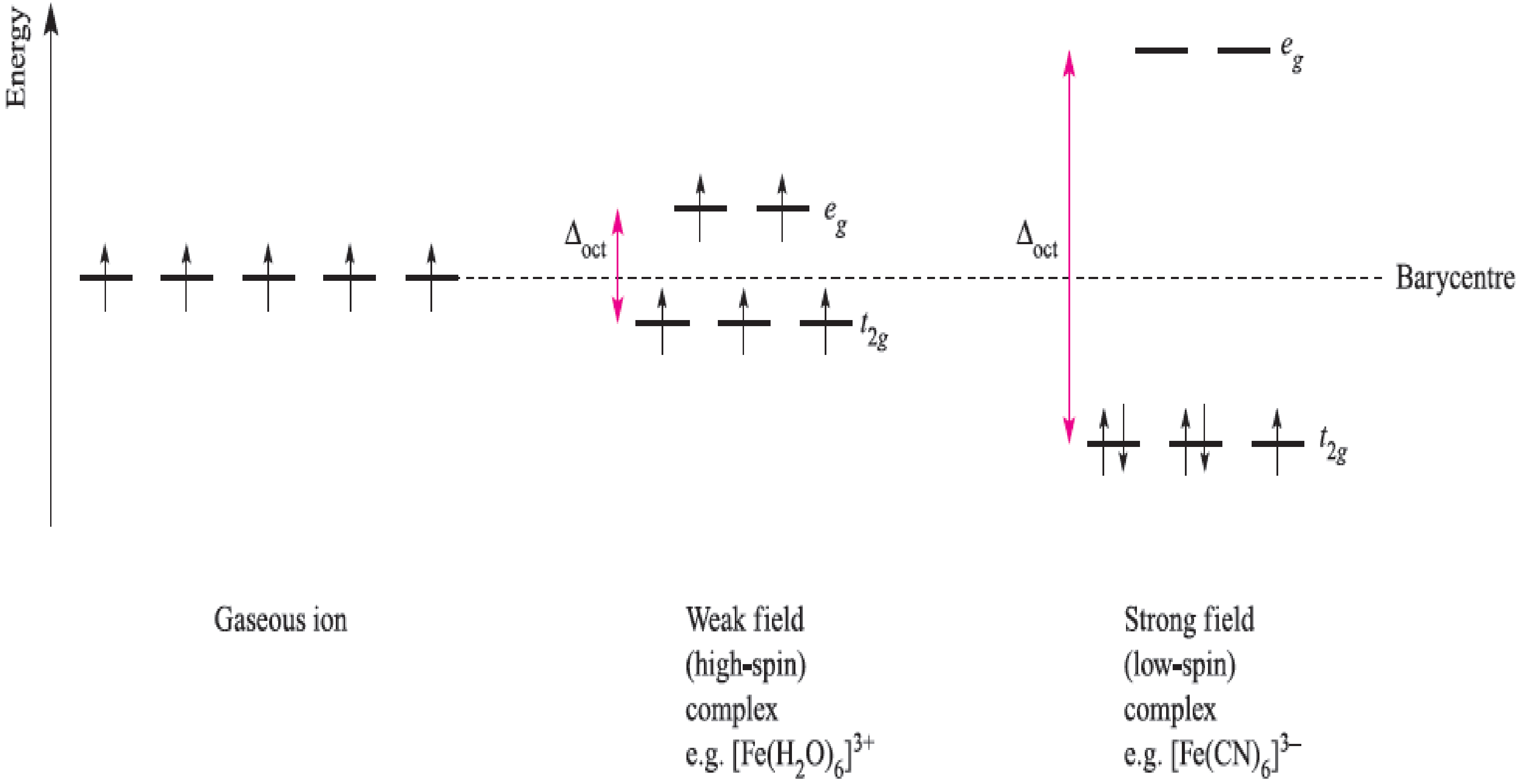
- The magnitude of Δ_{oct} is determined by the strength of the crystal field, the two extremes being called weak field and strong field.

- $\Delta_{oct}(\text{weak field}) < \Delta_{oct}(\text{strong field})$

- Factors governing the magnitude of Δ_{oct} are: the identity and oxidation state of the metal ion and the nature of the ligands. For octahedral complexes, Δ_{oct} increases along the following spectrochemical series of ligands.

$$\mathrm{I^- < Br^- < [NCS]^- < Cl^- < F^- < [OH]^- < [ox]^{2-}}$$
$$\mathrm{\approx H_2O < [NCS]^- < NH_3 < en < bpy < phen < [CN]^- \approx CO}$$

$$\text{weak field ligands} \xrightarrow[\text{increasing } \Delta_{oct}]{} \text{strong field ligands}$$



The occupation of the 3d orbitals in weak and strong field Fe^{3+} (d^5) complexes.

Crystal field stabilization energy

- For a given d^n configuration, the CFSE is the difference in energy between the d electrons in an octahedral crystal field and the d electrons in a spherical crystal field.
- For a d^1 system, the ground state corresponds to the configuration t_{2g}^1.
- With respect to the barycentre, there is stabilization energy of $-0.4\Delta_{oct}$; this is the so-called CFSE. For a d^2 ion, the ground state configuration is t_{2g}^2 and the CFSE = $-0.8\Delta_{oct}$.

- A d^3 ion (t_{2g}^3) has a CFSE = $-1.2\Delta_{oct}$. For a d^4 ion, two arrangements are available($t_{2g}3e_g{}^1$and $t_{2g}{}^4$)
- The preferred configuration is that with the lower energy and depends on P.

- Two terms contribute to the electron-pairing energy, P, the loss in the exchange energy which occurs upon pairing the electrons; the coulombic repulsion between the spin-paired electrons.

- For a low-spin d^4 configuration, the CFSE consists of two terms:a $-1.6\Delta_{oct}$ term, and a pairing energy, P.
- Now consider a d^6 ion, high-spin d^6 configuration ($t_{2g}{}^4e_g{}^2$).

