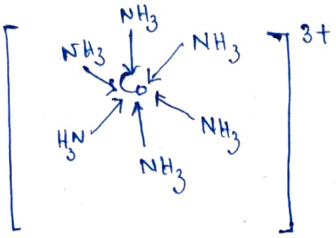
Theories in Co-ordination complexes

Sidgwick's Co-ordinate bond and effective atomic no:

Sidgwick (1927) extended the Lewis concept of co-valent bond and introduced a new concept of co-ordinate bond which is also some times called polar / dative bond. According to this Sidgwick's concept the ligand donate the electron pair to the central metal ion and thus form a co-ordinate bond., $M \leftarrow L$ which indicates that the ligand L (donar) has donated an electron pair to the metal ion, M (acceptor). This concept is based on the fact that all the ligands contain at least one lone pair of electrons. Thus on the basis of Sidgwick's concept, the structure of the complex ion $[Co(NH_3)_6]^{3+}$ is shown as



Evidently, the formation of bonds between the six ligands (which are NH_3 molecules) and the central metal ion, Co^{3+}, The N atom of each molecule donates an electron pair to Co^{3+} ion. Thus in all twelve electrons (i,e 6 $e^{\ominus}$ pair) are donated by six NH_3 ligands to Co^{3+} ion. The donation of an electron pair by NH_3 molecule has been represented by an arrow.

On the basis of his co-ordinate bond, Sidgwick suggested that after the ligands have donated a certain no. of electrons to the central metal ion through bonding, the total no. of electrons on the central atom, including those gained from ligands in the bonding is called effective atomic number (EAN) of the central metal ion and in many cases this total no. of electrons (i.e EAN) surrounding the central metal ion is equal to the atomic no. of the inert gases. which follow the central metal atom in the periodic table. This is called effective atomic number rule.

The EAN of the central metal atom / ion in a given complex ion is given by

$$EAN = (Z - x) + n \times y$$

where Z = atomic no. of the central metal atom
x = oxidation state of the central

(2)

n = no. of ligands
y = no. of electrons donated by one ligand

Calculation of EAN ~~of~~ to some metal complexes:

Metal carbonyls:

Carbonyl	atomic no.	$e^\ominus$ donated by terminal CO gr.	$e^\ominus$ donated by bridging CO group	$e^\ominus$ donated by M-M bond	EAN of the central metal atom
$Ni(CO)_4$	28	4×2	—	—	28+8 = 36
$Fe(CO)_5$	26	5×2	—	—	26+10 = 36
$Cr(CO)_6$	24	6×2	—	—	24+12 = 36
$Fe_2(CO)_9$	26	3×2	3×1	1×1	26+6+3+1 = 36
$Co_2(CO)_8$ (in soln.)	27	4×2	—	1×1	27+8+1 = 36
$Co_2(CO)_8$ (in solid)	27	3×2	2×1	1×1	27+6+2+1 = 36
$Mn_2(CO)_{10}$	25	5×2	—	1×1	25+10+1 = 36
$Fe_3(CO)_{12}$	26	4×2	—	2×1	28+8+2 = 36

Metal nitrosyls:

	Nitrosyl compounds	$e^\ominus$ donated by metal atom	$e^\ominus$ donated by $NO^+/NO^\ominus$	$e^\ominus$ donated by other ligand.	EAN of the metal atom
$NO^+ \approx 2e^\ominus$ donor	$Fe(NO)_2(CO)_2$	26+2 (Fe^{2-})	2×2 ($2NO^+$)	2×2 (2CO)	28+4+4 = 36
	$Mn(NO)_3(CO)$	25+3 (Mn^{3-})	3×2	1×2 (2CO)	28+6+2 = 36
	$Co(NO)(CO)_3$	27+1 (Co^-)	1×2	3×2	28+2+6 = 36
	$Fe(NO)_2(PR_3)_2$	26+2 (Fe^{2-})	2×2	2×2	28+4+4 = 36
	$Fe(NO)(CN)_5]^{2-}$	26-2 (Fe^{2+})	1×2	5×2	24+2+10 = 36
$NO^- \approx 2e^\ominus$ donor	$[Co(NO)(CN)_5]^{3-}$	27-3 (Co^{3+})	1×2 (NO^-)	5×2	24+2+10 = 36
	$[Co(NO)(NH_3)_5]^{2-}$	27-3 (Co^{3+})	1×2 (NO^-)	5×2	24+2+10 = 36
	$Fe(NO)_4$ / $(NO^+)_3Fe^{2-}(NO^-)$	26+2 (Fe^{2-})	3×2 ($3NO^+$) 1×2 (NO^-)	—	28+6+2 = 36

