COORDINATION COMPOUNDS

BONDING IN COORDINATION COMPOUNDS

BONDING IN COMPLEXES VALENCE BOND THEORY

It was developed by Pauling. The salient features of the theory are summarized below:

- (i) Under the influence of a strong field ligands, the electrons of central metal ion can be forced to pair up against the Hund's rule of maximum multiplicity.
- (ii) Under the influence of weak field ligands, electronic configuration of central metal atom / ion remains same.
- (iii) If the complex contains unpaired electrons, it is paramagnetic in nature, whereas if it does not contain unpaired electrons, then it is diamagnetic in nature and magnetic moment is calculated by spin only formula.

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

where n is the number of unpaired electrons in the metal ion.

Relation between unpaired electrons and magnetic moment

Magnetic moment (Bohr magnetons)	0	1.73	2.83	3.87	4.90	5.92
Number of unpaired electrons	0	1	2	3	4	5

Thus, the knowledge of the magnetic moment can be of great help in ascertaining the type of complex.

(iv) When ligands are arranged in increasing order of their splitting power then an experimentally determined series is obtained named as spectrochemical series.

< EDTA <
$$NH_3 \approx py$$
 < en < dipy < phen < NO_2 ^[]] CN⁻ < CO

(v) The central metal ion has a number of empty orbitals for accommodating electrons donated by the ligands.

The number of empty orbitals is equal to the co-ordination number of the metal ion for a particular complex.

- (vi) The atomic orbital (s, p or d) of the metal ion hybridise to form hybrid orbitals with definite directional properties. These hybrid orbitals now accept e⁻ pairs from ligands to form coordination bonds.
- (vii) The d-orbitals involved in the hybridization may be either inner (n 1) d orbitals or outer n d-orbitals. The complexes formed in these two ways are referred to as inner orbital complexes and outer orbital complexes, respectively.

Following table provides the types of hybridization with different coordination number.

Coordination number	Type of	Shape of complex
of metal	hybridization	
4	sp ³	Tetrahedral
4	dsp ²	Square planer
5	sp ³ d	Trigonal
		bipyramidal
6	Sp ³ d ²	Octahedral
6	d ² sp ³	Octahedral

It is to be noted that the type of hybridization of metal and shape of complex involved can be predicted conveniently, if some characteristic of the complex like magnetic nature, geometry or whether exhibits isomerism or not, etc., be known.

Coordination Number Six.

In the diamagnetic octahedral complex, $[Co(NH_3)_6]^{3+}$, the cobalt ion is in +3 oxidation state and has the electronic configuration represented as shown below.



Thus, the complex has octahedral geometry and is diamagnetic because of the absence of unpaired electron. Since in the formation of complex the inner d-orbital (3d) is used in hybridization, the complex is called an inner orbital or low spin or spin paired complex.

The complex $[FeF_6]^{4-}$ is paramagnetic and uses outer orbital (4d) in hybridization (sp^3d^2) ; it is thus called as outer orbital or high spin or spin free complex. So,



Six pairs of electrons from six F⁻ ions.

Coordination Number Four:

In the paramagnetic and tetrahedral complex $[NiCl_4]^{2-}$, the nickel is in +2 oxidation state and the ion has the electronic configuration $3d^8$. The hybridization scheme is as shown in figure.



sp⁻⁵ hybrid orbitals Four pairs of electrons from four Cl⁻ ions. The compound is paramagnetic since it contains two unpaired electrons. Similarly complex $[Ni(CO)_4]$ has tetrahedral geometry and is diamagnetic as it contains no unpaired electrons. The hybridization scheme is as shown in figure.