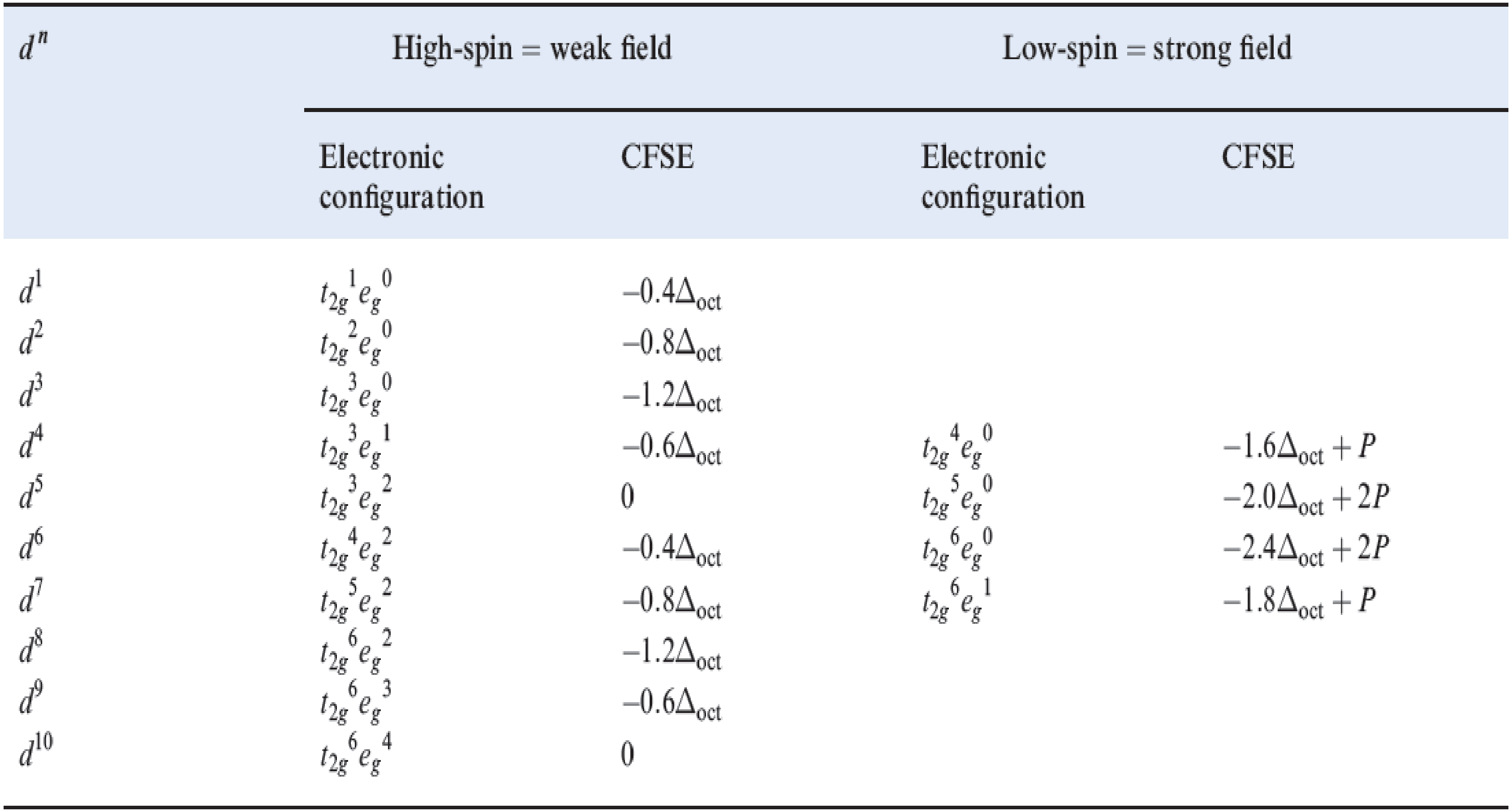
$$\text{CFSE} = -(4x\ 0.4)\Delta_{oct} + (2x\ 0.6)\Delta_{oct} = 0.4\Delta_{oct}$$

- For a low-spin d^6 configuration ($t_{2g}{}^6e_g{}^0$), the six electrons in the t_{2g} orbitals give rise to a $-2.4\Delta_{oct}$ term.
- A pairing energy term of 2P is added to $-2.4\Delta_{oct}$ in excess of the one in the high-spin configuration.

For high-spin: $\Delta_{oct} < P$

For low-spin: $\Delta_{oct} > P$

- Strong field ligands such as $[CN]^-$ favour the formation of low-spin complexes, while weak field ligands such as halides tend to favour high-spin complexes.
- However, we cannot predict whether high- or low-spin complexes will be formed unless we have accurate values of Δ_{oct} and P.



d^n	High-spin = weak field		Low-spin = strong field	
	Electronic configuration	CFSE	Electronic configuration	CFSE
d^1	$t_{2g}{}^1e_g{}^0$	$-0.4\Delta_{oct}$		
d^2	$t_{2g}{}^2e_g{}^0$	$-0.8\Delta_{oct}$		
d^3	$t_{2g}{}^3e_g{}^0$	$-1.2\Delta_{oct}$		
d^4	$t_{2g}{}^3e_g{}^1$	$-0.6\Delta_{oct}$	$t_{2g}{}^4e_g{}^0$	$-1.6\Delta_{oct} + P$
d^5	$t_{2g}{}^3e_g{}^2$	0	$t_{2g}{}^5e_g{}^0$	$-2.0\Delta_{oct} + 2P$
d^6	$t_{2g}{}^4e_g{}^2$	$-0.4\Delta_{oct}$	$t_{2g}{}^6e_g{}^0$	$-2.4\Delta_{oct} + 2P$
d^7	$t_{2g}{}^5e_g{}^2$	$-0.8\Delta_{oct}$	$t_{2g}{}^6e_g{}^1$	$-1.8\Delta_{oct} + P$
d^8	$t_{2g}{}^6e_g{}^2$	$-1.2\Delta_{oct}$		
d^9	$t_{2g}{}^6e_g{}^3$	$-0.6\Delta_{oct}$		
d^{10}	$t_{2g}{}^6e_g{}^4$	0		

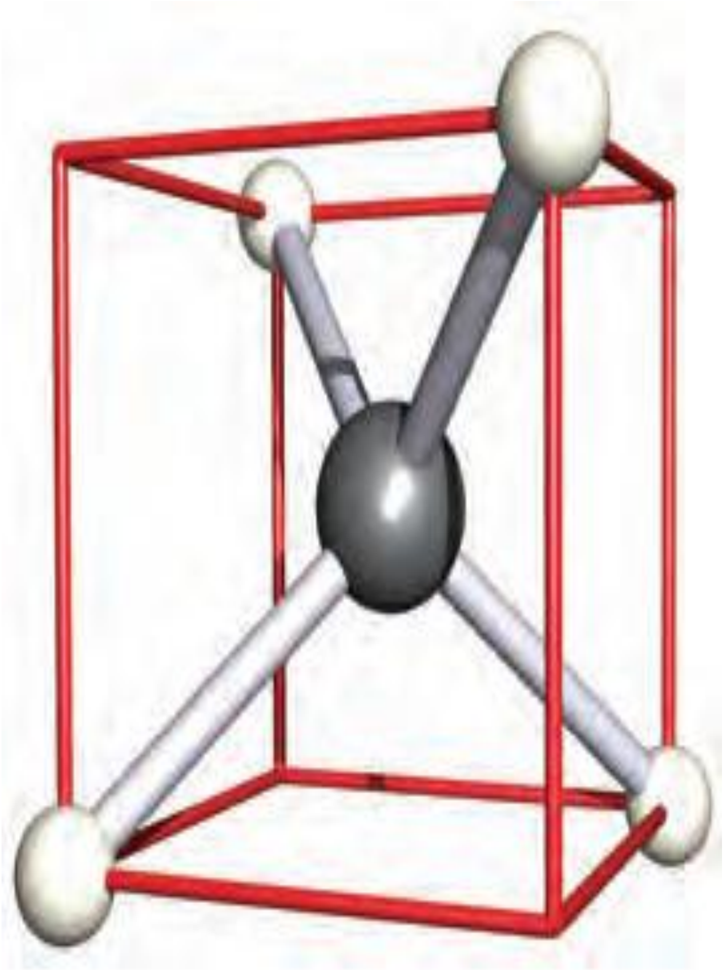
- Octahedral crystal field stabilization energies (CFSE) for d n configurations; pairing energy, P, terms are included where appropriate.

