



Chemistry of transition elements and complexes

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Chemistry of Transition Elements

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Introduction

The chemical elements in the periodic table are arranged together in blocks according to their outer electronic configurations. The elements with a half-filled or fully-filled outer s orbital comprise the s-block elements. Similarly, the elements with a partly filled or fully filled outer p orbitals comprise the p-block elements. The elements between these two blocks that

is, between the groups 3 and 12 in the periodic table have at most two electrons in the outermost s orbital, and incompletely filled d orbitals next to outermost orbital. These elements in which successive addition of electrons takes place progressively in the inner d orbitals are called as **d- block elements**. Similarly, the elements in which filling up of electrons takes place in inner to inner f orbitals are known as **f-block elements**. These two blocks of elements are generally called **transition elements**. However, the f-block elements are commonly known as **inner transition elements**. Here only the d-block elements will be considered for discussion.

Strictly speaking, the term transition element, as defined by IUPAC, is the one with a partly filled d orbitals in its ground state or in any of its oxidation state. This definition justifies the inclusion of Cu, Ag and Au as transition metals, since Cu(II) has a $3d^9$ configuration, Ag(II) has a $4d^9$ and Au(III) has a $5d^8$ configuration. By this definition, Zn, Cd and Hg are excluded from transition metals, as they have d^{10} configuration. However, being the end members of the series, they are often considered together with the transition elements.

The transition elements play important roles in our daily life and in keeping the living organisms alive. Many materials that we encounter each day contain transition elements such as iron, copper, chromium, nickel etc. in one form or the other. Production of various materials using chemical processes invariably involves catalysts which are mostly transition metals and their compounds. In order to understand roles of transition elements in biological systems or in chemical processes involving them, it is essential to understand the principles underlying the chemistry of these elements.

There are four series of transition elements :

- i) The first transition series : Scandium (Sc, $Z = 21$) to Zinc (Zn, $Z=30$) : addition of electrons in 3d orbitals.
- ii) The second transition series : Yttrium (Y, $Z =39$) to Cadmium (Cd, $Z = 48$) : addition of electrons in 4d orbitals.
- iii) The third transition series : Lanthanum (La, $Z=57$) to Hafnium (Hf, $Z=72$) through Mercury (Hg, $Z = 80$): addition of electrons in 5d orbitals.
- iv) The fourth transition series : Actinium (Ac, $Z=89$) to Rutherfordium (Rf, $Z=104$) through Ununbium (Uub, $Z=112$):addition of electrons in 6d orbitals.

The abundance of d- block elements in the Earth's crust vary considerably. Iron (6.30% by mass of the crustal rocks) is the fourth most abundant metal. Titanium (0.66%) and manganese (0.11%) are also quite abundant. Some of the heavier transition metals such as ruthenium(Ru), rhodium(Rh), iridium(Ir), osmium(Os) and gold(Au) are rather rare.The transition elements have several characteristic properties.

- All are metals with high tensile strength and good conductor of heat and electricity.
- All, except mercury (which is liquid at room temperature), appear as high melting point and boiling point lustrous solids. The high melting points are attributed to the involvement of greater number of electrons from (n-1) d orbitals in addition to the ns electrons in the interatomic metallic bonding. In a particular row, in general, the melting points rise to a maximum at d^5 , except for anomalous values of Mn and Tc, and fall regularly as the atomic number increases (Figure 1).

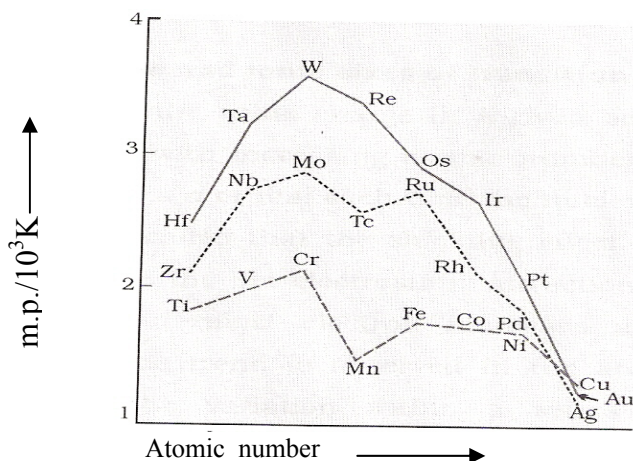


Figure - 1 The variation in melting points of transition metals across the series

- All have high enthalpy of atomization. The higher enthalpy values of atomization for the second and third series account for the occurrence of much more frequent metal – metal bonding in compounds of the heavy transition series.
- All form alloys with one another, and with metallic main group elements.
- Many of them are sufficiently electropositive to react with mineral acids to form salts, though some of them are rather inert in this respect.
- Most of them show more than one oxidation state (variable valence).
- Because of partly filled d orbitals some transition metal ions containing odd number of electrons form paramagnetic compounds.
- They have unparallel tendency to form coordination compounds with Lewis bases because of their small size, high charge and availability of low energy orbitals.
- Many form coloured compounds in one if not in all oxidation states; the absorption of visible light being associated with the presence of partly filled d orbitals.

The redox behavior, magnetic and optical properties of the transition elements are important features underlying their use in innumerable applications.

We shall be dealing with the electronic configurations, general characteristics, and complex forming tendency of transition elements.

Atomic Structures and Properties

Electronic configurations

The electronic configurations of the valence shells of the d-block elements can be given as $(n-1)d^{1-10} ns^{1-2}$, where $(n-1)$ stands for the inner d orbitals (Table 1). It is observed that the electron first enters in higher principal quantum number orbital (n) rather than in unoccupied $(n-1)d$ orbital. The reason for the preferential filling up of 4s in comparison to 3d can be understood in terms of the shielding effect and the effective nuclear charge. In fact, the relative energies of the atomic orbitals varies with increase in atomic number as shown in figure 2. In building up the elements from hydrogen ($Z=1$) to calcium ($Z=20$), the unoccupied 3d orbitals are effectively shielded from the increasing nuclear charge by the

electrons of (Ar) core. As a consequence, the energy of 3d orbitals remains fairly constant. In contrast, the energies of the 4s and 4p orbitals are declining as they penetrate the (Ar) core more. However, the 3d orbitals penetrate the 4s and 4p orbitals so that after Ca a 3d electron is not fully shielded from the increasing nuclear charge by the 4s electrons. Thus, by the time Sc ($Z=21$) is reached the energy of 3d orbitals fall below the level of 4p orbitals and close to that of 4s orbital. The next electron therefore enters the 3d orbital. Since the d electrons shield one another rather poorly from the nuclear charge, the energy of 3d orbitals continues to fall as Z_{eff} increases. Thus, by the time Ga ($Z=31$) is reached, the new filled d orbitals have fallen well below the 4s and 4p orbitals in energy and are no longer part of the valence shell, but become a core. The same sequence of events follow in the case of the heavier transition metal series.

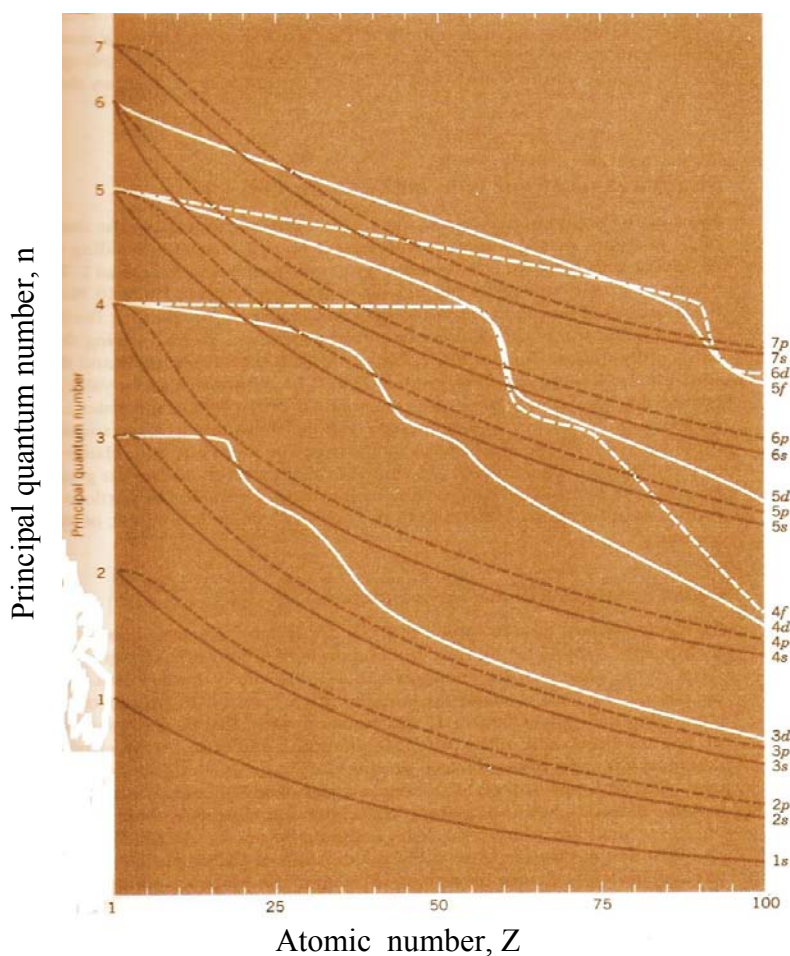


Figure - 2 The relative energies of the atomic orbitals as a function of atomic number

It is observed (Table 1) that the filling of d-orbitals is not always regular. These exceptions mostly occur at least in the first transition series because half- and fully - filled orbitals, impart unusual stability to the atoms due to exchange energy stabilization.

Table-1 Electronic configurations and some other properties of the transition elements
First series

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	
Atomic number	21	22	23	24	25	26	27	28	29	30	
Electronic configuration											
M	3d ¹ 4s ²	3d ² 4s ²	3d ³ 4s ²	3d ⁵ 4s ¹	3d ⁵ 4s ²	3d ⁶ 4s ²	3d ⁷ 4s ²	3d ⁸ 4s ²	3d ¹⁰ 4s ¹	3d ¹⁰ 4s ²	
M ⁺	3d ¹ 4s ¹	3d ² 4s ¹	3d ³ 4s ¹	3d ⁵	3d ⁵ 4s ¹	3d ⁶ 4s ¹	3d ⁷ 4s ¹	3d ⁸ 4s ¹	3d ¹⁰	3d ¹⁰ 4s ¹	
M ²⁺	3d ¹	3d ²	3d ³	3d ⁴	3d ⁵	3d ⁶	3d ⁷	3d ⁸	3d ⁹	3d ¹⁰	
M ³⁺	[Ar]	3d ¹	3d ²	3d ³	3d ⁴	3d ⁵	3d ⁶	3d ⁷	3d ⁸	3d ⁹	
Atomization enthalpy/ kJ mol⁻¹											
	326	473	575	397	281	416	425	430	339	126	
Ionisation enthalpy / kJmol⁻¹											
$\Delta_i H^\ominus$	I	631	656	650	653	771	762	758	737	746	906
	II	1235	1309	1414	1592	1509	1561	1644	1752	1958	1734
	III	2389	2650	2828	2990	3251	2957	3232	3489	3545	3289
Atomic/Ionic *radii, r/pm											
M	144	132	122	118	117	117	116	115	117	125	
M ²⁺	-	86	79	80	83	78	75	69	73	74	
M ³⁺	74.5	67	64	62	65	65	61	60	-	-	
Standard potential, E^o/V											
M ²⁺ /M	-	-1.63	-1.18	-0.90	-1.18	-0.44	-0.28	-0.25	+0.34	-0.76	
M ³⁺ /M ₂₊	-	-0.37	-0.26	-0.41	+1.57	+0.77	+1.97	-	-	-	
Density/g cm⁻³											
	3.43	4.1	6.07	7.19	7.21	7.8	8.7	8.9	8.9	7.1	

* Effective ionic radii with coordination number 6.

Radii of atoms and ions

In general, atomic radii (Table 1) of the elements show progressive decrease with increasing atomic number across a row in the transition series. This is because as the new electron enters a d orbital, each time the nuclear charge increases by unity. Since the shielding effect of a d electron is not that effective, the net electrostatic attraction between the nuclear charge and the outermost electron increases and hence a contraction in size. The same trend is observed in the ionic radii of a given series. However, the variation within a series is quite small. It may be attributed to the two opposing factors : one the increasing nuclear charge tending to decrease the size and the other electron-electron repulsion, because of addition of electrons in the same penultimate d shell, tending to increase the size.

An interesting feature emerges when atomic sizes of one series are compared with those of the corresponding elements in the other series. The data in Figure 3 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 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d 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.

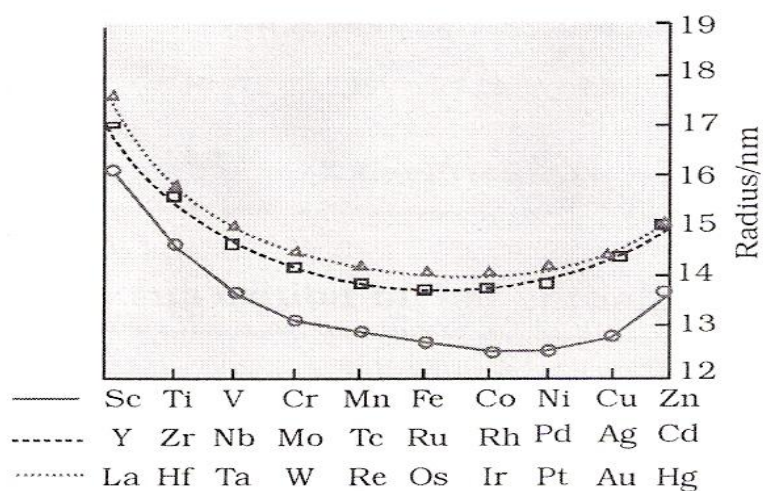


Figure - 3 The variation in atomic radii of transition metals across the series

The decrease in metallic radius coupled with increase in atomic mass results in a general increase in the density of these elements. Thus from titanium ($Z=22$) to copper ($Z=29$) the increase in the density is significant.

Ionisation enthalpies

With increasing nuclear charge, which accompanies the filling of the inner d orbitals, there is an increase in magnitude of ionisation enthalpy along each series of the transition elements from left to right. However, many small variations occur. Table 1 gives the values for the first three ionisation enthalpies corresponding to successive removal of electrons from outermost s orbital and d orbital of the first row elements. These values show that the successive enthalpies of these elements do not increase as steeply as in the main group elements. Although the first ionisation enthalpy (removal of electron from s orbital), in general, increase, the increase in the second and third ionisation enthalpies for the successive elements are not of the same magnitude. However, the trend is similar for the second ionisation enthalpies, which for the most part increase smoothly as the atomic number increases; the exceptions are chromium and copper for which these values are notably larger than those of their neighbours.

The irregular trend in the first ionisation enthalpy of the 3d metals, though of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of 4s and 3d orbitals. There is thus a reorganization energy accompanying ionisation with some gain in exchange energy as the number of electrons increases. In general, there is an expected increasing trend in the values as the effective nuclear charge

increases with the value of Cr being lower because of the absence of any change in the d configuration and the value of Zn being relatively high because of ionisation from the filled 4s 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 ionisation energies is required in addition to the enthalpy of atomization for each element. The dominant term is the second ionisation enthalpy which shows unusually high values for Cr and Cu where the d^5 and d^{10} configurations of the M^+ ions are disrupted, with considerable loss of exchange energy. The value for Zn is correspondingly low as the ionisation leads to the production of the stable d^{10} configuration. The trend in the third ionisation enthalpies is not complicated by the 4s 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 ionisation 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 difficulty in obtaining oxidation state greater than two for these elements.