Ni⁰, [Ar]
$$3d^8 4s^2$$
 $3d$
 $4s$
 $4p$

 [Ni(CO)_4]
 $1l$
 $1l$
 $1l$
 $1l$
 $1l$
 sp^3 hybrid orbitals
 as
 $4p$
 $4s$
 $4p$

Four pairs of electrons from four CO molecules. Complexes of Pd(II) and Pt (II) are usually four-coordinate, square planar, and diamagnetic and this arrangement is often found for Ni(II) complexes as well, e.g., in $[Ni(CN)_4]^{2-}$ (here nickel is in +2 oxidation state and has electronic configuration $3d^8$). In as much as the free ion is in the ground state each case is paramagnetic, the bonding picture has to include pairing of electrons as well as ligand-metal-ligand bond angles of 90° and this occurs via hybridization of one (n–1) d, one ns and two np orbitals to form four equivalent dsp² hybrid orbitals directed toward the corners of a square. These orbitals then participate in covalent coordinate σ bonds with the ligands, the bonding electron pairs being furnished by the ligands. The hybridization scheme for $[PtCl_4]^{2-}$ is as shown in figure.

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

$$[PtCl_{4}]^{2-}$$

$$[PtCl_{4}]^{2-}$$

$$[PtCl_{4}]^{2-}$$

$$[PtCl_{4}]^{2-}$$

dsp² hybrid orbitals Four pairs of electrons from four Cl[–] ions.

Similarly the hybridization scheme for $[Ni(CN)_4]^{2-}$ is as shown in figure.

dsp² hybrid orbitals

Four pairs of electrons from four CN⁻ ions.

It is found that $[Cu(NH_3)_4]^{2+}$ is square planar and paramagnetic with one unpaired electron in 4p-orbital. The hybridization scheme is as follow.

dsp² hybrid orbitals

Four pairs of electrons from four $\ensuremath{\mathsf{NH}}_3$ molecules.

Note. $[Ni(CN)_5]^{3-}$ is found to be diamagnetic with 2 types of Ni – C bond lengths, out of which four bond lengths are found to be equal and the fifth one is different. The hybridization scheme for $[Ni(CN)_5]^{3-}$ is as shown in figure.



dsp³ hybrid orbitals

Five lone pairs of electrons from five CN⁻-ions



square pyramidal.

Class-12th

While the valence bond theory, to a large extent, explains the formation, structures and magnetic behaviour of coordination compounds,

it suffers from the following shortcomings:

- **1.** A number of assumptions are involved.
- **2.** There is no quantitative interpretation of magnetic data.
- **3.** It has nothing to say about the spectral (colour) properties of coordination compounds.
- **4.** It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of coordination compounds.
- **5.** It does not make exact predictions regarding the tetrahedral and square-planar structures of 4-coordinate complexes.
- **6.** It does not distinguish between strong and weak ligands.

CRYSTAL FIELD THEORY (CFT) :

Crystal field theory is now much more widely accepted than the valence bond theory. It is assumed that the attraction between the central metal and ligands in a complex is purely electrostatic. The transition metal which forms the central atom cation in the complex is regarded as a positive ion of charge equal to the oxidation state. It is surrounded by negative ligands or neutral molecules which have a lone pair of electrons If the ligand is a neutral molecule such as NH₃, the negative end of the dipole in the molecule is directed toward the metal cation. The electrons on the central metal are under repulsive forces from those on the ligands. Thus, the electrons occupy the d orbital remain away from the direction of approach of ligands. In the crystal field theory, the following assumptions are made.

- (i) Ligands are treated as point charges.
- (ii) There is no interaction between metal orbitals and ligands orbitals.
- (iii) All the d orbitals on the metal have the same energy (that, is degenerate) in the free atom. However, when a complex, is formed, the ligands destroy the degeneracy of these orbitals, that is , the orbitals now have different energies. In an isolated gaseous metal ion, all five d orbitals have the same energy and are termed degenerate. If a spherically symmetrical field of ligands surrounds the metal ion, the d orbitals remain degenerate. However, the energy of the orbitals is raised because

of repulsion between the field of ligands and electrons on the metal. In most transition metal complexes, either six or four ligands surround the metal, giving octahedral or tetrahedral structures. In both these cases, the field produced by the ligands is not spherically symmetrical. Thus, the d orbitals are not all affected equally by the ligand field. In the an octahedral complex, the metal is at the centre of the octahedron and the ligands are at the six corners.