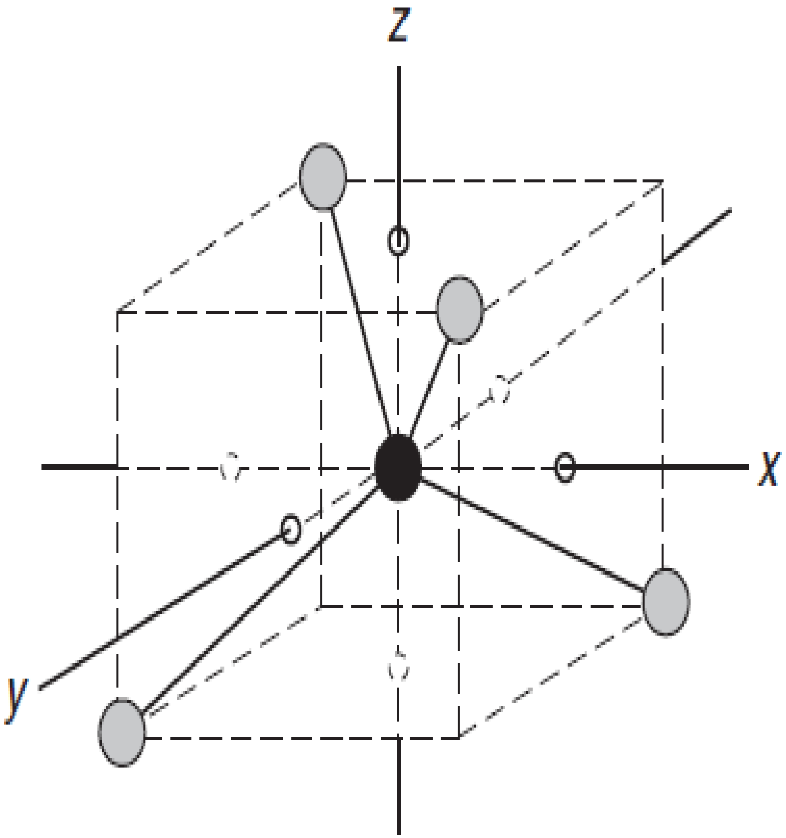
- On the other hand, with some experimental knowledge in hand, we can make some comparative predictions.

- If we know from magnetic data that $[Co(H_2O)_6]^{3+}$ is low-spin, then from the spectrochemical series we can say that $[Co(CN)_6]^{3-}$ will be low-spin.

- The only common high-spin cobalt(III) complex is $[CoF_6]^{3-}$.

The tetrahedral crystal field





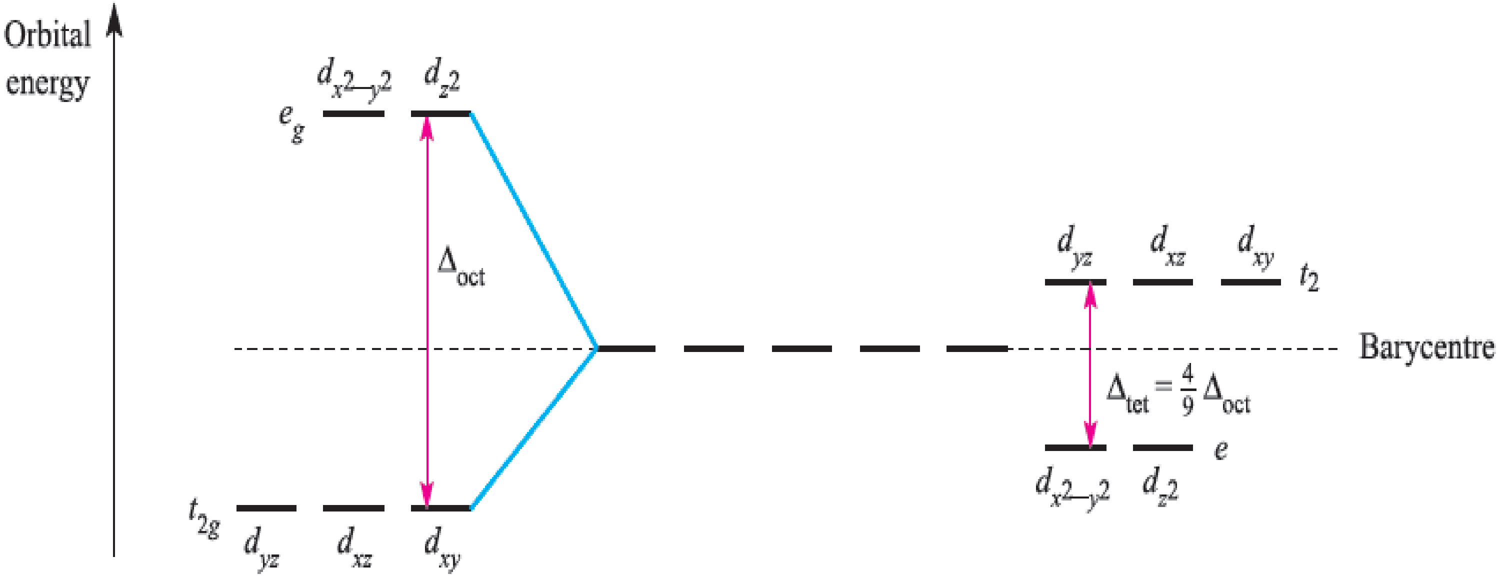
- The figure shows a convenient way of relating a tetrahedron to a Cartesian axis set.

- With the complex in this orientation, none of the metal d orbitals points exactly at the ligands, but the d_{xy}, d_{yz} and d_{xz} orbitals come nearer to doing so than the d_{z^2} and $d_{x^2-y^2}$ orbitals.

- For a regular tetrahedron, the splitting of the d orbitals is inverted compared with that for a regular octahedral structure, and the energy difference (Δ_{tet}) is smaller.

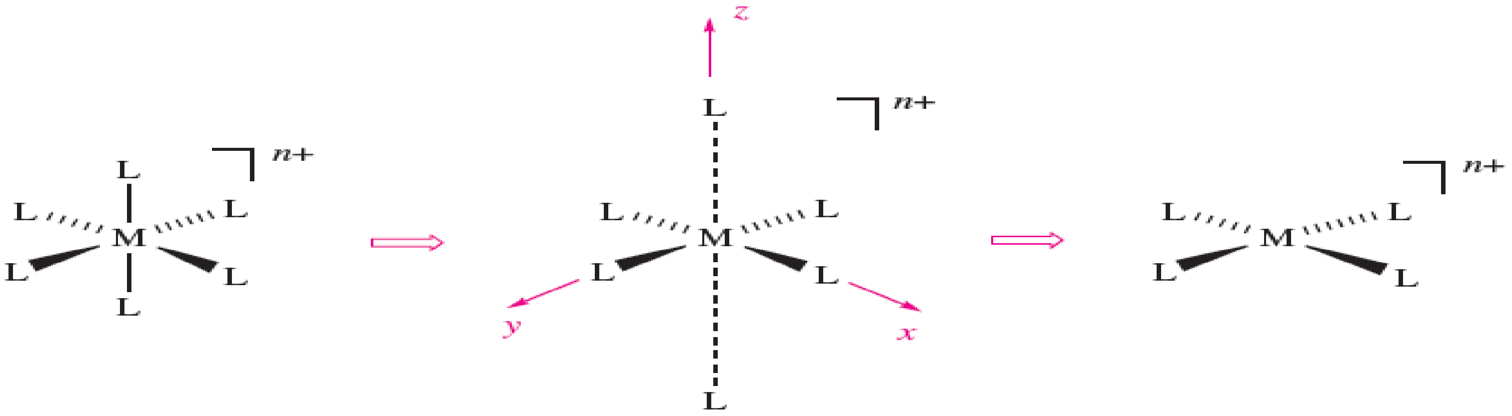
$\Delta_{tet} = 4/9\Delta_{oct} \approx 1/2\Delta_{oct}$

- Since Δ_{tet} is significantly smaller than Δ_{oct}, tetrahedral complexes are high-spin.
- Corresponding octahedral and tetrahedral complexes often have different colours.