Although ionisation enthalpies give some guidance concerning the relative stabilities of oxidation states, this problem is complicated by differing solvation (hydration) energies of different ions and, therefore not easily amenable for broad generalization .

Oxidation states

The oxidation states (or number) exhibited by the transition elements are shown in Table 2. The most common and important ones are shown in bold type. It is obvious that the transition metals exhibit a great variety of oxidation states. The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7. Ruthenium and Osmium commonly form compounds in +8 oxidation state, which is among the highest for isolable compounds. The lesser number of oxidation states at the extreme ends stems from either too few electrons to lose or share (Sc, Ti) or too many d electrons (hence fewer orbitals available for sharing electrons with others) for higher valence (Cu, Zn.). Thus, early in the series scandium(II) is virtually unknown and titanium(IV) is more stable than Ti(III) or Ti(II). At the other end, the only oxidation state of zinc is +2 (no d electrons are involved). The maximum oxidation states of reasonable stability correspond to the sum of the s and d electrons upto manganese (TiO_2 , VO_2^+ , CrO_4^{2-} , MnO_4^-) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are $Fe^{II,III}$, $Co^{II,III}$, Ni^{II} , $Cu^{I,II}$, Zn^{II} . It is mainly because the latter transition metals require more energy to remove the electrons.

Table-2 Oxidation states of the first row transition metals (the most common ones are in bold types)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
		+0 d^5	+0 d^6	+0 d^7	+0 d^8	+0 d^9	+0 d^{10}		
		+1 d^4	+1 d^5	+1 d^6	+1 d^7	+1 d^8	+1 d^9	+1 d^{10}	
	+2 d^2	+2 d^3	+2 d^4	+2 d^5	+2 d^6	+2 d^7	+2 d^8	+2 d^9	+2 d^{10}
+3 d^0	+3 d^1	+3 d^2	+3 d^3	+3 d^4	+3 d^5	+3 d^6	+3 d^7	+3 d^8	
	+4 d^0	+4 d^1	+4 d^2	+4 d^3	+4 d^4	+4 d^5	+4 d^6		
		+5 d^0	+5 d^1	+5 d^2		+5 d^4			
			+6 d^0	+6 d^1	+6 d^2				
				+7 d^0					

The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of d orbitals in such a way that their oxidation states differ from each other by unity, e.g. V^{II}, V^{III}, V^{IV}, V^V. This is in contrast with the variability of oxidation states of non-transition elements where oxidation states normally differ by units of two.

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.

The tendency of any element to form compounds in different oxidation states can be illustrated by considering its binary compounds. The transition elements form binary compounds with a wide variety of non-metals, and the stoichiometries of these compounds will depend upon the thermodynamics and electrostatics of compound forming process. Binary oxides, fluorides and chlorides of the transition elements reveal the oxidation states available to them (Table 3).

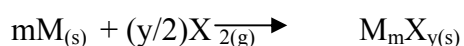
Table-3 Binary transition metal oxides, fluorides and chlorides

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Oxides									Cu ₂ O	
		TiO	VO		MnO	FeO	CoO	NiO	CuO	ZnO
	Sc ₂ O ₃	Ti ₂ O ₃	V ₂ O ₃	Cr ₂ O ₃	Mn ₂ O ₃	Fe ₂ O ₃	Co ₂ O ₃			
		TiO ₂	VO ₂	CrO ₂	MnO ₂			NiO ₂		
			V ₂ O ₅	CrO ₃						
					Mn ₂ O ₇					
Fluorides			VF ₂	CrF ₂	MnF ₂	FeF ₂	CoF ₂	NiF ₂	CuF ₂	ZnF ₂
	ScF ₃	TiF ₃	VF ₃	CrF ₃	MnF ₃	FeF ₃	CoF ₃			
		TiF ₄	VF ₄	CrF ₄	MnF ₄					
			VF ₅	CrF ₅						
				CrF ₆						
Chlorides									CuCl	
		TiCl ₂	VCl ₂	CrCl ₂	MnCl ₂	FeCl ₂	CoCl ₂	NiCl ₂	CuCl ₂	ZnCl ₂
	ScCl ₃	TiCl ₃	VCl ₃	CrCl ₃	MnCl ₃	FeCl ₃				
		TiCl ₄	VCl ₄	CrCl ₄						

Compound formation in maximum oxidation states

The highest oxidation state of an element is exhibited in its compounds with the two most electronegative and powerful oxidising elements – fluorine and oxygen. The less electronegative element, chlorine is expected to show slightly different range of oxidation states. The stoichiometric oxides, fluorides and chlorides of the d-block elements are summarized in Table 3 :

It reveals that the transition elements towards the left can attain maximum possible oxidation states, while at the right of the series oxidation state +2 becomes dominant. These trends in chemical behaviour are determined by the overall thermodynamics of the compound formation. For the reaction of a metal M, with a non-metallic elements, X₂, leading to the formation of M_mX_{y(s)} can be given by



Considering Born – Haber thermodynamic cycle, the various steps involved in the formation of the compound $M_mX_y(s)$ can be expressed as :

$$\Delta_f H^\theta_{(M_mX_y)} = m\Delta_a H^\theta_{(M)} + \Sigma^z \Delta_i H^\theta_{(M)} + y/2 \Delta_{diss} H^\theta_{(X)} + \Sigma^{(z/y)} \Delta_{eg} H^\theta_{(X)} + \Delta_u H^\theta_{(M_mX_y)}$$

where, $\Delta_f H^\theta_{(M_mX_y)}$ = enthalpy of formation for M_mX_y

$\Delta_a H^\theta_{(M)}$ = atomization enthalpy of $M_{(s)}$

$\Delta_i H^\theta_{(M)}$ = ionisation enthalpy of M to obtain $M^{z+}(g)$

$\Delta_{diss} H^\theta_{(X)}$ = bond dissociation enthalpy of $(X-X)$

$\Delta_{eg} H^\theta_{(X)}$ = electron gain enthalpy of $X_{(g)}$

$\Delta_u H^\theta_{(M_mX_y)}$ = lattice enthalpy of M_mX_y

Consider the formation of titanium chlorides in +2 and +4 oxidation states. Substituting the different parameter values for the formation of $TiCl_2(s)$, we get

$$\Delta_f H^\theta_{(TiCl_2)} = 473 + 1968 + 244 + (-698) + (-2501) = -514 \text{ kJmol}^{-1}$$

Similarly, for the formation of $TiCl_4(l)$, we get

$$\Delta_f H^\theta_{(TiCl_4)} = 473 + 8796 + 488 + (-1396) + (-9431) = -1070 \text{ kJmol}^{-1}$$

It is obvious from the above approximate calculations that the $TiCl_4$ is much more stable than the $TiCl_2$.

Such thermodynamic considerations are useful in explaining (i) the relative stabilities of compounds formed by an elements in its various oxidation states, and (ii) the formation of compounds in the highest oxidation state of a metal with fluorine and oxygen only and not with iodine.

Stability of compounds in aqueous solution

The relative stability of metal ion in its various oxidation states and those of different metal ions in the same oxidation state can be found by consideration of standard electrode potential values. The E^θ values for M^{2+}/M and M^{3+}/M^{2+} for first row transition metals are given in Table1. An examination of the E^θ values shows that Mn^{3+} and Co^{3+} ions are the strong oxidizing agents in aqueous solutions whereas Ti^{2+} , V^{2+} and Cr^{2+} are strong reducing agents.

The compound formed in a higher oxidation state of a metal is more covalent and acidic than that formed in its lower oxidation state. As a consequence, the higher oxidation state compound is more easily hydrolysed with water than that of lower oxidation state one. For example, $TiCl_4$ and VCl_4 are easily hydrolysed with water to give $TiOCl_2$ and $VOCl_2$ respectively, whereas $TiCl_3$ and VCl_3 in water form $[Ti(H_2O)_6]^{3+}$ and $[V(H_2O)_6]^{3+}$ ions.

Since the compounds in higher oxidation states are usually bonded covalently to electronegative elements such as O or F, they are often polyatomic ions, e.g. vanadate (VO_3^-), chromate (CrO_4^{2-}) and permanganate (MnO_4^-).

Magnetic properties

Many transition metal compounds are paramagnetic due to the presence of unpaired electrons. Magnetic moment of each such electron is associated with its spin angular momentum and orbital angular momentum. For the compounds of the first transition series, the orbital angular momentum quantum number is effectively quenched and hence is of no significance. For these the magnetic moment is determined by the number of electrons and is calculated by using 'spin-only' formula, i.e.,

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

where n is the number of unpaired electrons and μ_s is the magnetic moment in Bohr magneton (BM). A single 1s electron has a magnetic moment of 1.73 BM ($1 \text{ BM} = 9.2732 \times 10^{-24} \text{ A m}^2$).

Table-4 Calculated and observed magnetic moments (μ_s) of some first row transition metal ions

Ion	Configuration	Unpaired electron	Magnetic moment in BM	
			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	0

The magnetic moment increases with increasing number of unpaired electrons. Thus, the observed magnetic moment value gives a useful information about the number of unpaired electrons present in the species. The magnetic moments calculated from the 'spin-only' formula and those determined experimentally for some first row transition metal ions are given in Table 4.

Coloured ion formation

Many transition metal ions are coloured due to d-d transitions. The energy absorbed in excitation of an electron from a lower energy d orbital to a higher energy d orbital corresponds to the frequency which generally lies in the visible region. The colour observed

corresponds to the complementary colour of the light absorbed. The frequency of light absorbed is determined by the nature of ligand. The colour of some 3d transition metal ion in aqueous solution, where water molecule coordinate with the metal ions, are given in Table 5.

Table-5 Observed colours for some aqua species of the first row transition metal ions in +2 and +3

oxidation states

Element	+2	+3
Sc		$[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$, Colourless
Ti		$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, Violet
V	$[\text{V}(\text{H}_2\text{O})_6]^{2+}$, Violet	$[\text{V}(\text{H}_2\text{O})_6]^{3+}$, Green
Cr	$[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$, Blue	$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, Violet/green
Mn	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, Pink	$[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$, Violet
Fe	$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, pale green	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, Yellow/brown
Co	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, Pink	$[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, Blue
Ni	$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, Green	
Cu	$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, Blue	
Zn	$[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$, Colourless	

Alloy formation

The transition metals readily form alloys with each other because of similar radii. The alloys so formed are hard and have often high melting points. The best known are ferrous alloys; vanadium, chromium, molybdenum, tungsten and manganese are used for the production of variety of steels and stainless steel. Industrially important alloys of transition metals with non-transition metals are brass (copper-zinc), bronze (copper-tin) etc.

Interstitial compound formation

Many transition metals form interstitial compounds particularly with small non-metal atoms such as hydrogen, boron, carbon and nitrogen. These small atoms enter into the voids sites between the packed atoms of the crystalline metal. These interstitial compounds are non-stoichiometric, e.g. $\text{TiH}_{1.7}$, $\text{ZrH}_{1.9}$, $\text{VH}_{0.56}$, TiC , Fe_3C , $\text{Fe}_{0.94}\text{O}$ etc. They are hard and have higher melting points than those of pure metals. They retain metallic conductivity and are chemically inert.

Catalytic properties

The transition metals and their compounds show catalytic activity in a variety of chemical processes. This activity is ascribed to their ability to exhibit multiple oxidation states and to form complexes, alloys and interstitial compounds. One of the most popular example these

days is the heterogeneous catalyst used in car exhausts. This contains a Pt/Rh alloy supported on a ceramic matrix and converts the mixture of O₂, CO, NO_x and hydrocarbons in the exhaust gases to H₂O, CO₂, and N₂. Some other examples are the use of V₂O₅ in Contact process for manufacture of sulphuric acid, finely divided iron in Haber's process for manufacture of NH₃ and nickel in hydrogenation of oils.

An important example of homogeneous catalysis is provided by the Monsanto process in which the rhodium compound [Rh(CO)₂I₂]⁻ catalyses a reaction, resulting in the addition of CO to CH₃OH to form ethanoic acid (CH₃COOH).

Coordination Compounds

The transition metals and their ions have much higher tendency to form coordination compounds as compared to the s- and p- block elements. It is because of their relatively smaller sizes, higher ionic charges and the availability of d orbitals for bond formation. Coordination compounds, unlike normal compounds, retain their identity even when dissolved in water or any other suitable solvent. The properties of these compounds are totally different from those of their constituents.

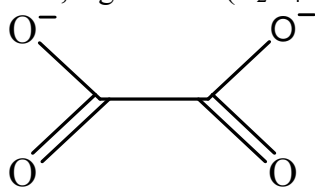
Alfred Werner can be considered to be the pioneer in the field of coordination chemistry and he received Nobel Prize in 1913 in recognition of his efforts. He showed that neutral molecules were bound directly to the metal so that complex salt such as CoCl₃.6NH₃ is correctly formulated as [Co(NH₃)₆]³⁺(Cl)₃. G.N. Lewis and N.V. Sidgwick proposed that a chemical bond required the sharing of an electron pair. This led to the idea that a neutral molecule with an electron pair can donate these electrons to a metal ion or other electron acceptor.

Thus, in a coordination compound, the metal species acts as electron acceptor (**Lewis acid**) and neutral molecule with lone pair of electrons or anion as electron donor (**Lewis bases**). A metal atom or ion when bonded directly to a fixed number of anions or molecules constitutes a **coordination entity**. For example, [Pt(NH₃)₂Cl₂] is a coordination entity in which platinum(II) is surrounded by two ammonia molecules and two chloride ions. Other examples are [Fe(CN)₆]⁴⁻, [Co(NH₃)₅Cl]²⁺, [Ni(CO)₄] etc. In a coordination entity, the atom/ion to which a fixed number of ions/ groups are bound in a definite geometrical arrangement around it, is called the **central atom or ion**. For example, the central atom in [Ni(NH₃)₆]²⁺ is Ni(II), in [Mo(CN)₈]³⁻, Mo(V), and in [Co(PR₃)₃Cl], Co(I). The charged ions or neutral molecules bound to the central atom in the coordination entity are called **ligands**. For example, PR₃ and Cl⁻ are ligands in [CoCl(PR₃)₃]. The number of ligand donor atoms directly bonded to the central atom is defined as the **coordination number**. For example, in the complex species [Mo(CN)₈]³⁻ and [CoCl(PR₃)₃], the coordination number of Mo and Co are 8 and 4, respectively. The central atom and the ligands bonded to it are enclosed in square bracket and is collectively termed as the **coordination sphere**. For example in the complex [Ni(NH₃)₆]Cl₂, the coordination sphere is [Ni(NH₃)₆]²⁺. The spatial arrangement of the ligands around the central atom is termed as **coordination polyhedron**. The most common coordination polyhedra are octahedral, tetrahedral and square planar.

