Bonding in co-ordination compounds.

Werner was able to explain the bonding in complex.

Primary valency (Pv) : This is non- directional and ionizable. In fact it is the positive charge on the metal ion.

Secondary valency (Sv) : This is directional and non- ionizable. It is equal to the number of ligand atoms co-ordinated to the metal (co-ordination number).

Example : $[Co(NH_3)_6]Cl_3$	or	$Co(NH_3)_6]^{3+} 3Cl^{-}$
$Pv \rightarrow 3Cl^{-}[3]$	Sv	$\rightarrow 6 NH_3(6)$
$[Co(NH_3)_5 Cl]Cl_2$	or	$\left[Co(NH_3)_5 Cl\right]^{2+} 2Cl^{-1}$
$Pv \rightarrow 2Cl^{-}(2)$	Sv	$\rightarrow 5 NH_3 + 1Cl^-(6)$
$[Co(NH_3)_4 Cl_2]Cl$	or	$[Co(NH_3)_4 Cl_2]^+ Cl^-$
$Pv \rightarrow Cl^{-}(1)$	Sv	$\rightarrow 4 NH_3 + 2Cl^-(6)$

Nature of the complex can be understood by treating the above complexes with excess of $AgNO_3$.

 $CoCl_3.6NH_3 \rightarrow 3AgCl, [Co(NH_3)_6Cl_3]$ (three chloride ion)

 $CoCl_3.5NH_3 \rightarrow 2AgCl$, $[Co(NH_3)_5Cl_2$ (two chloride ion)

 $CoCl_3.4NH_3 \rightarrow 1AgCl_1$ [$Co(NH_3)_4Cl_2$ (one chloride ion)

 $CoCl_3.3NH_3 \rightarrow no AgCl, [Co(NH_3)_3Cl_3 (no chloride ion)]$

The nature of bonding between central metal atom and ligands in the coordination sphere has been explained by the three well-known theories. These are :

(1) Valence Bond theory of coordination compounds

(i) The suitable number of atomic orbitals of central metal ion (s,p,d) hybridise to provide empty hybrid orbitals.

(ii) These hybrid orbitals accept lone pair of electrons from the ligands and are directed towards the ligand positions according to the geometry of the complex.

(iii) When inner d-orbitals i.e. (*n*-1) d orbitals are used in hybridization, the complex is called – *inner orbital*or*spin or hyperligated* complex.

(iv) A substance which do not contain any unpaired electron is not attracted by 2 magnet. It is said to be diamagnetic. On the other hand, a substance which contains one or more unpaired electrons in the electrons in the d-orbitals, is attracted by a magnetic field [exception O_2 and

NO]. It is said to be paramagnetic.

Paramagnetism can be calculated by the expression, $\mu_s = \sqrt{n(n+2)}$, where $\mu =$ magnetic moment.

s= spin only value and n= number of unpaired electrons.

Hence, if $n = 1, \mu_s = \sqrt{1(1+2)} = 1.73 B.M.$, if $n = 3, \mu_s = \sqrt{3(3+2)} = 3.87 B.M.$ and so on

On the basis of value of magnetic moment, we can predict the number of unpaired electrons present in the complex. If we know the number of unpaired electrons in the metal complex, then it is possible to predict the geometry of the complex species.

(v) There are two types of ligands namely strong field and weak field ligands. A strong field ligand is capable of forcing the electrons of the metal atom/ion to pair up (if required). Pairing is done only to the extent which is required to cause the hybridization possible for that Co-ordination number. A weak field ligand is incapable of making the electrons of the metal atom/ ion to pair up.

 $\begin{aligned} & \textit{Strong field ligands:} CN^-, CO, en, NH_3, H_2O, NO^-, Py \,. \\ & \textit{Weak field ligands:} I^-, Br^-, Cl^-, F^-, NO_3^-, OH^-, C_2O_4^{2-}, NH_3, H_2O \,. \end{aligned}$

Geometry (shape) **and magnetic nature of some of the complexes** (Application of valence bond theory)