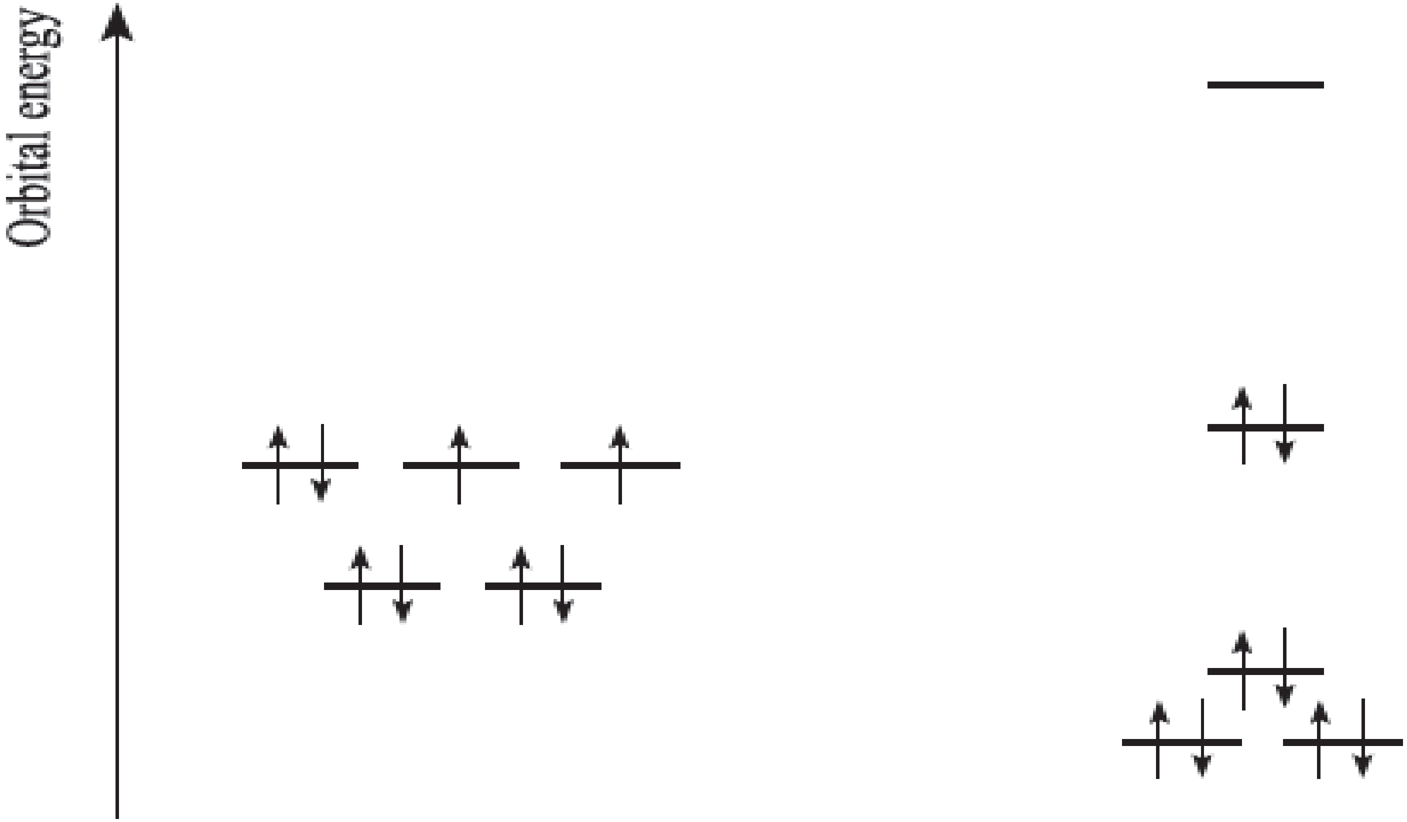


The square planar crystal field

- A square planar arrangement of ligands can be formally derived from an octahedral array by removal of two transligands.
- If we remove the ligands lying along the z axis, then the d_{z^2} orbital is greatly stabilized; the energies of the d_{yz} and d_{xz} orbitals are also lowered.

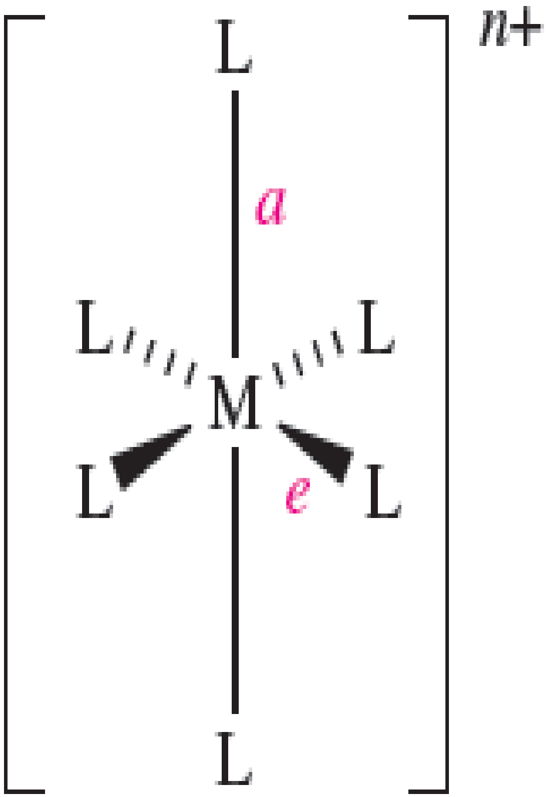


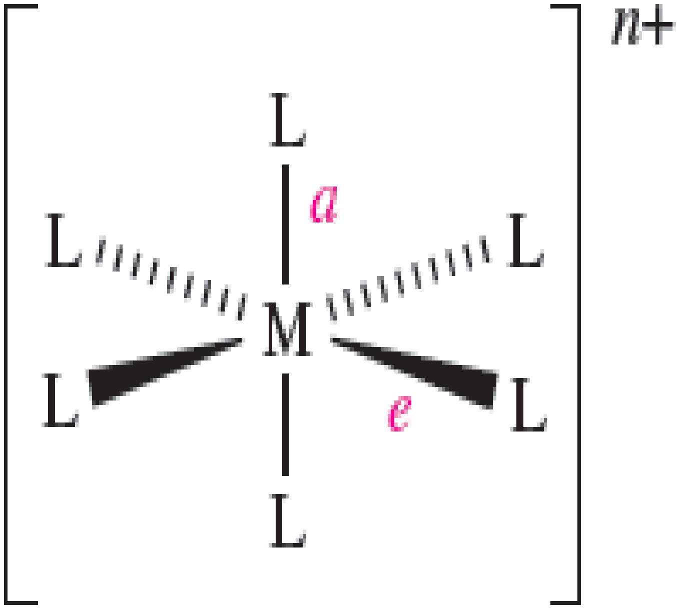
- The fact that square planar d^8 complexes such as $[Ni(CN)_4]^{2-}$ are **diamagnetic** is a consequence of the relatively large energy difference between the d_{xy} and d_{x2_y2} orbitals.