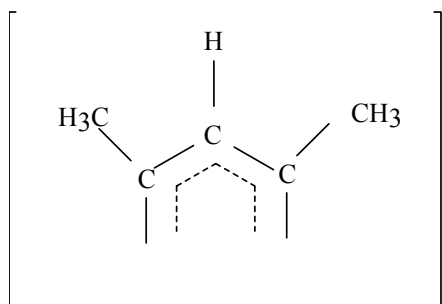
Types of ligands

The ligands can be classified structurally as follows:

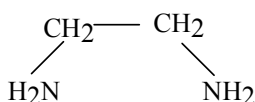
1. Unidentate ligands-These are ligands which bonds to the central metal atom through a single atom, e.g. ammonia (NH₃) which bonds to the central metal atom through nitrogen atom. Other examples are Cl⁻, CN⁻, H₂O etc.
2. Bidentate ligands- These are ligands which link to the central metal atom through two atoms, e.g. oxalato(C₂O₄²⁻), acetylacetonato (acac⁻), ethane -1, 2 diamine (en) etc.



(oxalato)



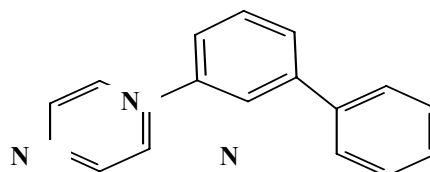
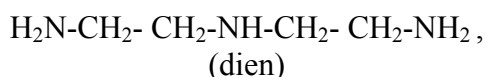
(acetylacetonato)



(en)

3. Polydentate ligands- These include all types of ligands with denticity higher than two. The various types of ligands included are :

- i) tridentate (denticity of 3), e.g. diethylenetriamine (dien), terpyridine (terpy) etc.



(terpy)

Here coordination to the metal atom can take place through the three nitrogen atoms.

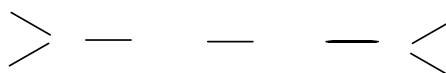
- ii) tetradentate (denticity of 4), e.g. triethylenetetramine (triene),

$$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$$

(triene)

Here coordination to the metal atom can take place through the four nitrogen atoms.

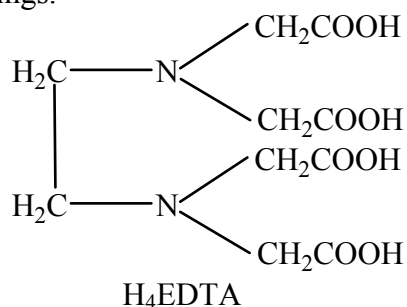
- iii) pentadentate ligand (denticity of 5), e.g. ethylenediaminetetraacetato,



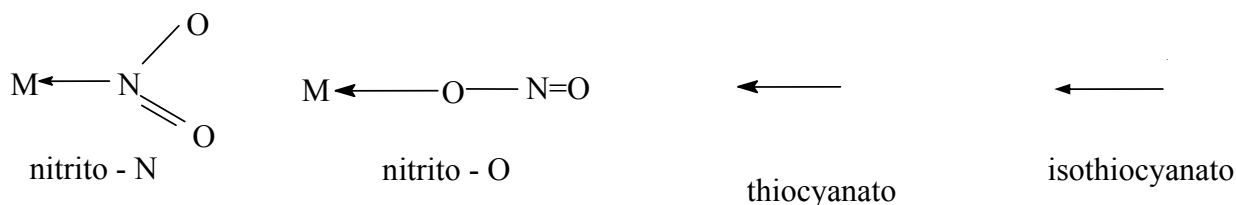
Here coordination to the metal atom can take place through the two nitrogen atoms and three oxygen atoms of the acetate group.

- iv) hexadentate ligand (denticity of 6), e.g. ethylenediaminetetraacetato (EDTA⁴⁻)
 Here coordination to the metal atom can take place through the two nitrogen atoms and four oxygen atoms of the acetate group.

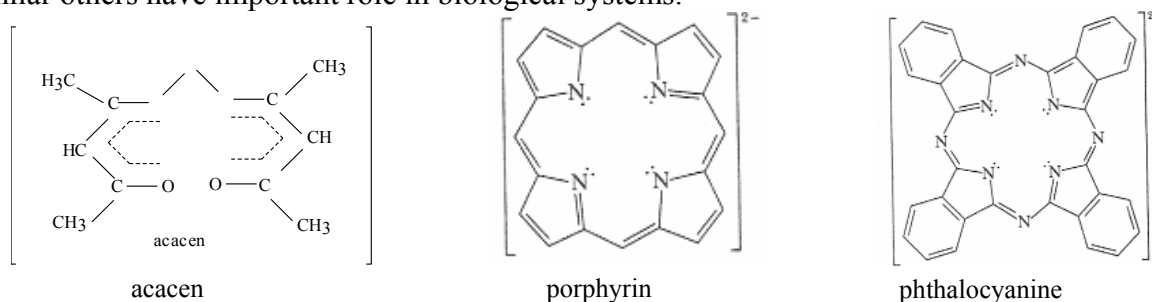
In many bidentate to polydentate ligands, the ligand is bonded to the same central metal atom at two or more places due to which a ring structure is formed. Such a ring structure formed by a bidentate (or polydentate) ligand is known as a chelate. The term chelate, derived from the Greek word **chela** meaning great claw of the lobster or other crustaceans, is suggested for the cliperlike groups which function as two associating units. Chelated complexes are known to have a higher stability as compared to ordinary complexes. Ethylenediaminetetraacetic acid (H_4EDTA) is an important chelating ligand. It binds the metal atom through two nitrogen and four oxygen atoms and hence acts as a hexadentate ligands and forms five rings.



Ligands which ligate to metal ions through two atoms of different elements present in it are called ambidentate ligands. Example of such ligands are NO_2^- and SCN^- ions. NO_2^- ion can coordinate either through nitrogen or through oxygen to a central metal. Similarly, SCN^- ion can coordinate through sulphur or nitrogen atom.



In addition there are macroacyclic and macrocyclic ligands of importance. Macroacyclic ligands derived from β – diketones and alkylamines are commonly known as Schiff bases, e.g. acacen. Macrocyclic ligands, such as porphyrin and its derivatives, phthalocyanine and similar others have important role in biological systems.



Designing of ligands to obtain desired geometry around a metal ion to use the metal complex for specific purpose has been an art.

Homoleptic and heteroleptic complexes

Homoleptic complexes are complexes in which all the ligands, which coordinate to central metal atom are the same, e.g. $\text{Cr}(\text{CO})_6$. In this complex the only ligand coordinating to cobalt is CO. On the other hand heteroleptic complexes are complexes in which two or more different type of ligands coordinate to the central metal atom, e.g. $[\text{Co}(\text{en})_2\text{Cl}_2]^+$. In this complex the ligands coordinating to cobalt are ethylenediamine (en) and chloride (Cl^-).

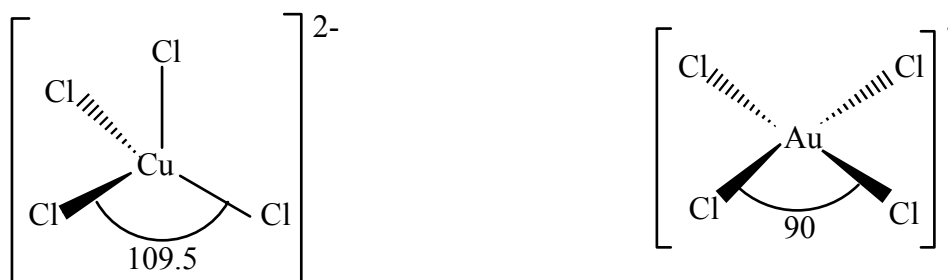
Coordination numbers and structures

The coordination number for a metal ion in a complex is the number of ligands that are directly attached to it. Mostly coordination numbers of 4 and 6 are observed, and 5 is of considerable interest, though coordination numbers can range from 2 to 12 and beyond.

Coordination number 4

There are two shapes available for a metal ion connected to four lone pairs.

- (i) Tetrahedral, e.g. the tetrachlorocopper(II) ion, $[\text{CuCl}_4]^{2-}$, where the internal bond angles are all 109.5° .

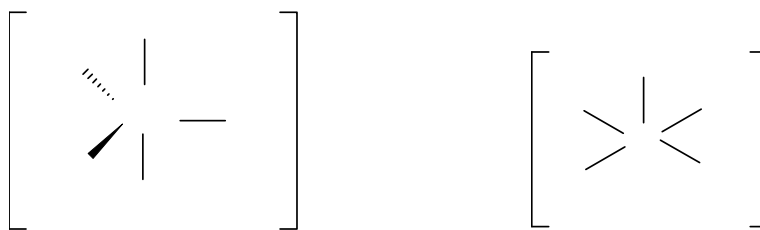


- (ii) Square planar, e.g. the tetrachlorogold(III) ion, $[\text{AuCl}_4]^-$, where the internal bond angles are all 90° .

Coordination number 5

Two shapes are

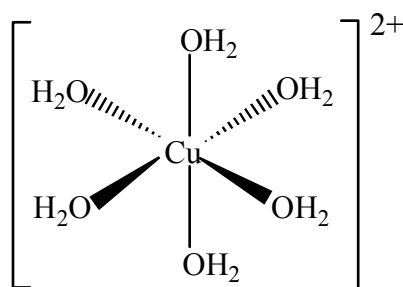
- (i) Trigonal bipyramid, e.g. pentachloro-cuprate(II), $[\text{CuCl}_5]^{3-}$



(ii) Square pyramid, e.g. pentacyano-nickelate(II), $[\text{Ni}(\text{CN})_5]^{3-}$

Coordination number 6

There is only one shape available for a metal ion surrounded by six lone pairs – octahedral, e.g. the hexaaquocopper(II) ion, $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$,

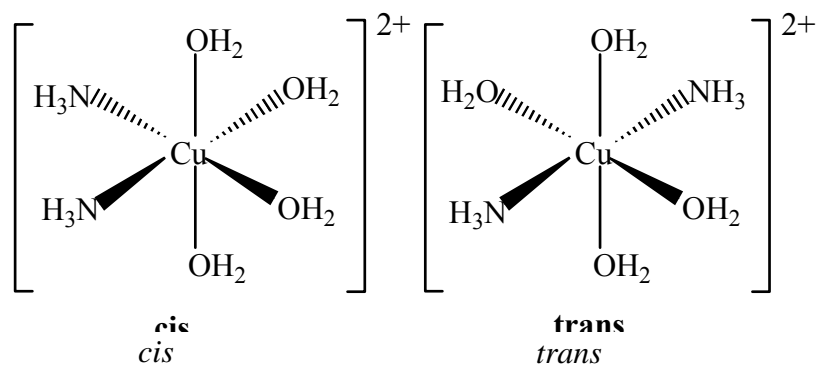


Isomerism in coordination compounds

Compounds having same chemical formula but different structures are called isomers. Many different types of isomerism occur because of complicated formulas of many coordination compounds, the variety of bond types and the number of shapes possible. These are described below.

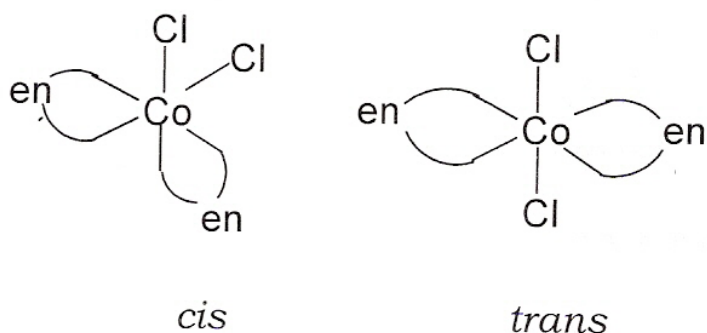
(1) Geometrical isomerism (or stereoisomerism)

Among the octahedral complexes of the types Ma_6 , Ma_5b , Ma_4b_2 , Ma_3b_3 , only the last two show two isomeric forms. In an octahedral (Ma_2b_4) complex (coordination number 6, a and b are unidentate ligands) there are two different positions that ligands can occupy relative to one another. In the two structures below it can be seen that the two ammonia ligands could be 90° or 180° relative to one another,

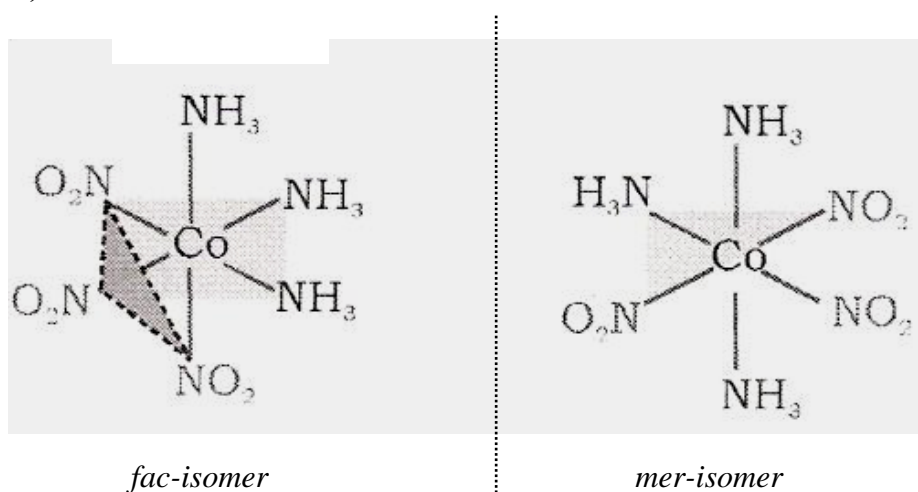


This gives a cis- isomer and a trans- isomer.

This type of isomerism also arises when bidentate ligands such as $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (en) are present in the complex, e.g. $[\text{CoCl}_2(\text{en})_2]$

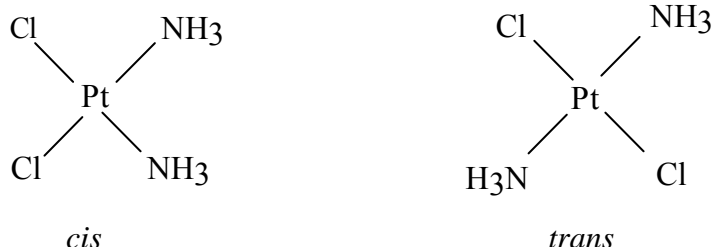


Among the complexes of the type Ma_3b_3 in octahedral geometry, another type of isomerism is observed in which the isomers are known as **facial (fac)** and **meridional (mer)** isomers. If the three ligands 'a', or 'b', all are in the same plane it gives a **meridional (mer)** isomer. On the other hand, if they are adjacent forming a triangular face of the octahedron it gives a **facial (fac)** isomer

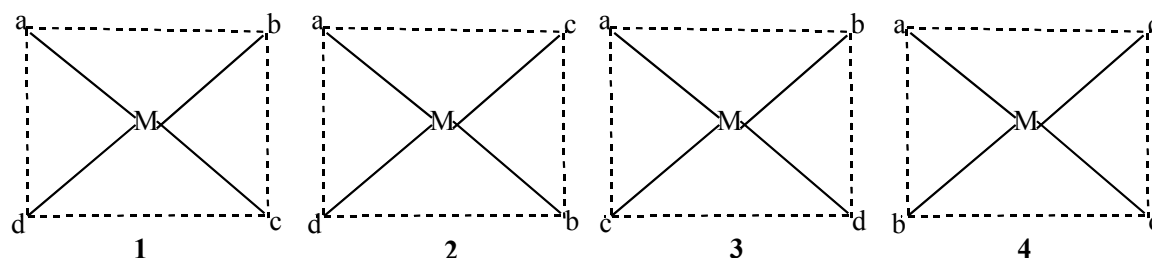


In the case of coordination number 4, out of tetrahedral and square planar only square planar geometry exhibits geometrical isomerism. This type of isomerism is exhibited by complexes of type Ma_2b_2 , Ma_2bc , $Mabcd$.