Atom/ion/ complex	Configuration	Oxidation state of metal	Type of hybridi- zation	Geometry shape	No. of unpaired electrons	Magnetic nature
(1)	. (2)	(3)	(4)	(5)	(6)	(7)
$Ni^{2+}(d^8)$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	+2			2	Paramagnetic
[NiCl ₄] ^{2–}	$\begin{array}{c} \uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \\ \hline \vdots \\ sp^3 \end{array}$	+2	sp ³	Tetrahedral	2	Paramagnetic
[Ni(CN) ₄] ²⁺	$f \downarrow f \downarrow f \downarrow f \downarrow \downarrow \bullet$ \bullet \bullet \bullet Rearrangement dsp^2	+2	dsp ²	Square planar	0	Diamagnetic
Ni		0			2	Paramagnetic
Ni(CO) ₄	$\uparrow\downarrow\uparrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow$ \bullet \bullet Rearrangement sp^3	0	sp ³	Tetrahedral	0	Diamagnetic
[Ni(NH ₃) ₆] ²⁺	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	+2	sp ³ d ² (Outer)	Octahedral	2	Paramagnetic
$\mathrm{Mn}^{2+}(d^5)$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	+2			5	Paramagnetic
[Mn(CN) ₆] ^{4–}	$\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \bullet \downarrow \bullet$ \bullet \bullet \bullet \bullet Rearrangement d^2sp^3 d^2sp^3 d^2sp^3	+2	d ² sp ³ (Inner)	Octahedral	1	Paramagnetic
[MnCl ₄] ^{2–}	$\begin{array}{c} \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \\ \hline \vdots \\ sp^3 \end{array}$	+2	sp ³	Tetrahedral	5	Paramagnetic
$\operatorname{Cu}^{2+}(d^9)$		+2			1	Paramagnetic
$\left[\operatorname{CuCl}_4\right]^{2-}$	$\begin{array}{c} $	+2	sp ³	Tetrahedral	1	Paramagnetic
$[Cu(NH_3)_4]^{2+}$		+2	dsp ²	Square planar	1	Paramagnetic
	One electron is shifted from $3d$ - to $4p$ -orbital					

(1)	(2)	(3)	(4)	· (5)	(6)	(7)
$\operatorname{Cr}^{3+}(d^3)$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	+3			3	Paramagnetic
[Cr(NH ₃) ₆] ³⁺	$\underbrace{\uparrow \uparrow \uparrow \uparrow \underbrace{\bullet} \bullet \bullet}_{d^2 s p^3} \underbrace{\bullet \bullet \bullet}_{d^2 s p^3}$	+3	d ² sp ³ (Inner)	Octahedral	3	Paramagnetic
[Cr(H ₂ O) ₆] ³⁺	$\begin{array}{c c} \uparrow \uparrow \uparrow \uparrow \uparrow \\ \hline \hline \\ \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	+3	sp ³ d ² (Outer)	Octahedral	3	Paramagnetic
$\operatorname{Co}^{3+}(d^6)$		+3			4	Paramagnetic
[CoF ₆] ³⁻	$\begin{array}{c} \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \\ \hline \vdots \\ sp^{3}d^{2} \end{array}$	+3	sp ³ d ² (Outer)	Octahedral	4	Paramagnetic
$[Co(NH_3)_6]^{3+}$	Rearrangement d^2sp^3	+3	d ² sp ³ (Inner)	Octahedral	0	Diamagnetic
$\operatorname{Co}^{2+}(d^7)$		+2			3	Paramagnetic
[Co(H ₂ O) ₆] ²⁺	$\begin{array}{c} \uparrow \downarrow \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \uparrow \\ \hline \vdots \\ sp^3d^2 \end{array}$	+2	sp ³ d ² (Outer)	Octahedral	3	Paramagnetic
$\operatorname{Fe}^{2+}(d^6)$		+2			4	Paramagnetic
[Fe(CN) ₆] ^{4–}	Image: the second s	+2	d ² sp ³ (Inner)	Octahedral	0	Diamagnetic
$[Fe(H_2O)_6]^{2+}$		+2	sp ³ d ² (Outer)	Octahedral	4	Paramagnetic
$[Fe(NH_3)_6]^{2+}$	Same	+2	sp ³ d ² (Outer)	Octahedral	4	Paramagnetic
$Fe^{3+}(d^5)$		+3			5	Paramagnetic
[Fe(CN) ₆] ³⁻	$f \downarrow f \downarrow f \downarrow f \downarrow \bullet $	+3	d ² sp ³ (Inner)	Octahedral	1	Paramagnetic
Fe		0			4	Paramagnetic
Fe(CO) ₅		0	dsp ³ (Inner)	Trigonal bipyramidal	0	Diamagnetic

(2) **Ligand field theory :**According to this theory when the ligands come closer to metal atom or ion, a field is created. This field tends to split the degenerate *d*-orbitals of the metal atom into different energy levels. The nature and number and number of lignads determine the extent of splitting on the basis of which the magnetic and spectroscopic properties of the complex can be explained.