Jahn–Teller distortions

- Octahedral complexes of d^9 and high-spin d^4 ions are often distorted.





- For a high-spin d^4 ion, one of the e_g orbitals contains one electron while the other is vacant.
- If the singly occupied orbital is in the dz^2, the complex suffers elongation along the z axes.
- Conversely, occupation of the dx^2-y^2 orbital would lead to elongation along the x and y axes as in structure.
- A similar argument can be put forward for the d^9 configuration.

- The corresponding effect when the t_{2g} set is unequally occupied is expected to be very much smaller.
- Distortions of this kind are called **Jahn–Teller distortions.**

- The Jahn–Teller theorem states that any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy, thereby removing the degeneracy.

Crystal field theory: uses and limitations

- CFT can bring together structures, magnetic and electronic properties.
- Trends in CFSEs provide some understanding of thermodynamic and kinetic aspects of d-block metal complexes.
- CFT is surprisingly useful when one considers its simplicity.
- However, it has limitations.

- For example, although we can interpret the contrasting magnetic properties of high- and low-spin octahedral complexes on the basis of the positions of weak- and strong-field ligands in the spectrochemical series,
- CFT provides no explanation as to why particular ligands are placed where they are in the series.

σ

Molecular Orbital Theory(MOT)

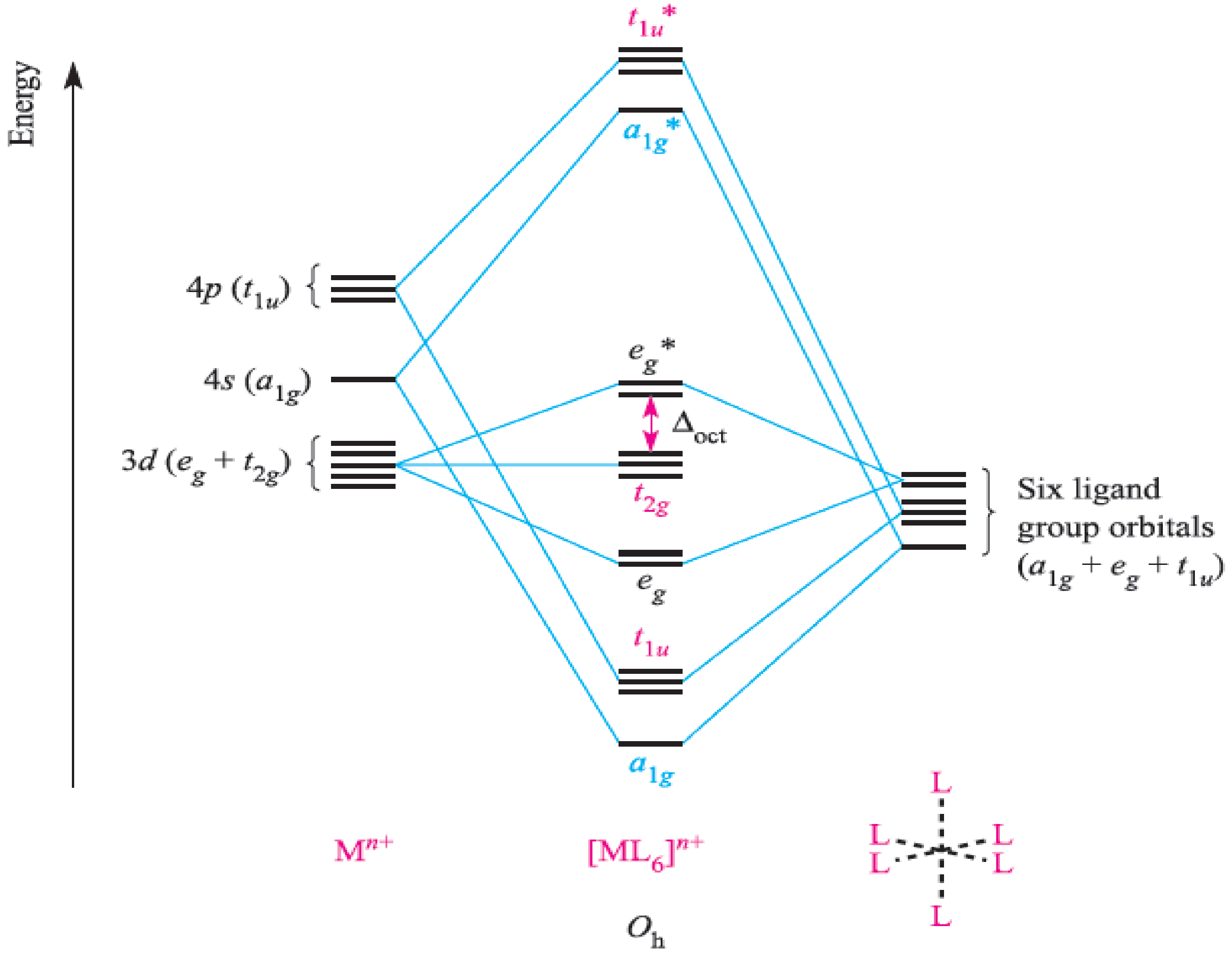
- In contrast to CFT, the MOM considers **covalent** interactions between the metal centre and ligands.

Complexes with no metal–ligand π–bonding

- consider an octahedral complex such as$[Co(NH_3)_6]^{3+}$ in which metal–ligand σ -bonding is dominant.
- For a first row metal, the valence shell atomic orbitals are 3d, 4s and 4p.
- Under O_h symmetry, the s orbital has a_{1g} symmetry, the p orbitals are degenerate with t_{1u} symmetry, and the d orbitals split into e_g and t_{2g} symmetries.

- Each ligand provides one orbital and derivation of the ligand group orbitals for the O_h L_6 fragment is analogous to those for the F_6 fragment in SF_6.
- These LGOs have a_{1g}, t_{1u} and e_g symmetries.
- Symmetry matching between metal orbitals and LGOs allows the construction of a MO diagram.
- The metal d_{xy}, d_{yz} and d_{xz} atomic orbitals have $\mathbf{t_{2g}}$ symmetry and are non-bonding.
- The a_{1g} and t_{1u} MOs are **stabilized** to a greater extent than the e_g MOs.

- In an O_h complex with no π-bonding, the energy difference between the t_{2g} and e_g^* levels corresponds to Δ_{oct} in CFT.