In square planar Ma_2b_2 , the two ligands 'a' may be arranged adjacent to each other, in a **cis** isomer, or opposite to each other, in a **trans** isomer as depicted below :



The following are the different geometrical isomers of complex of the type $Mabcd$.

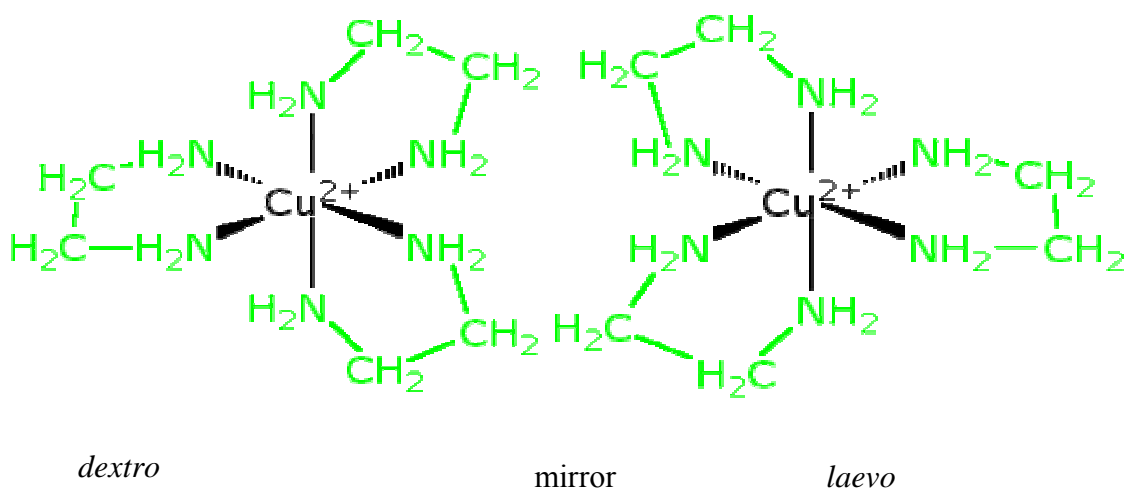


Of these, the isomers 3 and 4 being identical, only three geometrical isomers for this type of complexes exist. Similarly, geometrical isomers for complexes of the type Ma_2bc are possible.

Geometrical isomerism is not observed for lower coordination number complexes.

(2) Optical isomerism

With certain ligands an octahedral complex ion can exhibit optical isomerism. This has nothing to do with the idea of a central carbon atom surrounded by four different groups, as in organic chemistry. However, it does have to do with the idea of two molecules that are not superimposable onto each other. They are also known as *enantiomers*. Shown below are two different complex ions formed when 1,2-diaminoethane is used as the ligand with copper(II) ions.



The left hand molecule cannot be rotated so that it matches exactly the right hand molecule, and therefore the complex exhibits stereoisomerism. The two forms are called **dextro**(*d*) or **laevo** (*l*) depending upon the direction they rotate the plane of polarized light in a polarimeter (*d* rotates to the right, and *l* to the left).

3. Ionisation isomerism

This type of isomerism arise due to difference in the position of groups being inside or out the coordination sphere of the complex, e.g. $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$ (complex 1). and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$ (complex 2). There is interexchange of Br and SO_4 in the isomers and since the two isomers on ionisation give different ions these are called ionisation isomers. Complex 1 on ionisation will give rise to $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ and SO_4^{2-} ions while complex 2 on ionisation will give rise to $[\text{Co}(\text{NH}_3)_5\text{SO}_4]^+$ and Br^- ions. Another pair of complex exhibiting this type of isomerism is $[\text{Co}(\text{NH}_3)_5\text{Cl}_2]\text{NO}_2$ and $[\text{Co}(\text{NH}_3)_5(\text{Cl})(\text{NO}_2)]\text{Cl}$.

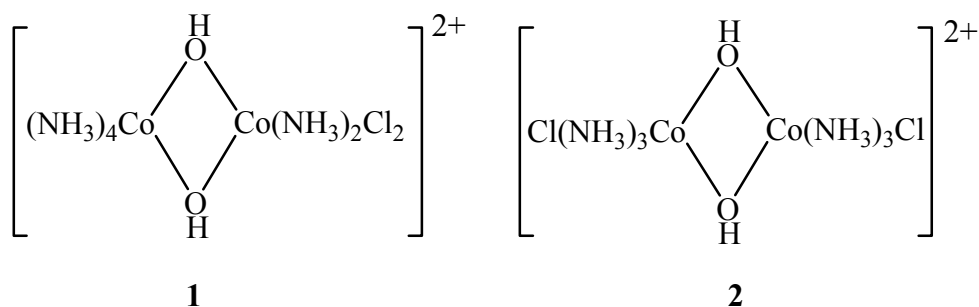
4. Solvate isomerism

This type of isomerism is similar to ionisation isomerism. This isomerism is known as 'hydrate' isomerism when arises due to replacement of a coordinated group by water of hydration. An example to illustrate this type of isomerism is: $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$, $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$. These are three isomers which differ largely from one another in their physical and chemical properties. While the coordination number of chromium is 6 in all the three cases, the isomers contain different number of coordinated water molecules.

5. Coordination isomerism

This type of isomerism is observed in case of compounds in which both, anionic and cationic parts of the coordination compound are complex. An example is provided by $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$, in which the NH_3 are bound to Co^{3+} and the CN^- to Cr^{3+} and $[\text{Co}(\text{CN})_6][\text{Cr}(\text{NH}_3)_6]$ where the NH_3 are bound to Cr^{3+} and the CN^- to Co^{3+} , both the anionic and cationic parts are complex ions.

A special case of coordination isomerism is coordination position isomerism which involves different placements of ligands in a bridged complex as shown below.



Here ammonia and chloro ligands are differently placed relative to the two cobalt atoms.

6. Linkage isomerism

Linkage isomerism arises in coordination compounds containing ambidentate ligand. For example, in NO_2^- the nitrogen as well as oxygen atom can donate their lone pair. An example to illustrate this type of isomerism is $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]$ and $[\text{Co}(\text{NH}_3)_5(\text{ONO})]$. In the first complex coordination occurs through nitrogen of the NO_2 group while in the second complex coordination occurs through oxygen.

Nomenclature of Coordination Compounds

The nomenclature system as recommended by the IUPAC (International Union of Pure and Applied Chemistry) is outlined in this section. The names of co-ordination compounds are derived by following the principles of additive nomenclature. The groups that surround the central atom or structure must be identified in the name.

1. Order of naming ions

In ionic complexes, the cation is named first and then the anion irrespective whether the cation or the anion is the complex species (which is enclosed in square brackets). No spaces are left between parts of the name that refer to the same coordination entity. For example:

$\text{K}_4[\text{Fe}(\text{CN})_6]$ is named as potassium hexacyanoferrate(II)

$[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ is named as hexaamminenickel(II) chloride

$[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{Cl}$ is named as pentaamminecarbonatocobalt(III) chloride

Non-ionic complexes are given a one word name, e.g. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$ is named as diammine tetrachloroplatinum(IV).

2. Names of ligands

In the complex ion, the name of the ligand(s) precedes that of the central metal atom. (This procedure is reversed from writing formulas).

Neutral ligands are named as the molecules. However, water molecule is named as 'aqua', ammonia as 'ammine', carbon monoxide as 'carbonyl' and nitric oxide as 'nitrosyl'. Negative ligands generally end in **o** as illustrated below with a few examples :

Cl^- - chloro, CN^- - cyano, H^- - hydrido

(Note that the 2004 draft on naming coordination compounds has recommended that the anionic ligands ending in 'ide', 'ite' or 'ate', the final 'e' is replaced by 'ido', 'ito' and 'ato', respectively; thus, Cl^- - chlorido, CN^- - cyanido, H^- - hydrido, CH_3COO^- - acetato or ethanoato)

3. Order of naming ligands

If more than one ligand is present in the complex species, then the ligands are named in alphabetical order without any separation by hyphens. For example, $[\text{Pt}(\text{NH}_3)_4(\text{Cl})(\text{NO}_2)]\text{SO}_4$ is named as tetramminechloronitroplatinum(IV)sulphate; $[\text{Cu}(\text{CH}_3\text{NH}_2)_2\text{Cl}_2]$ is named as dichloro-bis(methylamine)copper(II). (This is in accordance with the 1971 rule. Some texts still say that ligands are named in the order: neutral then anionic).

4. Numerical prefixes to indicate number of ligands

Two kinds of numerical prefix are used for indicating the number of each type of ligand within the name of the coordination entity.

- i) If ligands have simple names such as chloro, iodo, nitro etc., their number is indicated by prefixes such as di, tri, tetra, penta etc.
- ii) If the ligands have complex names, their number is given by prefixes such as bis, tris, tetrakis etc. for examples :

$[\text{Co}(\text{CH}_2\text{NH}_2)_2\text{Cl}_2]_2\text{SO}_4$ is named as dichlorobis(ethylenediamine)cobalt(III) sulphate.
 $[\text{Cr}\{(\text{CH}_2\text{NH}_2)_2\}_3]\text{Cl}_3$ is named as *d* or *l* tris(ethylenediamine)chromium(III)

5. Ending of names

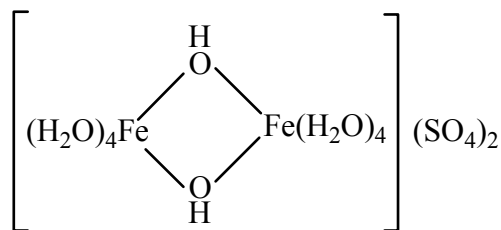
The name of an anionic complex which ends in 'ate', e.g. $\text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3]$ is named as potassium trioxalatoaluminate(III). In case of cationic and neutral complexes, the name of the metal is written without any characteristic ending. For example, $[\text{Fe}(\text{H}_2\text{O})_6]\text{SO}_4$, which contains the cationic complex $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, is named as hexaaquoiron(II)sulphate. Coordination compound $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_5]$ having the anionic complex $[\text{Pt}(\text{NH}_3)\text{Cl}_5]^-$ is named as potassium amminepentachloroplatinate(IV).

6. Oxidation states of the central ion

The oxidation state of the central ion is designated by a roman numeral i.e., I, II, III, IV etc. in parentheses at the end of the name of the central metal atom. For zero oxidation state, the letter 0 is written in parentheses. A number of examples have already been given to illustrate this rule.

7. Bridging groups in bidentate ligands

Ligands which link two central metal atoms are usually separated from the rest of the complex by a hyphen and is/are denoted by the Greek letter μ . This is repeated before the name of each bridging group in the complex. The following example illustrates the rule.



This coordination compound is named as octaaquo- μ -dihydroxodiiron(III) sulphate and written as $[(\text{H}_2\text{O})_4\text{Fe}(\mu_2\text{-OH})_2\text{Fe}(\text{H}_2\text{O})_4] (\text{SO}_4)_2$.

8. Abbreviations for complicated molecules

While writing the structure of complex for complicated molecules, generally abbreviations are used. For example, en for ethylenediamine, py for pyridine.

Stability of complexes

The formation of complexes and their relative stabilities in a aqueous solution is a matter of great importance in inorganic and analytical chemistry as well as in biochemistry. Many methods in chemical analysis and analytical separation are based on the formation of metal complexes in solution. Designing of drugs for specific purposes is also based on the relative stabilities of the metal complexes. Thus this aspect of coordination chemistry has a variety of applications.

When discussing the concept of stability of coordination compounds it is necessary to distinguish between thermodynamic and kinetic stability. Here we concentrate on **thermodynamic stability** and look at the changes in the Gibbs energy, enthalpy and entropy during the reaction.

A metal ion in solution does not exist in isolation, but in combination with ligands (such as solvent molecules or simple ions) or chelating groups, giving rise to complex ions or coordination compounds. Complexes may be non-ionic (neutral) or cationic or anionic, depending on the charges carried by the central metal ion and the coordinated groups.

Stability of a complex in solution refers to the degree of association between the two species involved in a state of equilibrium. Qualitatively, the greater the association, the greater is the stability of the compound. The magnitude of the **(stability or formation) equilibrium constant** for the association, quantitatively expresses the stability. Thus, ignoring the solvent molecules associated with metal ion and the charge on the metal ion, in a reaction of the type:



the larger the stability constant, the higher the proportion of ML_4 that exists in the solution. The solvent molecules initially associated with metal ion will compete with the ligand molecules, L, and be successively replaced by them. The four constants can be expressed as follows:

1. $\text{M} + \text{L} \rightleftharpoons \text{ML} \quad K_1 = [\text{ML}] / [\text{M}] [\text{L}]$
2. $\text{ML} + \text{L} \rightleftharpoons \text{ML}_2 \quad K_2 = [\text{ML}_2] / [\text{ML}] [\text{L}]$
3. $\text{ML}_2 + \text{L} \rightleftharpoons \text{ML}_3 \quad K_3 = [\text{ML}_3] / [\text{ML}_2] [\text{L}]$

4. $ML_3 + L \rightleftharpoons ML_4$ $K_4 = [ML_4] / [ML_3] [L]$
 where K_1, K_2 etc. are referred to as "**stepwise stability constants**".
 Alternatively, we can write the "**overall stability constant**" thus:



The stepwise and overall stability constants are therefore related as follows:

$$\beta_4 = K_1 \cdot K_2 \cdot K_3 \cdot K_4$$

or more generally,

$$\beta_n = K_1 \cdot K_2 \cdot K_3 \cdot K_4 \dots K_n$$

Consider the following steps involved in the formation of the cuprammonium ion :



etc. where K_1, K_2 are the stepwise stability constants.

Also:

$$\beta_4 = [Cu(NH_3)_4^{2+}] / [Cu^{2+}] [NH_3]^4$$

The addition of the four ammine groups to copper shows a pattern found for most formation constants, in that the successive stability constants decrease. In this case, the four constants are:

$$\log K_1 = 4.0, \log K_2 = 3.2, \log K_3 = 2.7, \log K_4 = 2.0 \text{ or } \log \beta_4 = 11.9$$

The **reciprocal** of the formation constant is called the **instability constant** or the **dissociation constant** of coordination complexes.