⊛ Some metal complexes:

Complex ion	Atomic no. of metal atom (Z)	O.S of the central metal atom (x)	Electron donated by the ligand = n × y	EAN of the central metal ion = (Z − x) + ny
Pd $(NH_3)_6]^{4+}$	46	+4	6×2	(46−4)+12 = 54 (Xe)
$[Fe(CN)_6]^{4-}$	26	(+2)	6×2	(26−2)+12 = 36 (Kr)
$[Co(NH_3)_6]^{3+}$	27	(+3)	6×2	(27−3)+12 = 36 (Kr)
$[Pt(NH_3)_6]^{4+}$	78	(+4)	6×2	(78−4)+12 = 86 (Rn)
$[Ag(NH_3)_4]^{+}$	47	(+1)	4×2	(47−1)+8 = 54 (Xe)
$[Cu(CN)_4]^{3-}$	29	(+1)	4×2	(29−1)+8 = 36 (Kr).

Exceptions of EAN rules:

Though in many cases EAN is the same as the atomic no. of the next inert gas, yet it is not always so. (i) Complexes of Ni(II), Co(II), Ag(I) etc. which have more than one co-ordination no. depending on the nature of the ligand generally do not follow the EAN rule.

(ii) Some metal atoms such as Fe(III) which has its coordination no. equal to 4 in $[FeCl_4]^-$ and equal to 6 in $[Fe(CN)_6]^{3-}$ never follow this rule.

Some examples, where EAN rule do not follow, are given below

Complex ion	Atomic no. of metal atom	O.S of the central metal atom	e^- donated by the ligand	EAN of metal atom.
$[Fe(CN)_6]^{3-}$	26	+3	6×2	(26−3)+12 = 35
$[Cr(NH_3)_6]^{3+}$	24	+3	6×2	(24−3)+12 = 33
$[Ni(NH_3)_6]^{2+}$	28	+2	6×2	(28−2)+12 = 38
$[Mn(H_2O)_6]^{2+}$	25	+2	6×2	(25−2)+12 = 35
$[Ni(en)_3]^{2+}$	28	+2	3×4	(28−2)+12 = 38
$[Co(CN)_6]^{4-}$	27	+2	6×2	(27−2)+12 = 37
$[Pt(NH_3)_2Cl_2]$	78	(+2)	2×4	(78−2)+8 = 84
$[Cu(NH_3)_4]^{2+}$	29	(+2)	4×2	(29−2)+8 = 35
$[FeCl_4]^-$	26	(+3)	4×2	(26−3)+8 = 31

(ii)

~~Central~~ complex ion	Atomic no. (z)	O.S of metal ion (x)	$e^{\ominus}$ donated by ligand = ny	EAN of metal atom
$Ni(CN)_4]^{2-}$	28	(+2)	4 × 2	(28 − 2) + 8 = 34
$[PdCl_4]^{2-}$	46	(+2)	4 × 2	(46 − 2) + 8 = 52
$[Pt(NH_3)_4]^{2+}$	78	(+2)	4 × 2	(78 − 2) + 8 = 84
$[AgX_2]^-$	47	(+1)	2 × 2	(47 − 1) + 4 = 50
$[Ag(NH_3)_2]^+$	47	(+1)	2 × 2	(47 − 1) + 4 = 50
$[CuCl_2]^-$	29	(+1)	2 × 2	(29 − 1) + 4 = 32
$[Cr(NO)(CN)_5]^{3-}$	24	(+1)	1 × 2 (NO^+) 5 × 2 (CN^-)	(24 − 1) + 12 = 35
$[Mn(NO)(H_2O)_5]^{2-}$	25	(+2)	1 × 2 5 × 2	(25 − 2) + 12 = 35
$[Fe(NO)(H_2O)_5]^{2-}$	26	(+1)	1 × 2 5 × 2	(26 − 1) + 12 = 37.