- In low-spin $[Co(NH_3)_6]^{3+}$, 18 electrons occupy the a_{1g}, t_{1u}, e_g and t_{2g} Mos.
- Whether a complex is high- or low-spin depends upon the energy separation of the t_{2g} and e_g^* levels.
- Notionally, in a σ-bonded O_h complex, the 12 electrons supplied by the ligands are considered to occupy the a_{1g}, t_{1u} and e_g orbitals.
- Occupancy of the t_{2g} and e_g^* levels corresponds to the number of valence electrons of the metal ion, just as in **CFT**. 313

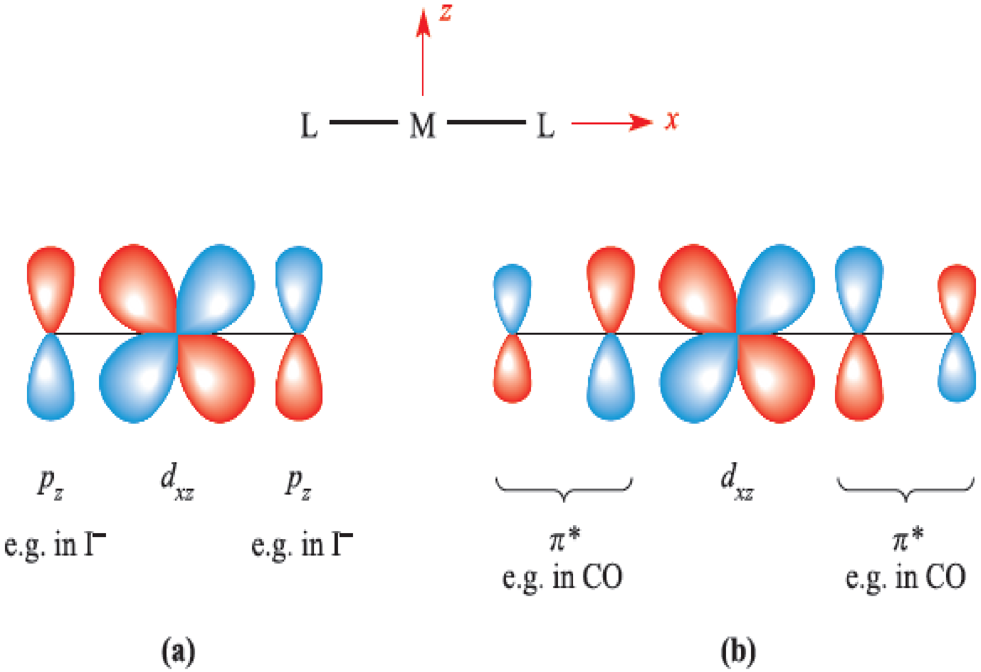
Complexes with metal–ligand π -bonding

- The metal d_{xy}, d_{yz} and d_{xz} atomic orbitals are nonbonding in an $[ML_6]^{n+}$, σ-bonded complex and these orbitals may overlap with ligand orbitals of the correct symmetry to give π - interactions.
- Two types of ligand must be differentiated: π-donor and π–acceptor ligands.
- π- donor ligands donates electrons to the metal centre in an interaction that involves a filled ligand orbital and an empty metal orbital.

- A π–acceptor ligand accepts electrons from the metal centre in an interaction that involves a filled metal orbital and an empty ligand orbital.

- π-donor ligands include Cl^-, Br^- and I^- and the metal–ligand π-interaction involves transfer of electrons from filled ligand p orbitals to the metal centre.

- π-acceptor ligands are CO, N_2, NO and alkenes, and the metal–ligand π-bonds arise from the back donation of electrons from the metal centre to vacant antibonding orbitals on the ligand.



π-bond formation in a linear L-M-L unit in which the metal and ligand donor atoms lie on the x axis:

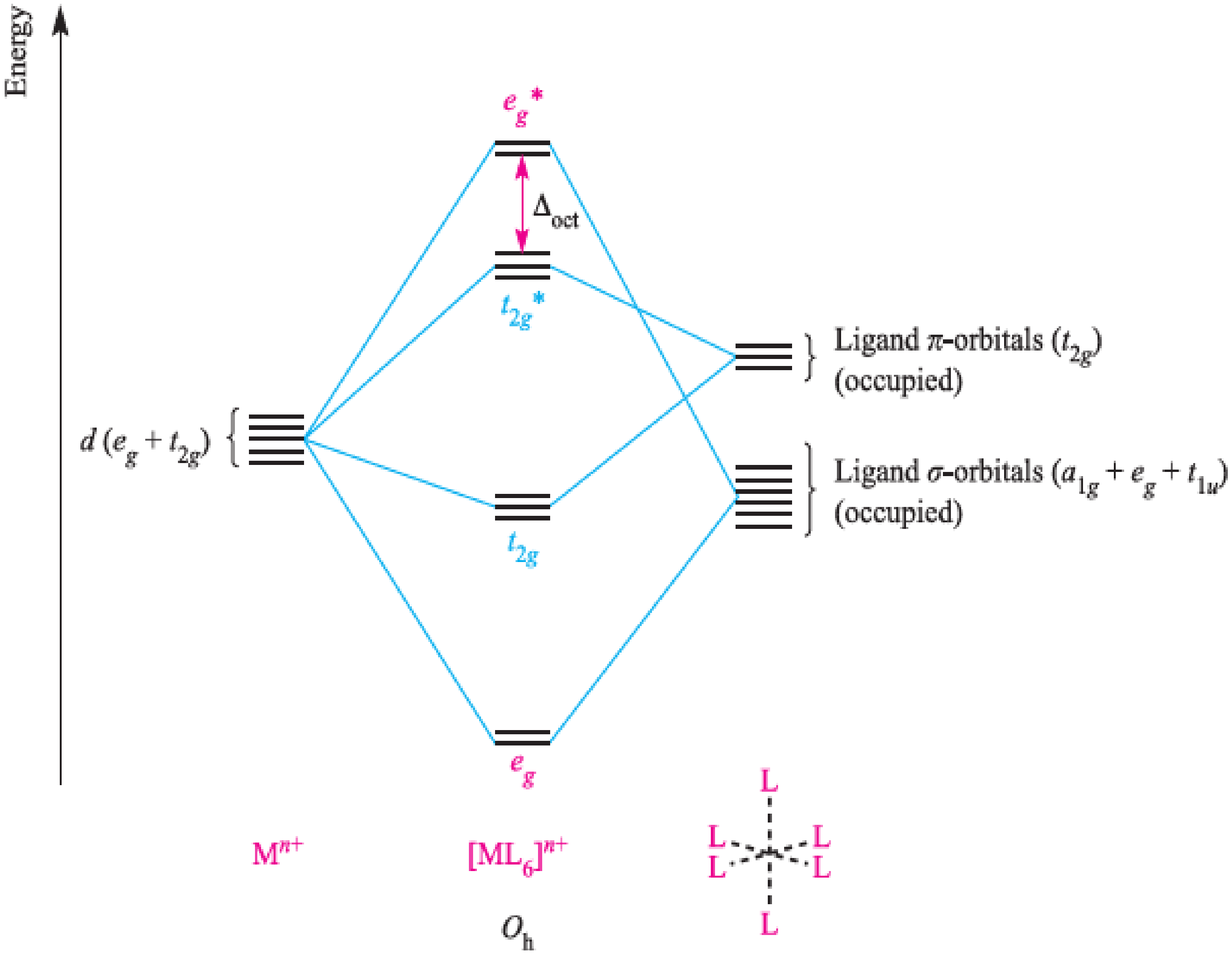
(a) between metal d_{xz} and ligand p_z orbitals as for (a), an example of a π-donor ligand; and