The direction x, y and z point to three adjacent corners of the octahedron as shown fig. The lobes of the e_g orbitals (d_{x2-y2} and d_{z2}) point along the axes x,y and z. The lobes of the t_{2g} orbitals (d_{xy} , d_{xz} and d_{yz}) point in between the axes. If follows that the approach of six ligands along the x,y,z, -x, -y, and -z directions will increase the energy of the $d_{x2} - y_2$ and d_{z2} orbitals (which point along the axes) than it increases the energy of the dxy, dxz and dyz orbitals (which points between the axes). Thus, under the influence of an octahedral ligand field the d orbitals split into two groups of different energies. Rather than referring to the energy level of a isolated metal atom. The difference in energy between the two d levels is given by the symbols Δ_0 or 10 Dq.



It follows that the eg orbitals are +0.6 Δ_0 above the average level, and the t_{2g} orbitals -0.4 Δ_0 below the average level.



Fig. Diagram of the energy levels of d -orbitals in a octahedral field Tetrahedral Complexes A regular tetrahedron is related to a cube. One atom is at the centre of the cube, and four of the eight corners of the cube are occupied by ligands as shown in Fig. The direction x,y and z point to the centres of the faces of the cube. The e_g orbitals point along x,y and z (that is , to centres of the faces.)



Fig. Relation of tetrahedron to a cube

The approach of the ligands raised the energy of both sets of orbitals. The energy of the t_{2g} orbital raised most because they are closest to the ligands. This crystals field splitting is opposite to that in octahedral complexes. The t_{2g} orbitals are 0.4 t above the average energy of the two groups (the Bari centre) and the e_g orbitals are 0.6 t below the average level.



Free metal ion (five degenerate d orbitals)

Fig Crystal field splitting of energy levels in a tetrahedral field

Stability of complexes

A co-ordination compound is formed in solution by the stepwise addition of ligands to a metal ion. Thus, the formation of the complex, ML_n (M = central metal cation, L = monodentate ligand and n=co-ordination number of metal ion) supposed to take place by the following n consecutive steps.

$$M + L \rightleftharpoons ML; K_1 = \frac{[ML]}{[M][L]}$$
$$M + L \rightleftharpoons ML_2; K_2 = \frac{[ML_2]}{[ML][L]}$$
$$ML_2 + L \rightleftharpoons ML_3; K_3 = \frac{[ML_3]}{[ML_3][L]}$$

$$\mathsf{ML}_{n-1} + \mathsf{L} \rightleftharpoons \mathsf{ML}_n; \mathsf{K}_n = \frac{[\mathsf{ML} \cdot]}{|\mathsf{ML}_{n-1} \parallel \mathsf{L}|}$$

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 K_1 , K_2 , K_3 K_n are called stepwise stability constants. With a few exceptions, the values of successive stability constants decrease regularly from K_1 to K_n . The overall stability constant K is given as

$$M + nL \rightleftharpoons ML_n;$$

$$K = K_1 K_2 K_3 \dots K_n = \frac{[ML_r]}{[M][L]'}$$

The higher the overall stability constant value of the complex, the more stable it is. Alternatively, 1/K values called instability constant explain the dissociation of the complex into metal ion and ligands in the solution. The value of the stability constant for some of the complexes are given in Table. Stability constants of complexes

Complex	Stability constant		
$[Cu(NH_3)_4]^{2+}$	4.5×10^{11}		
[Ag(NH ₃) ₂]+	1.6×10^{7}		
[Co(NH ₃) ₆] ²⁺	1.12×10^{6}		
[Co(NH ₃) ₆]+	5.0× 10 ³³		
[AgCl ₂]-	1.11×10^{5}		
[AgBr ₂]-	1.28×10^{7}		
[Ag(CN) ₂]-	1.0×10^{22}		
[Cu(CN) ₄] ²⁻	$2.0 imes 10^{27}$		
[Fe(CN) ₆] ³⁻	$7.69 imes 10^{43}$		