The metal-binding process is usually represented by a series of stepwise equilibria which lead to stability constants that may vary numerically from hundreds to enormous values such as 10^{35} and more. For this reason, they are commonly reported as logarithms. It is additionally useful to use logarithms, since $\log(K)$ is directly proportional to the Gibbs energy of the reaction.

$$\Delta G^\theta = -RT \ln \beta \text{ or } -2.303 RT \log_{10} \beta$$

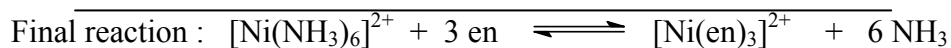
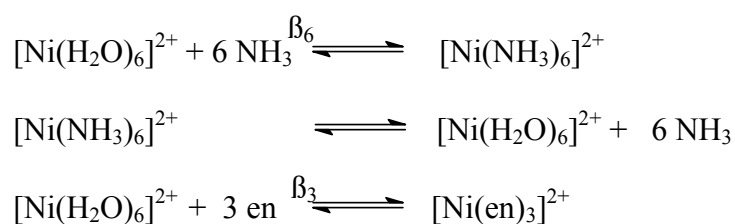
$$\Delta G^\theta = \Delta H^\theta - T \Delta S^\theta$$

The chelate effect

The chelate effect can be seen by comparing the reaction of a chelating ligand and a metal ion with the corresponding reaction involving comparable monodentate ligands. For example, comparison of the binding of 2,2'-bipyridine with pyridine or 1,2-diaminoethane (ethylenediamine=en) with ammonia.

It has been known for many years that keeping the coordination number of the metal ion same, the complex resulting from coordination with the chelating ligand is **much more thermodynamically stable** as compared to that formed with monodentate ligand. This can be seen by looking at the values for adding two monodentate ligands compared with adding one didentate ligands, or adding four monodentates compared to two didentates, or adding six monodentates compared to three didentates.

The complex formation of Ni^{2+} with ammonia or 1,2-diaminoethane, can be expressed by the following equations :



The overall stability constant value for the Ni(II) complex with three chelate rings is about 10^{10} more than that formed with six monodentate ligands. In order to find various factors responsible for this observation, let us examine the contributions of enthalpy and entropy in the process.

Table-6 Thermodynamic data on reaction of ammonia and 1,2-diaminoethane (en) with Ni^{2+}

Number of ligands	log β	ΔG° (kJmol ⁻¹)
1 NH ₃	2.8	-16
2 NH ₃ (1 en)	5.0 (7.51)	-28.5 (-42.8)
3 NH ₃	6.6	-37.7
4 NH ₃ (2 en)	7.87 (13.86)	-44.9 (-79.1)
5 NH ₃	8.6	-49.1
6 NH ₃ (3 en)	8.61 (18.28)	-49.2 (-104.4)

Using the equilibrium constant for the final reaction (Table 6) where the three didentate ligands replace the six monodentate ligands, we find that at a temperature of 298 K :

$$\begin{aligned}
 \Delta G^\circ &= -2.303 RT \log_{10} (K) \\
 &= -2.303 R T (18.28 - 8.61) \\
 &= -54 \text{ kJ mol}^{-1}
 \end{aligned}$$

Based on measurements made over a range of temperatures, it is possible to break down the ΔG° term into the enthalpy and entropy components. The result is that:

$$\begin{aligned}
 \Delta H^\circ &= -29 \text{ kJ mol}^{-1} \\
 -T\Delta S^\circ &= -25 \text{ kJ mol}^{-1}, \text{ and at } 298\text{K} \\
 \Delta S^\circ &= +88 \text{ J K}^{-1} \text{ mol}^{-1}
 \end{aligned}$$

Thus, the breakdown of the ΔG into ΔH and $T\Delta S$ shows that the two terms are nearly equal. The entropy term found is still much larger than for reactions involving a non-chelating ligand substitution at a metal ion.

In order to explain this enhanced contribution from entropy, one explanation is to count the number of species on the left and right hand side of the equation above. It will be seen that on the left-hand-side there are 4 species, whereas on the right-hand-side there are 7 species.

Thus a net gain of 3 species occurs as the reaction proceeds. This can account for the increase in entropy since it represents an increase in the disorder of the system.

An alternative view could be based on our understanding as to how the reactions might proceed. To form a complex with 6 monodentate ligands requires 6 separate favourable collisions between the metal ion and the ligand molecules. On the contrary, the tris-bidentate metal complex requires an initial collision for the first ligand to attach by one arm, the other arm is always going to be nearby and only requires a rotation of the other end to enable the ligand to form the chelate ring. Thus in the process of dissociation, when a monodentate group is displaced, it is lost into the bulk of the solution. On the other hand, if one end of a bidentate group is displaced the other arm is still attached and it is only a matter of the arm rotating around and it can be reattached again.

Both sets of conditions favour the formation of the complex with didentate groups rather than monodentate groups.

Consideration of data for a large number of such reactions, with many different metal ions and ligands, show that enthalpy contributions to the chelate effect are sometimes favourable, sometimes unfavourable, but always relatively small. The general conclusion is that the chelate effect is essentially an entropy effect.

Bonding in Transition Metal Complexes

Many approaches have been put forth to explain the nature of bonding in complexes. Important ones are:

1. Valence Bond Approach (VBA)
2. Crystal Field Approach (CFA).
3. Ligand Field Approach (LFA)
4. Molecular Orbital Approach (MOA)

First two theories will be discussed in this chapter.

Valence Bond Approach

This approach of coordination compounds was mainly developed by Linus Pauling. According to this approach, the formation of a complex is considered to be a reaction between a Lewis base (ligand) and a Lewis acid (metal or metal ion) with the formation of a coordinate covalent bond between the ligand and the metal.

The metal atom or ion under the influence of ligands can use $(n-1)d$, ns , np or ns , np , nd orbital for hybridization to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral, square planar and so on (Table 7).

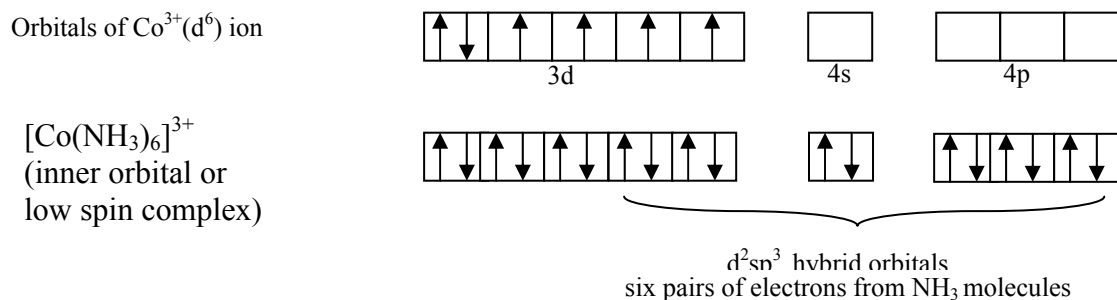
Table-7 Number of orbitals and type of hybridizations

Coordination	Type of hybridization	Distribution of hybrid orbitals in space
4	sp^3	Tetrahedral
4	dsp^2	Square planar

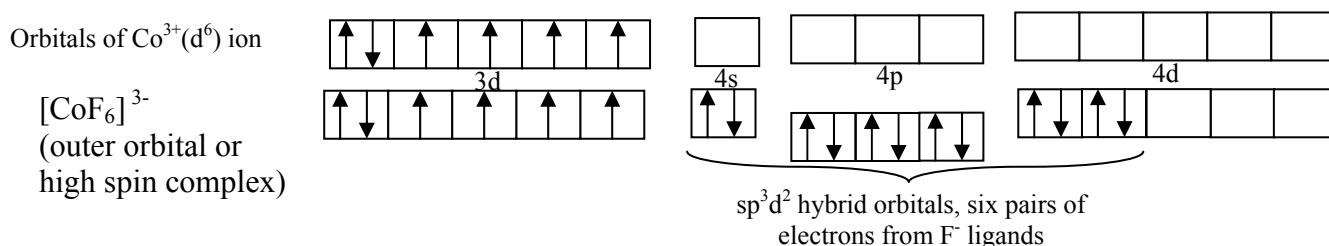
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

These hybridized orbitals are allowed to overlap with those of ligand orbitals that can donate an electron pair for bonding. Let us take some examples to explain this approach.

In the octahedral complex, $[\text{Co}(\text{NH}_3)_6]^{3+}$. The cobalt(III) has the electronic configuration $3d^6$. The complex is diamagnetic. The hybridization scheme can be given as :

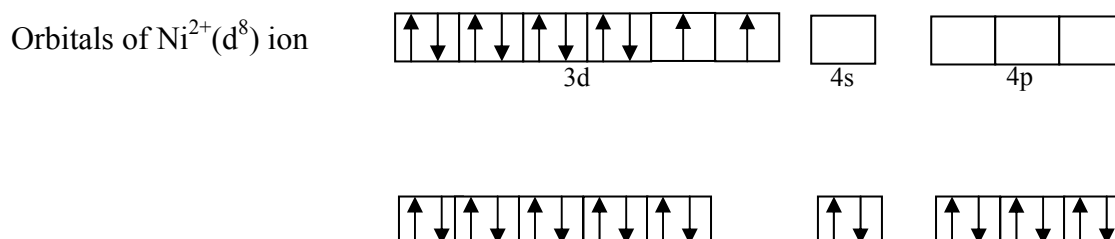


Six pairs of electrons, one from each NH_3 molecule occupy the six hybrid orbitals. Thus, the complex has octahedral geometry and its diamagnetic character is justified because of the absence of unpaired electron. Since in the formation of the complex, the inner d-orbitals (3d) are used in hybridization, the complex, $[\text{Co}(\text{NH}_3)_6]^{3+}$ is called an **inner orbital or low spin or spin paired complex**. Similar octahedral complex, $[\text{CoF}_6]^{3-}$ is, however, paramagnetic. In such a situation Co^{3+} can be considered to use outer d orbitals (4d) in hybridization (sp^3d^2) and leaving four unpaired electrons to satisfy its paramagnetic nature. It is thus called **outer orbital or high spin or spin free complex**.



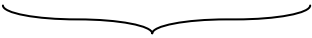
In tetrahedral complexes one s and three p-orbitals are hybridized to form four equivalent orbitals oriented tetrahedrally. This is illustrated below for a paramagnetic $[\text{NiCl}_4]^{2-}$. Here nickel(II) has the electronic configuration $3d^8$.

The hybridization scheme is as follows :



$[\text{NiCl}_4]^{2-}$
(High spin complex)

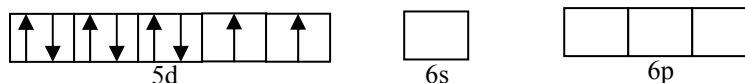
3d


sp³ hybrid orbitals, four pairs of
electrons from Cl⁻ ligands

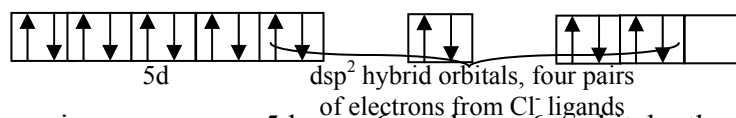
Each Cl⁻ ion donates a pair of electrons. The compound is paramagnetic since it contains two unpaired electrons. The $[\text{Ni}(\text{CO})_4]$ also has a tetrahedral geometry but is diamagnetic since it contains no unpaired electron. The two electrons of 4s orbital under the influence of CO ligand molecules pair up with the two unpaired electrons of the 3d orbitals leaving the 4s orbital vacant. The four pairs of electrons from 4 CO molecules then occupy the sp³ hybrid orbitals.

Complexes of Pd²⁺ and Pt²⁺ having d⁸ configuration are 4-coordinate, square planar and diamagnetic and this arrangement is found in Ni²⁺ (e.g. $[\text{Ni}(\text{CN})_4]^{2-}$) as well. Since the complexes are diamagnetic, the ligands in these complexes must cause pairing up the two unpaired electrons. Consider the example of $[\text{PtCl}_4]^{2-}$, where the hybridization scheme can be given as follows :

Orbitals of Pt²⁺(d⁸) ion



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



Since the 4 donated electron pairs occupy one 5d, one 6s and two 6p orbitals, the complex $[\text{PtCl}_4]^{2-}$ involves dsp² hybridization. As a consequence the geometry of the complex is square planar with platinum at the centre and the chloride ions at the four corners.

The coordination entities like $[\text{PtCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ on one side and $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CO})_4]^0$ on the other side illustrate the useful generalization called, the **magnetic criteria of the bond type**, this is, the geometry of the coordination entity can be predicted if its magnetic behavior is known.

In the above cases, we find that diamagnetic species are square planar while the paramagnetic species are tetrahedral.

It is important to note that the hybrid orbitals are conceived by a combination of atomic orbitals using mathematical manipulation of the respective wave functions involved.

Magnetic properties of coordination compounds

The magnetic moment coordination compounds can be measured by the magnetic susceptibility experiments. The results can be used to obtain information about the structures adopted by metal complexes.

The magnetic moment is expressed in Bohr magnetons (B.M.). A Bohr magneton is given by the expression

$$\text{B.M.} = e h / 4 \pi m c$$

where h is the planck's constant, e is the electronic charge, c is the velocity of light and m is the mass of electron. The magnetic moment of an electron arises from its spin motion and its

orbital motion. The effective (or resultant) magnetic moment of a substance is made up of two components:

- i) contribution due to the orbital motion of the electron, and
- ii) contribution due to spin of the electron.

In case of transition metal ions the unpaired electrons are in the outer valence shell. Due to strong ligand field the orbital motion of the transition metal ions in the complex is quenched and hence only the spin contribution is significant. As a consequence, the magnetic moment is directly related to the number of unpaired electrons, n by the following expression:

$$\mu_{\text{eff}} = (n(n+2))^{1/2}$$

The effective magnetic moments of the various d configurations in the octahedral and tetrahedral cases are given later in the Tables 8 and 9 while discussing their geometry.

The magnetic moment data agree in many cases, especially with coordination compounds containing d^1 , d^2 and d^3 ions. However, with species containing d^4 to d^7 ions there are complications. For example, among Fe(III), d^5 ion complexes, $[\text{Mn}(\text{CN})_6]^{3-}$ has magnetic moment equivalent to two unpaired electrons while $[\text{MnCl}_6]^{3-}$ has a magnetic moment equivalent to four unpaired electrons. $[\text{Fe}(\text{CN})_6]^{3-}$ has magnetic moment of a single unpaired electron while $[\text{FeF}_6]^{3-}$ has a paramagnetic moment indicating five unpaired electrons. Similarly, among Co(III), d^6 ion complexes, $[\text{CoF}_6]^{3-}$ is paramagnetic with four unpaired electrons while $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ is diamagnetic. These apparent anomalies are explained by valence bond theory in terms of formation of **inner orbital** and **outer orbital** coordination entities. $[\text{MnCl}_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$ are inner orbital complexes involving d^2sp^3 hybridization and are paramagnetic and diamagnetic, respectively. On the other hand, $[\text{FeF}_6]^{3-}$ and $[\text{CoF}_6]^{3-}$ are outer orbital complexes involving sp^3d^2 hybridization and are paramagnetic corresponding to four, five and four unpaired electrons, respectively.

Limitations of Valence Bond Approach

While the VB approach, to a larger extent offers explanation of structure and magnetic behaviour of coordination compounds, it has following shortcomings:

- i) It involves a number of assumptions.
- ii) It does not give quantitative interpretation of magnetic data.
- iii) It does not explain the colour exhibited by coordination compounds.
- iv) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
- v) It does not make exact predictions regarding the tetrahedral and square planar structures of 4-coordinate complexes.
- vi) It does not distinguish between weak and strong ligands.