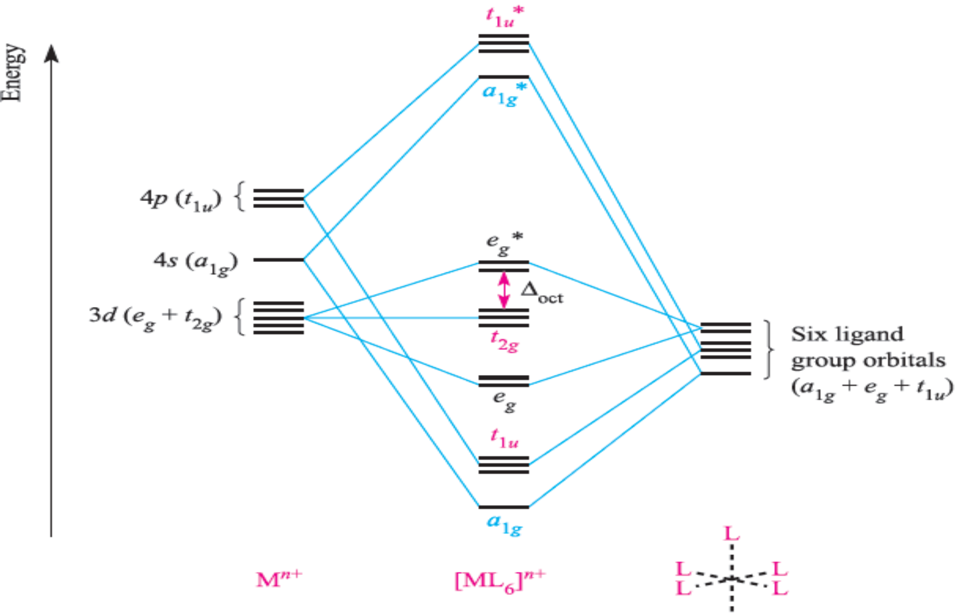
(b) between metal d_{xz} and ligand π-orbitals as for L = CO, an example of a π-acceptor ligand.

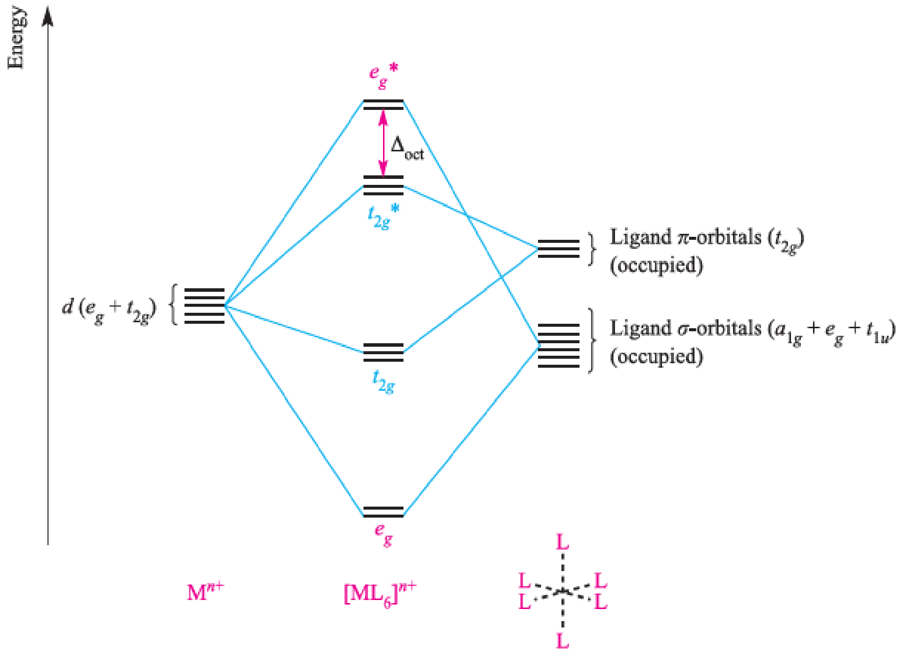
- π-acceptor ligands can stabilize low oxidation state metal complexes.
- The interaction of ligand π-orbitals with the metal t_{2g} atomic orbitals leads to bonding (t_{2g}) and antibonding (t_{2g}^*) MOs.
- The energy separation between the t_{2g}^* and eg^* levels corresponds to Δ_{oct}.
- In the interaction between a metal ion and six π-acceptor ligands:- the vacant ligand π^*-orbitals lie significantly higher in energy than the ligand -orbitals.
- Orbital interaction leads to B(t_{2g}) and AB(t_{2g}^*) MOs as before, but now the t_{2g}^* MOs are at high energy.

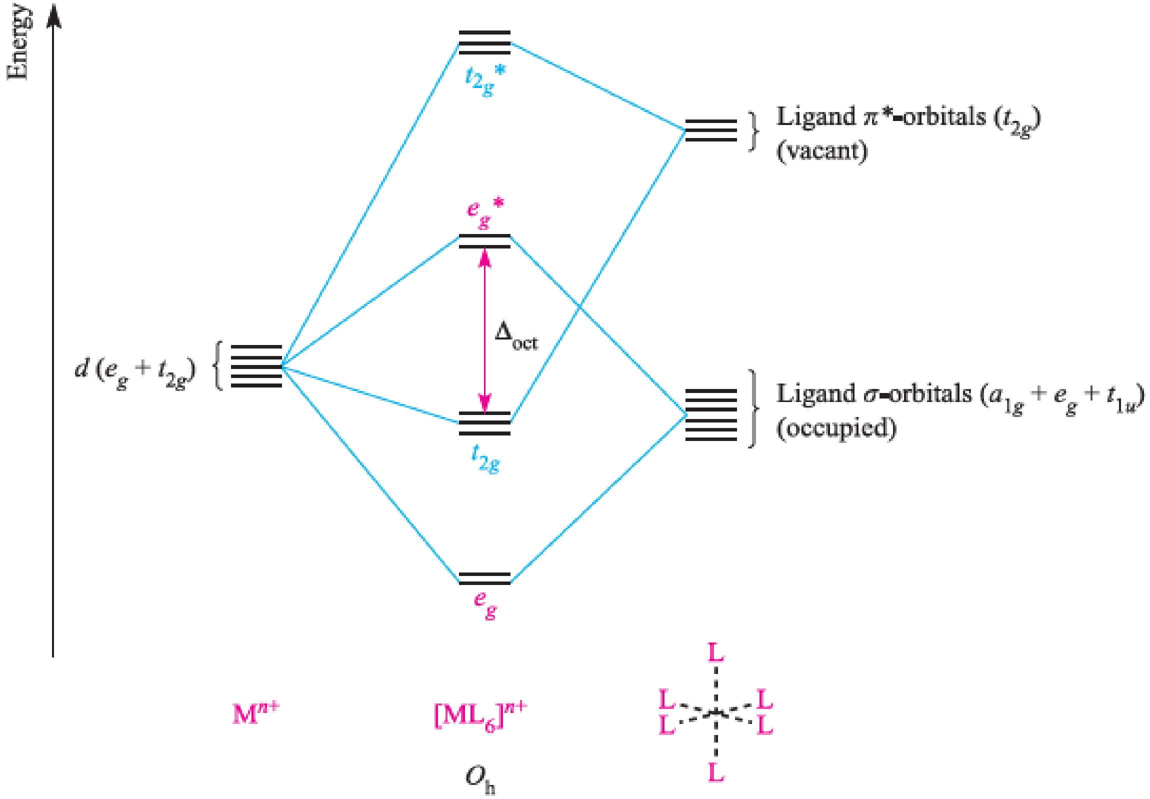
- Δ_{oct} is identified as the energy separation between the t_{2g} and $e_g{}^*$ levels.