COLOUR IN COORDINATION COMPOUNDS

Coordination compounds of transition metals have fascinating colours. According to the crystal field theory the colour is due to the d-d transition of electron under the influence of ligands. We know that the colour of a substance is due to the absorption of light at a specific wavelength in the visible part of the electromagnetic spectrum (400 to 700 nm) and transmission or reflection of the rest of the wavelengths. An object that absorbs all visible light appears black. The mechanism of light absorption in coordination compounds is that photons of appropriate energy can excite the coordination entity from its ground state to an excited state. Consider the Ti(III) ion in solution, that is $[Ti(H_20)_6]^{3+}$. This is a violet colour octahedral complex, where in the ground state of the complex a single electron is present in t_{2g} level. The next higher state available for the transition is the empty e_g level. If the light corresponding to the energy of yellow-green is absorbed by the complex, it would excite the electron from t_{2g} level to e_g level. Consequently, the complex appears violet in colour. In case of copper (II) ions in solution, for example, it can be imagined that one of the d-electrons from the t_{2g} set $(d_{XV}, d_{VZ}, d_{XZ}$ orbitals) gets excited to the eg set (orbitals). In this case since high energy light is transmitted it means that low energy light (red region) is absorbed. For copper (II) ions in aqueous solution, the

energy gap Δ_{t} is relatively small. Table below gives the relationship of the wavelength

of light absorbed and the colour observed.

Relationship between the wavelength of light absorbed and the colour observed In some coordination entitles

Coordination entity	Wavelength of light	Colour of light	Colour of coordination
	absorbed (nm)	absorbed	entity
[CoCl(NH ₃) ₅] ²⁺	535	Yellow	Violet
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue Green	Red
$[Co(NH_3)_6]^{3+}$	475	Blue	Yellow Orange
[Co(CN0 ₆] ³⁻	310	Ultraviolet	Pale Yellow
$[Cu(H_2O)_4]^{2+}$	600	Red	Blue
$[Ti(H_2O)_6]^{3+}$	498	Blue Green	Purple

Note :

(a) In absence of ligand, crystal field splitting does not occur and as a consequence the substance appears colourless.

For example;

- (i) removal of water from violet coloured complex [Ti(H₂O)₆]Cl₃ on heating makes it colourless,
- (ii) similarly anhydrous copper sulphate (CuSO₄) is white, but hydrated copper sulphate (CuSO₄.5H₂O) is blue coloured.
- (b) The nature of the ligand and the molar ratio of metal : ligands also influence the colour of the complex.

For example; in the pale green complex of $[Ni(H_2O)_6]$, the colour change is

observed when ethylenediamine is progressively added to it.

Molar ratio of en : Ni	Coloured obs erved
1:1	Pale blue
1:1	Blue/Purple
1:1	Violet

Chemistry

Note: Ruby is Al_2O_3 in which 0.5–1% Cr³⁺ ions (d³ electron system) are randomly distributed in the positions normally occupied by Al^{3+} . We may consider Cr(III) species as octahedral Cr(III) complexes incorporated into the alumina lattice; d-d transition of electron at these centres/points give rise to the colour (red).

Emerland is the mineral beryl ($Be_3Al_2Si_6O_{18}$) in which Cr^{3+} ions occupy octahedral sites, but in this case low energy corresponding to yellow red and blue is absorbed and light corresponding to green region is transmitted.

FACTORS AFFECTING STABILITY OF COMPLEX COMPOUNDS

- (i) The values of stability constant differ widely depending on the nature of the metal ion and the ligand in general higher the charge density on the central ion. The greater the stability of its complexes.
- (ii) the more basic a ligands, the greater is the ease with which it can donate its lone pairs of electrons and therefore, greater is the stability of the complexes formed by it.
- **Ex.** The cyano and ammine complexes are far more stable than those formed by halide ions. This is due to the fact that NH₃ and CN⁻ are strong Lewis bases.
- (iii) The higher the oxidation state of the metal, the more stable is the complex. The charge density of Co^{3+} ion is more than Co^{2+} ion and thus, $[Co(NH_3)_6]^{3+}$ is more stable than $[Co(NH_3)_6]^{2+}$. Similarly, $[Fe(CN)_6]^{3-}$ is more stable than $[Fe(CN)_6]^{4-}$.
- (iv) Chelating ligands form more stable complexes as compared to monodentate ligands.