Crystal Field Approach

The crystal field approach (CFA) is an electrostatic model which considers the metal – ligand bond to be ionic arising purely from electrostatic interactions between the metal ion and the ligand. The transition metal (central metal atom) is regarded as a positive ion and is surrounded by negative or neutral ligands which have a lone pair of electrons. If the ligand is neutral like NH_3 , the negative end of the dipole in the molecule is directed towards the metal atom. The electrons on the central metal atom are under repulsive forces from the ligands, hence they occupy the d orbital furthest from the direction of the ligands (Figure 4).

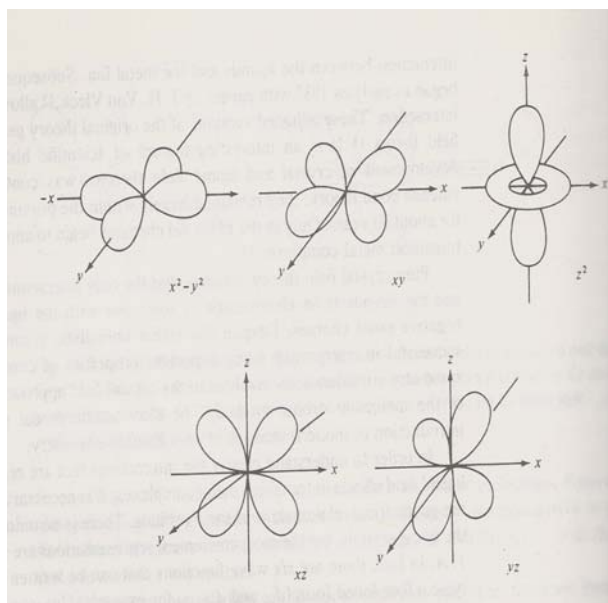


Figure - 4 Representation of the five d orbitals

In crystal field approach the following assumptions are made.

1. Ligands are treated as point charges.
2. There is no interaction between metal orbitals and ligand orbitals.
3. The d orbitals on the metal atom which were of same energy (degenerate) in an isolated atom, have their degeneracy removed by the ligands when a complex is formed. It results in splitting of d orbitals. The pattern of splitting depends on the nature of the crystal fields induced by ligands.

Octahedral complexes

In an octahedral complex, the metal is at the centre of the octahedron and ligands are at the six corners. The x, y, z axes point to the corners of the octahedron. The e_g orbitals ($d_{x^2-y^2}$ and d_{z^2}) are directed along the axes and t_{2g} orbitals (d_{xy} , d_{yz} , d_{xz}) point in between the axes (Figure 4). Therefore the approach of ligands along the x, y, z, -x, -y and -z directions increases the energy of the $d_{x^2-y^2}$ and d_{z^2} orbitals much more than that of d_{xy} , d_{yz} and d_{xz} orbitals. Thus under the influence of an octahedral ligand field the d orbitals split into two groups of different energy (Figure 5). Instead of referring to the energy level of an isolated metal atom, the weighted mean of these two sets of perturbed orbitals is taken as zero. The zero energy level is also known as barycentre. The difference in the energy between the two d levels is given by Δ_o or $10Dq$. The two e_g orbitals are $0.6\Delta_o$ (or $6Dq$) above the average level and three t_{2g} orbitals are $0.4\Delta_o$ (or $4Dq$) below the average.

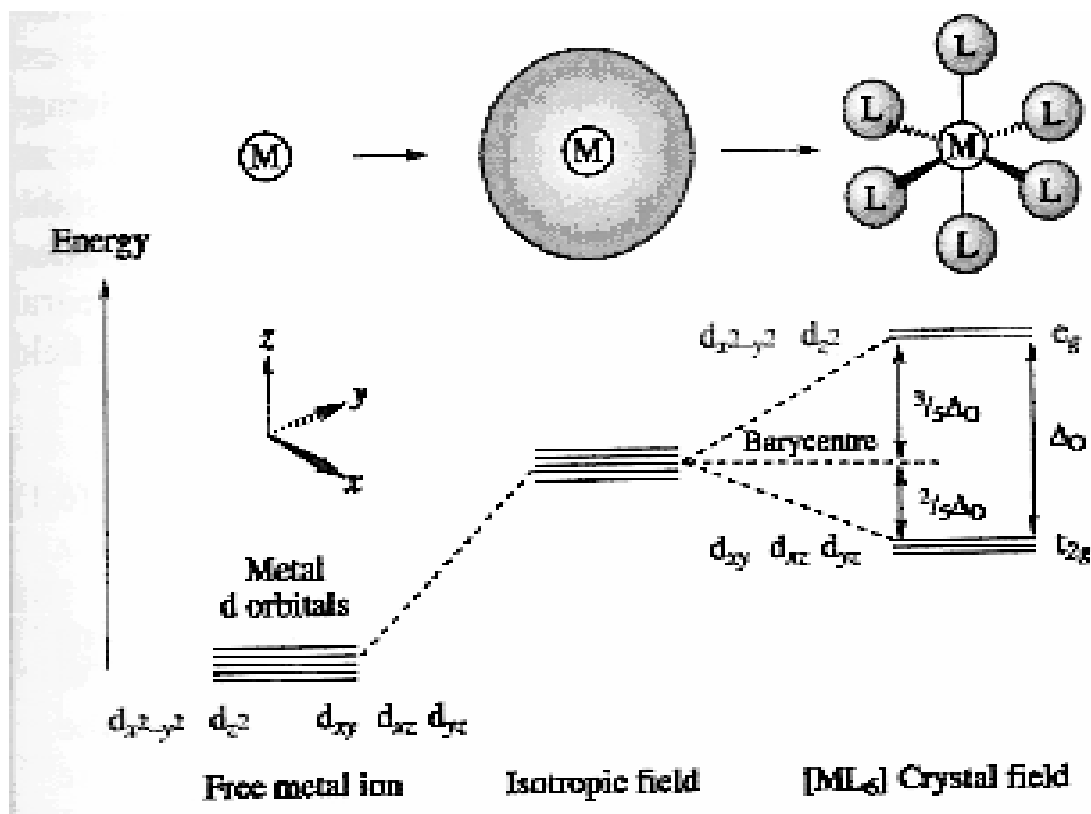


Figure - 5 The effect of an octahedral crystal field on the energies of d orbitals

The magnitude of Δ_0 depends on the following factors.

i) Nature of ligand

Studies have shown that keeping the same central metal atom, on varying the ligands attached to it, the magnitude of Δ_0 is different in each case. Ligands which cause only a small degree of splitting are termed weak field ligands and those which cause a large splitting are called strong field ligands. The common ligands are arranged in order of their strength and the series is called the **spectrochemical series**.

Weak field

$\text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{F}^- < \text{Cl}^- < \text{NO}_3^- < \text{OH}^- < \text{H}_2\text{O} \approx \text{C}_2\text{O}_4^{2-} < \text{EDTA}^{4-} < \text{NH}_3 \approx \text{pyridine} < \text{ethylenediamine} < \text{dipyridyl} < \text{o-phenanthroline} < \text{NO}_2^- < \text{CN}^- < \text{CO}$.

Strong field

ii) Charge on the metal atom

The magnitude of Δ_0 increases as the charge on central metal atom increases and in general M^{3+} complexes have double the value than that of M^{2+} complexes.

iii) Position of the metal in the transition series

The magnitude of Δ_0 increases on descending down the group of transition metals.

Depending upon the d electron configuration of the metal ion, and under specific environment around it, its complex acquires stability.

Crystal field stabilization energy(CFSE)

The crystal field stabilization energy (CFSE) is the energy by which the complex is stabilized relative to the free metal atom where there is no splitting of d orbitals. It can be calculated by:

$$\text{CFSE} = \{(n_{e_g} \times 3/5) - (n_{t_{2g}} \times 2/5)\} \Delta_0$$

where n_{e_g} = number of electrons in e_g orbitals and $n_{t_{2g}}$ = number of electrons in t_{2g} orbitals.

Consider the case of d^{10} ion (Table 8) where under the influence of an octahedral ligand field four electrons will move to higher energy e_g orbitals and six electrons to lower energy t_{2g} orbitals. Thus, the result for d^{10} system (eg. Zn^{2+}) is no change in energy.

$$\text{CFSE} = \{(4 \times 3/5) - (6 \times 2/5)\} \Delta_0 = 0$$

A similar result would be obtained for a d^0 (e.g. Sc^{3+}) and a d^5 (e.g. Mn^{2+} , Fe^{3+}) electron configuration. In other words such ions would not be affected by the field of the ligands. Let us consider the other cases.

Taking for example $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ in which metal ion has d^1 configuration the CFSE is $-0.4\Delta_0$. Similarly for d^2 configuration (as in $[\text{V}(\text{H}_2\text{O})_6]^{3+}$) the CFSE is $-0.8\Delta_0$ and in d^3 (Cr^{3+}) and d^8 (Ni^{2+}) it will be $-1.2\Delta_0$. (Table 8)

Table-8 Electronic configurations in octahedral crystal field and CFSE

d electron configuration	Arrangement in weak field ligand					Arrangement in strong field ligand					Net gain in strong field ligand				
	t _{2g}			e _g	CFSE (Δ _o)	Spin only magnetic moment	t _{2g}			e _g		CFSE (Δ _o)	Spin only magnetic moment		
d ¹	↑					-0.4	1.73	↑					-0.4	1.73	0
d ²	↑	↑				-0.8	2.83	↑	↑				-0.8	2.83	0
d ³	↑	↑	↑			-1.2	3.87	↑	↑	↑			-1.2	3.87	0
d ⁴	↑	↑	↑	↑		-0.6	4.9	↑↓	↑	↑			-1.6+PE	2.83	-1+PE
d ⁵	↑	↑	↑	↑	↑	0	5.92	↑↓	↑↓	↑			-2+2PE	1.73	-2+2PE
d ⁶	↑↓	↑	↑	↑	↑	-0.4	4.9	↑↓	↑↓	↑↓			-2.4+2PE	0	-2+2PE
d ⁷	↑↓	↑↓	↑	↑	↑	-0.8	3.87	↑↓	↑↓	↑↓	↑		-1.8+PE	1.73	-1+PE
d ⁸	↑↓	↑↓	↑	↑	↑	-1.2	2.83	↑↓	↑↓	↑↓	↑	↑	-1.2	2.83	0
d ⁹	↑↓	↑↓	↑↓	↑↓	↑	-0.6	1.73	↑↓	↑↓	↑↓	↑↓	↑	-0.6	1.73	0
d ¹⁰	↑↓	↑↓	↑↓	↑↓	↑↓	0	0	↑↓	↑↓	↑↓	↑↓	↑↓	0	0	0

It can be assumed that the electrons added beyond d³ will occupy e_g orbitals in preference to pairing up in t_{2g} orbitals. This is not unreasonable, since there is a pairing energy (PE) associated with bringing electrons close to form a pair in an orbital. However, if the interaction between the metal ion and the ligands is sufficiently large so that Δ_o>PE, it becomes more energetically favourable for the fourth electron added to occupy a t_{2g} orbital. Ligands which produce this effect are known as **strong-field ligands** and the complexes they form are called **low-spin** complexes. Whereas ligands for which Δ_o<PE are known as **weak-field ligands** and they form **high-spin** complexes. Thus, when calculating the CESE of a strong-field low-spin complex it is necessary to include the pairing energies associated with the additional electron pairs. In such cases CFSE for a low-spin complex (CFSE_L) can be written as :

$$CFSE_L = \{(n_{e_g} \times 3/5) - (n_{t_{2g}} \times 2/5)\} \Delta_0 + n(PE)$$

where, $n(\text{PE})$ = number of additional electron pairs for a low-spin case.

It is important to note that for a given metal ion the pairing energy (PE) is constant. Thus, when the configuration is d^4 , two cases arise: high-spin case and low-spin case.

(i) d^4 high spin case

This case arises when the ligands attached to the metal are weak field ligands. The electronic configuration of d orbitals in this case is $t_{2g}^3 e_g^1$ and the CFSE will be $(3 \times -0.4\Delta_o) + 0.6\Delta_o = -0.6\Delta_o$

(ii) d^4 low spin case

This case arises when the ligands attached to the metal are strong field ligands. The electronic configuration of d orbitals in this case is $t_{2g}^4 e_g^0$ and the CFSE will be $(4 \times -0.4\Delta_o) = -1.6\Delta_o + (\text{PE})$.

This case violates the Hund's rule.

The two cases differ in the number of unpaired electrons. The CFSE in the second case is higher than in the first case.

Similar situation can be observed in complexes of metal ions with d^5 , d^6 and d^7 configurations. High- and low- spin configurations in an octahedral crystal field for d^6 (Fe^{2+}) is shown in Figure 6.

Pairing energy, PE, depends mainly on the electronic distribution of the central metal ions and its value can be obtained from the atomic spectra of the elements. The Δ_o , which depends on metal ion, ligand and the geometry of the complex, is obtained from the electronic spectra of the complex. Consideration of the data related to PE and Δ_o for metal ions of d^4 to d^7 configurations (Table 9) show that when $\Delta_o > P$, low-spin complexes are formed and when $\Delta_o < P$ then high-spin complexes are formed.

Table-9 Crystal field splittings, Δ_o , and mean electron-pairing energies, PE, for some transition metal ions

Configuration	Ion	PE cm^{-1}	Ligand	Δ_o cm^{-1}	Spin State	
					Predicated	Observed
D^4	Cr^{2+}	23,500	6 H_2O	13,900	High	High
	Mn^{3+}	28,000	6 H_2O	21,000	High	High
D^5	Mn^{2+}	25,500	6 H_2O	7,800	High	High
	Fe^{3+}	30,000	6 H_2O	13,700	High	High
D^6	Fe^{2+}	17,600	6 H_2O	10,400	High	High
			6 CN^-	33,000	Low	Low
	Co^{3+}	21,000	6 F^-	13,000	High	High
			6 NH_3	23,000	Low	Low
D^7	Co^{2+}	22,500	6 H_2O	9,300	High	High

The CFSE, electronic configuration and spin only magnetic moment (in Bohr magneton) in octahedral complexes are given in Table 8. The crystal field stabilization energy increases the thermodynamic stability of the complexes.

Tetragonal distortion of octahedral complexes (Jahn-Teller distortion)

The stereochemistry or shape of transition metal complexes is determined by the tendency of electron pairs to occupy positions as far away from each other as possible. If the d electrons are symmetrically arranged with respect to an octahedral field they will repel all the six ligands equally and a regular octahedral geometry is achieved. The various symmetrical electronic arrangements are observed in d^0 (strong and weak field), d^3 (strong and weak field), d^5 (weak field), d^6 (strong field), d^8 (weak field) and d^{10} (strong and weak field). (see Table 8)

In all other cases the electronic arrangements are unsymmetrical. As the t_{2g} orbitals point in between the ligands, the asymmetric filling of these orbitals has little effect on the shape of the complex. However, the e_g orbitals point directly towards the ligands and as a result the asymmetric filling of these orbitals leads to more repulsion of some ligands compared to others. This leads to a significant deviation from octahedral geometry. The reason for this is that in an octahedral environment if e_g orbitals, $d_{x^2-y^2}$ and d_{z^2} are unsymmetrically filled (for example $t_{2g}^3 e_g^1$, $t_{2g}^6 e_g^1$ and $t_{2g}^6 e_g^3$) their degeneracy is removed and the two orbitals become unequal in energy. Out of the two orbitals, the d_{z^2} orbital has its two lobes pointing towards z and $-z$ axes while the $d_{x^2-y^2}$ has four lobes pointing towards x, y, $-x$ and $-y$ axes. In order to minimize the repulsion with the ligands the single e_g electron will occupy the d_{z^2} orbital. Therefore two ligands approaching along the z and $-z$ axes will experience greater repulsion than the four ligands along the other four axes. This situation results in tetragonal distortion or strictly speaking **tetragonal elongation** of octahedral complexes with four short and two long bonds. Examples of this distortion include CrF_2 and MnF_3 where metal ions of d^4 configuration are octahedrally surrounded by six weak field ligands, F^- ions.