π-donor ligands diagram

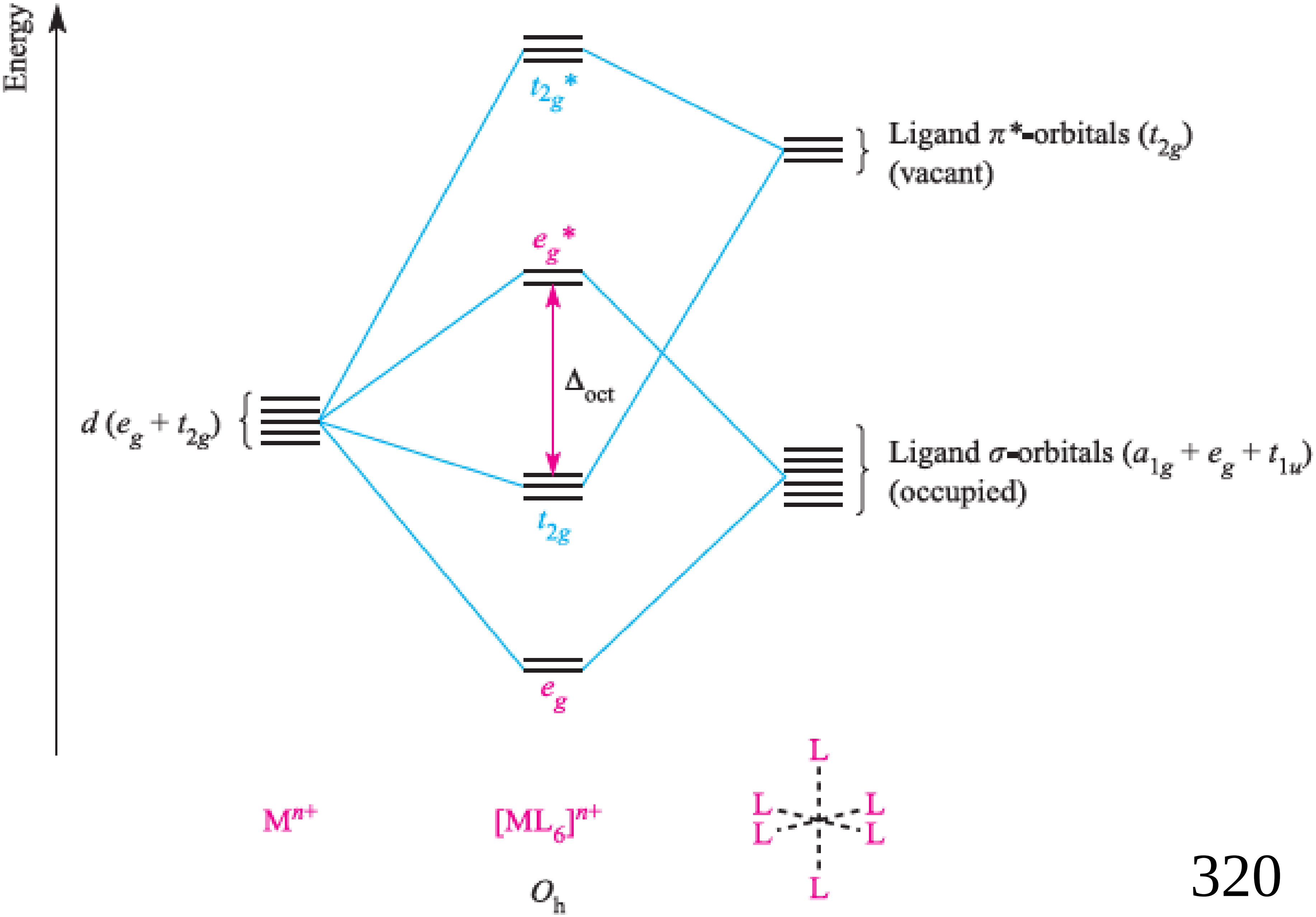



Energy
t_{1u}^*
a_{1g}^*
$4p\ (t_{1u})$
$4s\ (a_{1g})$
e_g^*
Δ_{oct}
$3d\ (e_g + t_{2g})$
t_{2g}
Six ligand group orbitals $(a_{1g} + e_g + t_{1u})$
e_g
t_{1u}
a_{1g}
L
L
L
L
L
M^{n+}
$[ML_6]^{n+}$


Energy
e_g^*
Δ_{oct}
t_{2g}^*
Ligand π-orbitals (t_{2g}) (occupied)
$d\ (e_g + t_{2g})$
Ligand σ-orbitals $(a_{1g} + e_g + t_{1u})$ (occupied)
t_{2g}
e_g
L
L
L
L
L
L
M^{n+}
$[ML_6]^{n+}$


Energy
t_{2g}^*
Ligand π*-orbitals (t_{2g}) (vacant)
e_g^*
Δ_{oct}
$d\ (e_g + t_{2g})$
Ligand σ-orbitals $(a_{1g} + e_g + t_{1u})$ (occupied)
t_{2g}
e_g
L
L
L
L
L
L
M^{n+}
$[ML_6]^{n+}$
O_h

π-acceptor ligands diagram



- The above figures reveal important differences between octahedral $[ML_6]^{n+}$ complexes containing σ-donor, π-donor and π –acceptor ligands:

- ✓ Δ_{oct} **decreases** in going from a σ-complex to one containing π-donor ligands;

- ✓ for a complex with π-donor ligands, increased π–donation stabilizes the t_{2g} level and destabilizes the t_{2g}^*, thus decreasing Δ_{oct}; Δ_{oct} values are relatively large for complexes containing π-acceptor ligands, and such complexes are likely to be low-spin.

- For a complex with π -acceptor ligands, increased π -acceptance stabilizes the t_{2g} level, increasing Δ_{oct}.

Occupancies of the MOs in above figures

- Six π- donor ligands provide 18 electrons (12 σ- and six π-electrons)

✓ and these can notionally be considered to occupy the a_{1g}, t_{1u}, e_g and t_{2g} orbitals of the complex.

- The occupancy of the t_{2g}^* and eg^* levels corresponds to the number of valence electrons of the metal ion.
  - Six π-acceptor ligands provide 12 electrons and, formally, we can place these in the a_{1g}, t_{1u} and e_g orbitals of the complex.

- The metal valence electrons then corresponds to the occupancy of the t_{2g} and $e_g{}^*$ levels.
- Since occupying antibonding MOs is **detrimental** to metal π–ligand bond formation, it follows that, for example, O_h complexes with π-acceptor ligands will not be favoured for metal centres with d^7, d^8, d^9 or d^{10} configurations.
- d-block metal organometallic and related complexes tend to obey the ***effective atomic number rule or 18-electron rule.***