Similarly, many $Cu(II)$ complexes (e.g. $[Cu(NO_2)_6]^{4-}$), where Cu^{2+} has $t_{2g}^6 e_g^3$ configuration, show tetragonally distorted octahedral structures. Here also to minimize repulsion with the ligands, two electrons occupy the d_{z^2} orbital and one occupies the $d_{x^2-y^2}$ orbital (Figure 7).

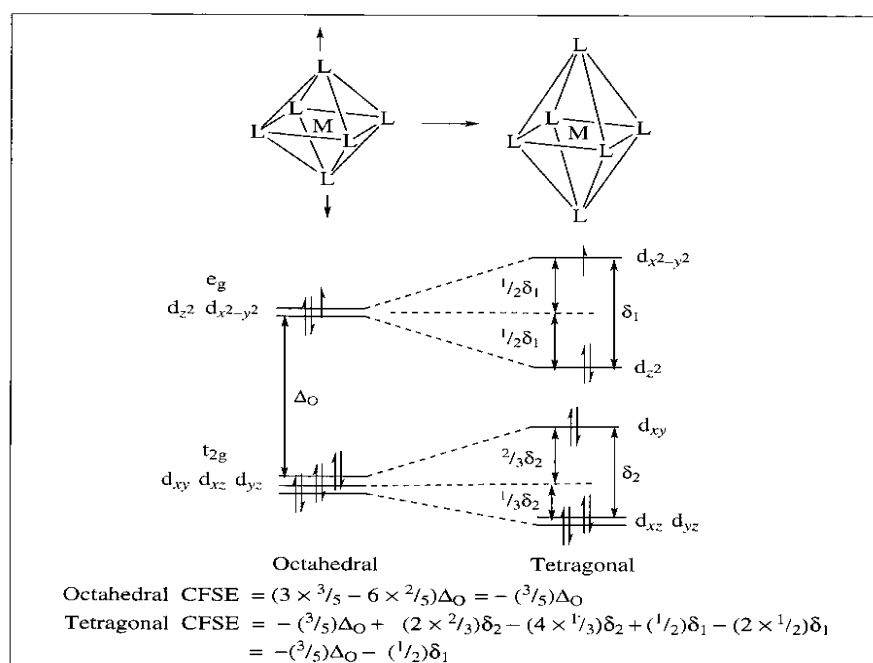


Figure – 7 The effect and the effect of a tetragonal distortion of an octahedral crystal field on the energies of d orbitals: The Jahn-Teller

In case where the $d_{x^2-y^2}$ orbital contains the extra electron, then the elongation will occur along the x and y axes and, therefore, ligands approach more closely along the z axis. Thus there will be four long bonds and two short bonds. This means compression of octahedron along the z-axis and is called tetragonal compression. The tetragonal elongation is much more common.

From this discussion one can say that when there is unequal filling of d_z^2 and $d_{x^2-y^2}$ orbitals, distortion occurs. This is known as **Jahn-Teller distortion**. The theorem states that "any nonlinear molecular system in a degenerate electronic state will be unstable, and will undergo some sort of distortion to lower its symmetry and remove the degeneracy".

Square planar complexes

If the central metal atom in a complex has a d^8 configuration, six electrons will occupy t_{2g} orbitals and the rest two will go to the e_g orbitals irrespective of whether ligand is weak or strong field.

Now taking the case of very strong field ligand, the single electron in $d_{x^2-y^2}$ orbital is repelled by four ligands while electron in d_z^2 orbital is repelled by only two ligands (Figure 8). As a result the energy of $d_{x^2-y^2}$ orbital increases relative to the other orbital. If ligand field is strong enough, the difference in energy between these two orbitals becomes larger than the energy needed to pair up electrons. Therefore pairing up of electrons in d_z^2 orbital takes place leaving the other orbital empty. Now four ligands along x, y, -x and -y axes can approach metal atom without any difficulty but ligands approaching along z and -z axes meet very strong repulsive forces. As a result only four ligands succeed in bonding to the metal and a square planar complex is formed. Square planar complexes are formed by d^8 ions with strong field ligands, e.g. $[\text{Ni}(\text{CN})_4]^{2-}$. The CFSE is large for heavier elements and in highly charged species, and as a consequence all complexes of Pt^{2+} , Pd^{2+} and Au^{3+} are square planar, whether with strong or weak field. Square planar is also common for complexes of the d^9 ion, Cu^{2+} e.g. $[\text{Cu}(\text{py})_4]^{2+}$. For this only one electron has to be placed in the high energy $d_{x^2-y^2}$ orbital. This geometry also arise in d^4 ions in weak field (e.g. mononuclear S-coordinated complex : $[\text{Mn}(\text{S}_2\text{C}_6\text{H}_3\text{Me})_2]^-$)

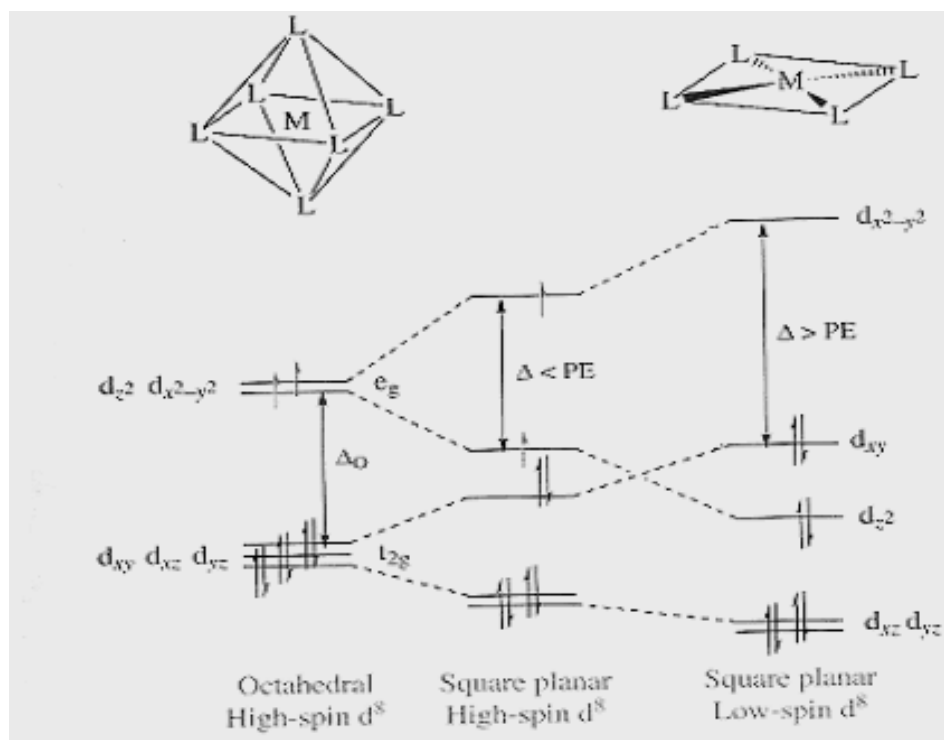


Figure - 8 The effect of a square planar crystal field on the energies of d orbitals.

Tetrahedral complexes

A regular tetrahedron is related to the cube with the metal ion occupying the centre and ligands occupy alternate corners of the cube. The e_g orbitals point along x, y and z axes and t_{2g} orbitals point in between the axes. The three axes point to the centres of the faces of the cube. Therefore the direction of approach of the ligands does not coincide with either of the two set of orbitals. The angle between an e_g orbital, the central metal and the ligand is half of the tetrahedral angle i.e., $54^\circ 44'$. The angle between a t_{2g} orbital, the central metal and the ligand is $35^\circ 16'$. Thus, the t_{2g} orbitals are nearer to the ligands as compared to the e_g orbitals. Although the approach of the ligands raises the energy of all the d orbitals but since the t_{2g} orbitals are nearer to the ligands they are raised more in energy. Therefore the crystal field splitting is opposite to that in case of octahedral complexes. The t_{2g} orbitals in tetrahedral case are raised by $0.4\Delta_t$ above the zero point energy while the other set of orbitals are $0.6\Delta_t$ below the average (Figure 9).

The magnitude of crystal field splitting in tetrahedral complexes (Δ_t) is considerably less than in octahedral complexes. Since there are only four ligands, the ligand field is only $2/3$ times of the octahedral field and since the orbitals do not coincide with the direction of the ligands, the crystal field splitting is further reduced by a factor of $2/3$. Therefore the crystal field splitting in tetrahedral complexes (Δ_t) is approximately $4/9$ of the octahedral field (Δ_o). Unlike the octahedral complexes, where a strong field ligand causes a larger splitting compared to weak field ligand, the tetrahedral Δ_t is always very small and energetically not favourable to pair electrons. Therefore all tetrahedral complexes are high spin complexes.

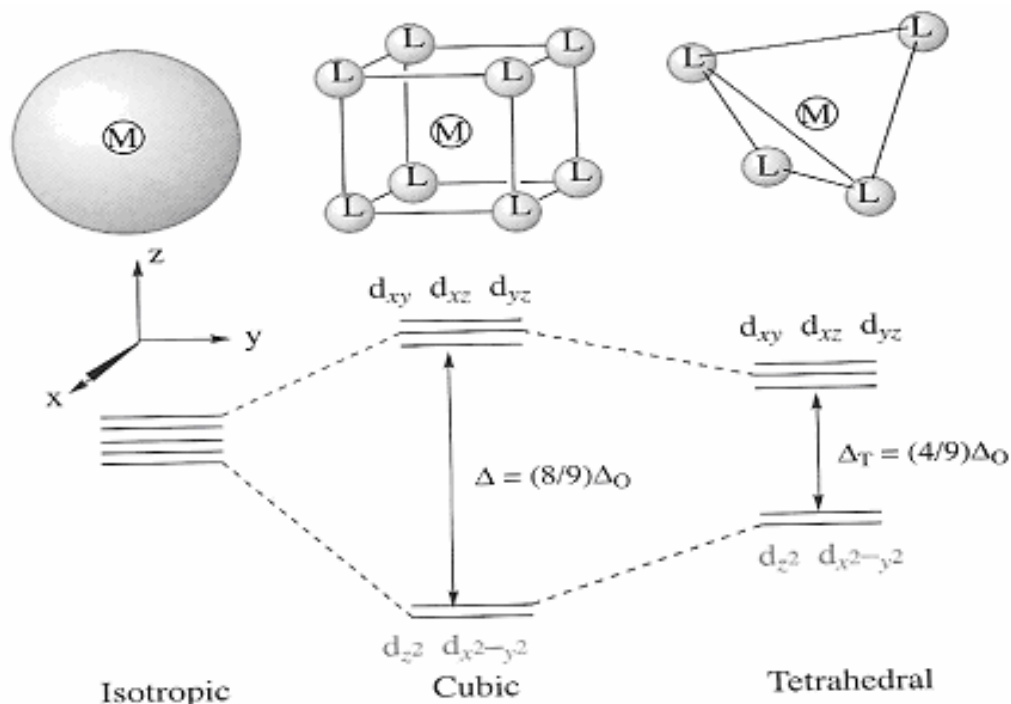


Figure - 9 The effect of cubic and tetrahedral crystal fields on the energies of d orbitals

The CFSE for tetrahedral complexes and its comparison with the octahedral CFSE is given in Table 10. The CFSE for d^0 , d^5 and d^{10} configurations is zero in both octahedral and tetrahedral cases. In all other cases the octahedral CFSE is greater than that of tetrahedral CFSE. Overall octahedral complexes are more stable and more common than tetrahedral complexes, partly because of the formation of six bonds instead of four and also because of larger CFSE.

Table-10 Electronic configurations in tetrahedral field and CFSE

d electron configuration	Arrangement of electrons					Spin only magnetic moment (in B.M.)	Tetrahedral CFSE(Δ_t)	Tetrahedral CFSE on octahedral CFSE scale ($\Delta_t = 4/9 \Delta_0$)	Octahedral CFSE	
	e_g		t_{2g}						Weak field	Strong field
D^1	↑					1.73	-0.6	-0.27	-0.4	-0.4
D^2	↑	↑				2.83	-1.2	-0.53	-0.8	-0.8
D^3	↑	↑				3.87	-0.8	-0.36	-1.2	-1.2
D^4	↑	↑	↑	↑		4.90	-0.4	-0.18	-0.6	-1.6
D^5	↑	↑	↑	↑	↑	5.92	0	0	0	-2.0
D^6	↑↓	↑	↑	↑	↑	4.90	-0.6	-0.27	-0.4	-2.4
D^7	↑↓	↑↓	↑	↑	↑	3.87	-1.2	-0.53	-0.8	-1.8

D ⁸	↑↓	↑↓	↑↓	↑	↑	2.83	-0.8	-0.36	-1.2	-1.2
D ⁹	↑↓	↑↓	↑↓	↑↓	↑	1.73	-0.4	-0.18	-0.6	-0.6
D ¹⁰	↑↓	↑↓	↑↓	↑↓	↑↓	0	0	0	0	0

Tetrahedral complexes are favoured when

- (i) the ligands are large and bulky and could cause crowding in an octahedral complex,
- (ii) the ligands are weak field, so that the loss in CFSE is not that important,
- (iii) the central metal has a low oxidation state and as a result the magnitude of Δ_t is small, and
- (iv) the electronic configuration of the central metal is d^0 , d^5 or d^{10} as there is no CFSE in these cases or d^1 or d^6 where the loss in CFSE is small.

Electronic spectra of transition metal complexes

In the electronic spectrum of a transition metal complex, d-d bands arise from electronic transitions which are largely localized on the metal ion. The magnitude of the energy gap Δ_o between the t_{2g} and e_g levels can be measured by recording UV – visible spectrum of the complex. The simplest example for a d-block element is presented by a d^1 ion such as Ti^{3+} . Consider a complex like $[Ti(H_2O)_6]^{3+}$ which is violet in colour. In this the electron will occupy the orbital with the lowest energy, that is one of the t_{2g} orbitals in the ground state of the complex. The next higher energy state available for the electron is the empty e_g orbitals. If light of frequency ν , which is equal to Δ_o/h , where h is Planck's constant and Δ_o is the energy difference between the t_{2g} and e_g orbitals, strikes the solution, it should be possible for such an ion to capture a quantum of radiation to excite the electron from the t_{2g} to the e_g orbital (i.e., the change in configuration from $t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$). The absorption band that results from this process is found in the visible spectrum of the hexaaquatitanium(III) ion (Figure 10) and is responsible for its violet colour.

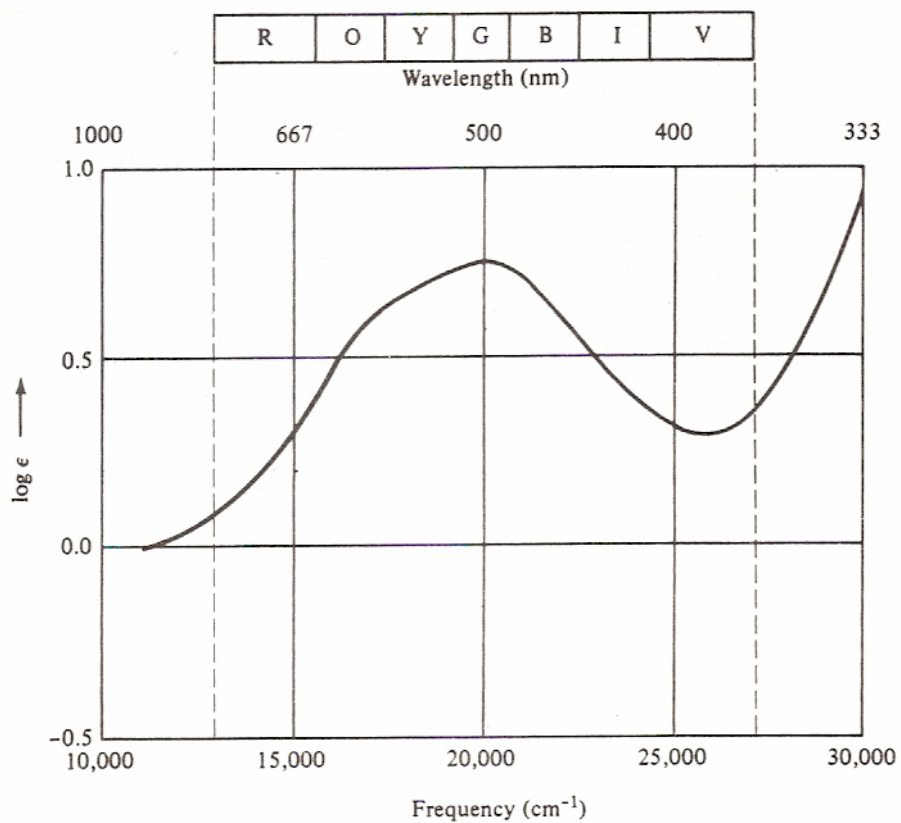


Figure - 10 The electronic absorption spectrum of $\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

The position of the absorption band in the spectrum, its intensity and width are the three important features of the spectrum. The position of the absorption band ($20,300\text{ cm}^{-1}$) gives the value of Δ_0 in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$. Knowing that $1\text{kJmol}^{-1} = 83.7\text{ cm}^{-1}$, the ($20,300\text{ cm}^{-1}$) value of Δ_0 for this complex is $20300/83.7 = 243\text{ kJmol}^{-1}$.

The solution containing $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ absorbs yellow and green lights (which excite the d^1 electron from t_{2g} to e_g orbital) and thus transmits the complementary colour red-violet. Further, the single d electron in this complex ion occupies an energy level $2/5 \Delta_0$ below the average energy of d orbitals. Since the determined Δ_0 value is 243 kJmol^{-1} , the CFSE comes out to be $2/3 \times 243 = 97\text{ kJmol}^{-1}$.

The maximum molar absorbance value (~ 5) indicates that the band is very weak. The molar absorbance values for one-electron theoretically “allowed” transitions are of the order of 10^4 - 10^5 . This suggests that the d - d transitions (i.e. transitions between the same orbitals) are not “allowed” but “**forbidden**” according to the quantum theory. However, due to slight distortion in octahedral geometry (Jahn-Teller effect) and vibrations of the ligands which removes the centre of symmetry, the rigorous requirement is relaxed and, consequently low intensity broad bands appear.

Appearance of d - d transitions in visible region is useful for quantitative determination of metal ions by spectrophotometric method. Broad shape of these bands minimize the chances of error in metal ion determination as slight wavelength variation in recording the absorbance will not have any significant effect.

In the case of tetrahedral compounds, the structures lack a centre of symmetry. As a result the d - d transitions become **non-forbidden**. Thus the tetrahedral complexes, in general, show considerably more intense d - d absorption bands than those of octahedral complexes; the increase in intensity is often by a factor of 10 or more. This explain why, for example, the pale red colour of the octahedral $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ion is changed by addition of Cl^- ions to the intense blue colour of the tetrahedral $[\text{CoCl}_4]^{2-}$ ion.

Limitations of crystal field approach

Although the CFA successfully explains many of the properties of transitional metal complexes such as their electronic spectra and colour, it fails to account for some important observations. In particular, spectroscopic measurement have been used to define a relative order of ligands in terms of the magnitude of the crystal field splitting they induce. This order, known as spectrochemical series, is based on measurement with a variety of metal ions and so represents an averaged ordering of ligands which may not be exactly correct for any given metal ion but represents the general picture. Since the CF model is an ionic model based on the electrostatic effect of the ligands on the energies of the metal ion d orbitals, it is surprising to find that anionic ligands such as Br^- , F^- and OH^- should be weaker-field than neutral ligand such as CO , NH_3 and PR_3 . This anomaly arises because the CFA model does not take account of covalence in metal-ligand bonding.

Modifications to the CFA model in the **ligand field approach (LFA)** model take accounts of these facts. **Molecular orbital approach (MOA)** takes into account both ionic as well as covalent contributions in the formation of complexes. This extensively involves symmetry and group theory applications.

The Chemistry of the Heavier Transition Metals

The second and third transition metal series are commonly referred to as the heavier transition metals collectively.

In general the ionic radii are larger by about 15-20 pm compared to the corresponding first transition series metals. As a result of this the coordination number of the elements of the second and third transition metal series tend to be higher than for the first transition metal series. Due to this tendency to show four coordination is considerably less frequent although it is present in certain cases, e.g. $[\text{ReO}_4]^-$. Square planar geometry is found in d^8 species such as Pd^{2+} , Pt^{2+} and Au^{3+} which are stabilized by CFSE. In general octahedral geometry is quite common and coordination numbers of 7, 8, 9 and even 10 are fairly common among the heavier transition metals.

These heavier transition metals exhibit pronounced tendency towards higher oxidation states. The +2 state that is a common among the metals of the first transition series, except scandium, is fairly uncommon among the heavier congeners. Cadmium(Cd) is the only one to be restricted to the +2 oxidation state and Hg^{2+} , Pd^{2+} and Pt^{2+} are the only other examples of this oxidation state. While cobalt(Co) exists in +2 and +3 oxidation states commonly, its heavier congeners i.e., rhodium(Rh) and iridium(Ir) are limited to +3 and higher oxidation states. The most stable oxidation state of chromium is +3 but both molybdenum(Mo) and tungsten(W) are strongly reducing in this state and the most important state for these is +6 oxidation state. In general the highest oxidation state is quite stable in the heavier transition metals. Compounds such as WCl_6 , ReF_7 , RuO_4 , OsO_4 and PtF_6 have no analogs in the first series. Unlike the lighter congeners Pd^{4+} , Pt^{4+} and Au^{3+} are fairly commonly known.

In case of complexes the heavier transition metals have a large tendency towards spin pairing and high spin complexes are not very common. Therefore, while nickel(Ni) in +2 oxidation state forms complexes in tetrahedral, square planar, square pyramidal, trigonal bipyramidal and octahedral geometries, Pd^{2+} and Pt^{2+} with all the ligands form only low spin square planar complexes.

Another important point of difference is with regard to the magnetic properties. Due to the extensive spin orbit coupling, the spin only approximation is no longer applicable. As a result of extensive temperature dependent paramagnetism the simple approximation of magnetic moment in terms of number of unpaired electrons applicable to the first transition metal series cannot be extended to the heavier congeners.

Special features of the heavier transitions elements

Some important features of the heavier transition metals compared with those of the first series are as follows :

- Isopoly and heteropoly acids and salts
This is a special features particularly of molybdenum and tungsten. They form a number of polymolybdic(VI) and polytungstic(VI) acids and their salts. Nb^{+5} and Ta^{+5} also show comparable behavior but to a very limited extent.

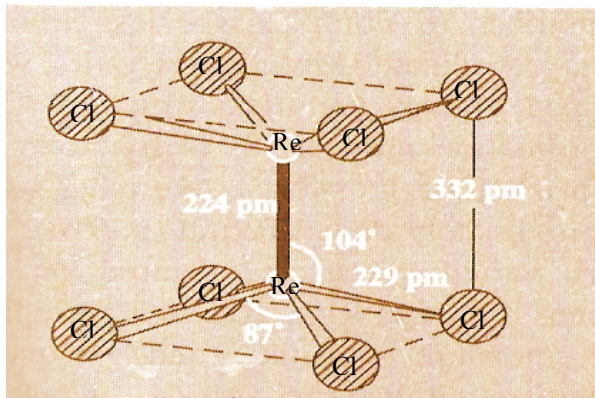
The polyacids of molybdenum and tungsten are of two types :

- i) isopoly acids and their related anions, which contain only molybdenum or tungsten with oxygen and hydrogen, e.g. $\text{Mo}_7\text{O}_{24}^{6-}$.

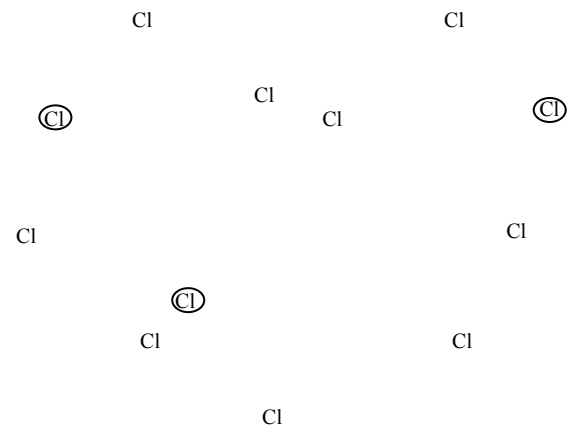
- ii) heteropoly acids and anions which contain one or two atoms of another element along with those in isopoly acids, e.g. $[\text{PMo}_{12}\text{O}_{40}]^{3-}$.
- Multiple metal-metal bonds

Although single and to an extent double metal-metal bonds are fairly common among metals of first transition series but triple and quadruple bonds are not very common. Here also molybdenum contains a large number of examples.

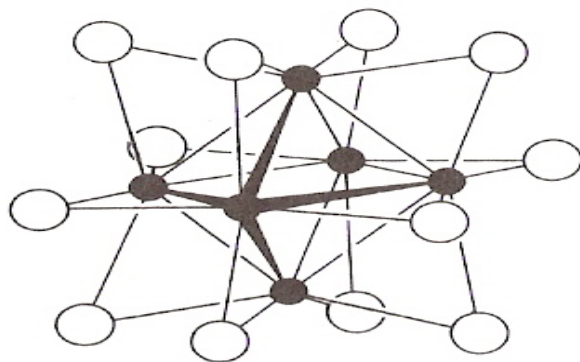
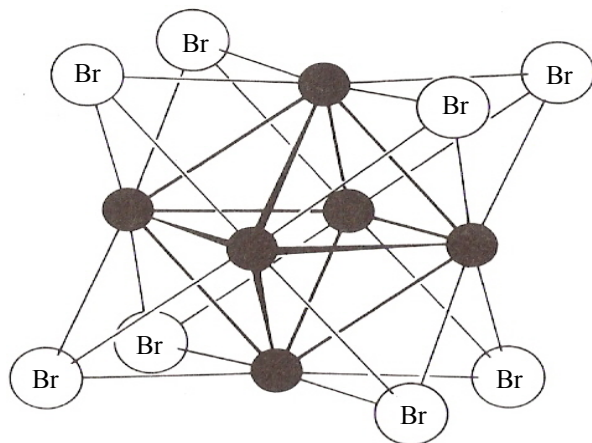
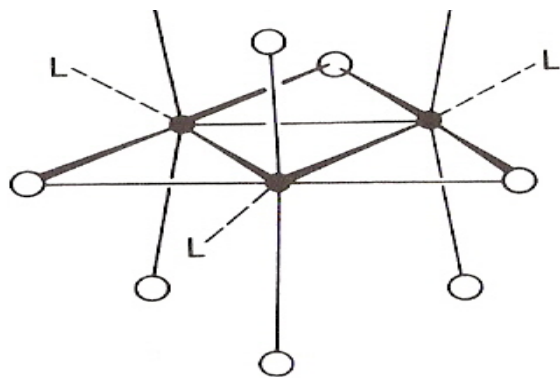
 - i) Triple bond – These are found mainly in compounds of stoichiometry M_2X_6 . An important example of these type of triple bond containing compounds is $\text{M}_2(\text{NR}_2)_6$. Among the metals involved, major number of example belong to molybdenum(Mo) and tungsten(W), e.g. $\text{W}_2(\text{NMe}_2)_6$.
 - ii) Quadruple bond – Molybdenum, tungsten, rhenium and technetium form a number of quadruple bond containing compounds, e.g. $\text{Mo}_2\text{Cl}_8^{2-}$, $\text{Re}_2\text{Cl}_8^{2-}$ (Figure 11a).
- Metal clusters - There are a number of compounds containing three or more than three metal atoms bonded to each other thereby forming a cluster.
 - i) Trinuclear cluster – In this type of cluster, three metal atoms are bonded to each other, e.g. $\text{Re}_3\text{Cl}_{12}^{3-}$ (Figure 11b). Here each rhenium is bonded to the other two rhenium atoms directly by metal – metal bonds.
 - ii) Tetranuclear cluster – Here four atoms are bonded to each other, e.g. $\text{Mo}_4\text{Cl}_8(\text{PR}_3)_4$. Here the molybdenum atoms are bonded to each other by alternating single and triple bonds.
 - iii) Octahedral cluster – Cluster containing six atoms have been reported for molybdenum, niobium tantalum and rhenium. There are two types of these clusters. One where an octahedron of six molybdenum atoms is coordinated by eight bromide ions, e.g. $\text{Mo}_6\text{Br}_{12}$ (Figure 11c), and the other where the octahedron is coordinated by twelve halide ions. Niobium and tantalum from this type of clusters (Figure 11d).



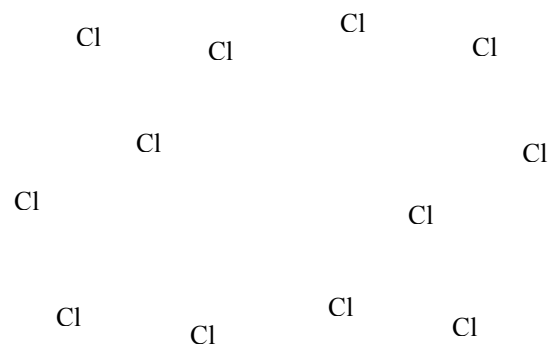
(a)



(b)



(c)



(d)

Figure - 11 Structures of (a) $[\text{Re}_2\text{Cl}_8]^{2-}$ (b) $[\text{Re}_3\text{Cl}_{12}]^{3-}$ (c) $[\text{Mo}_6\text{Br}_8]\text{Br}_4$, and (d) $[\text{Nb}_6\text{Cl}_{12}]^{2+}$

Suggested readings:

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Significant keywords:

d-Block elements, transition metals, coordination compounds, crystal field stabilization energy.