Application of EAN rule:

With the help of EAN rule, the magnetic property of the complex ions can be predicted. It has been observed that the complex ion whose central metal atom obey EAN rule are diamagnetic and it is experimentally varified.

The complex ions whose central metal atom does not obey EAN rule are generally paramagnetic. The no. of unpaired $e^{\ominus}s$ present in the complex ion is equal to the difference between the EAN of the central metal atom and the atomic no. of the inert gas which follow the central metal atom in the periodic table. With the help of these unpaired electrons ~~of~~ the value of magnetic moment (μ) can be calculated and it has found to be almost equal to the experimental value (μ_{exp}).

Limitation of Sidgwick's concept or Co-ordinate bond:

(i) The donation of $e^{\ominus}$ pair by each of the ligand to the central metal ~~atom~~ ion to form L→M co-ordinate bond in complexes accumulates −ve charge on the central metal ion which is most unlikely.

e.g $[Co(NH_3)_6]^{3+}$

Co^{3+} ⟶ +3

$e^{\ominus}$ pair from ligand −6

−3 (charge on metal ~~at~~ ion)

(ii) Another objection is that electron pair used by H_2O, NH_3 and many other neutral ligand for donation purpose is $2s^2$ electron pair. This $2s^2$ electron pair has no bonding characteristics, and if these electrons, in order to make them useful for bonding purpose, are excited to higher energy levels, there is required more energy than what is actually available in the bond formation. The answer to this objection may lie in the reorganisation of energy levels in the bonding atom to form hybrid orbitals.

(iii) Finally, there are complexes which are predominantly ionic in character and hence the forces acting between the central atom and the ligands may be regarded as essentially electrostatic. Fluoro complexes of metal provide examples of such ~~th~~ type of complexes.

Pauling suggested that the accumulation of undue −ve charge on the central metal ion can be prevented if it is assumed that the metal-ligand bond has some ionic character (electro-neutrality principle) and in addition to σ-bond, the central atom also forms a π-bond with the ligand (π-bonding in complexes).

Electroneutrality principle:

Pauling's electroneutrality principle states that in a complex species the charge tend to get distributed in such a manner so that no atom in a complex has a resultant charge greater than about ±1.

A complex would be most stable when the electronegativity of ligand allows sharing of the electron pairs such that the metal achieves a condition of essentially zero net electrical charge.

The distribution of electron charge over the complex species may be estimated from the % ionic character of the bonds on the basis of the difference of electronegativity between linked atoms.

$$\left[\%\text{ of ionic character} = 18 \times (\chi_A - \chi_B)^{1.4} \quad \text{or} \quad 16(\chi_A - \chi_B) + 3.5(\chi_A - \chi_B)^2 \right]$$

The following examples illustrate the application of the principle

$[Be(H_2O)_4]^{2+}$ Electronegativity of Be = 1.5

" " O = 3.5

Difference = 2.0

∴ % of ionic character of Be—O bond = 48.

Hence, the bonds are approximately 52% covalent. Hence the 4 oxygen atoms actually donate a total of $4 \times .52 = 2.08$ valence $e^{\ominus}$ to the Be^{2+}.

Thus the netcharge on Be^{2+} ion is $-2.08 + 2 = -0.08$.

Correspondingly, each O atom may be supposed to gain $+0.52e$ charge for each Be–O linne. Actually, this is partly neutralised by the H atoms joined to them. The O–H bond is 29% ionic (from electronegativity difference = $3.5 - 2.1 = 1.4$). Now, if the O–H bond were 100% ionic, each H atom would donate one "full electron to an adjacent O. Since, the O–H bonds are only 29% ionic, the O-atom recieves in effect only $0.29e$ charge from each of two hydrogens, maxing a total of $0.58e^{\ominus}$. The 'net charge' on each O is then $0.52e \div 0.58 = -0.06e$. The net charge on each hydrogen is $+0.29e^{\ominus}$.

Thus,

Be $-.08$

4O: $4 \times -.06 = -0.24$

8H: $8 \times +0.29 = +2.32$

$[Be(H_2O)_4]^{2+}$ Total $= +2.00$.

The very low net charge nearing electroneutrality explain the existance of $[Be(H_2O)_4]^{2+}$.

For $[Be(H_2O)_6]^{2+}$.

Be : -1.12
6 O : -0.36
12 H : $+3.48$

Total : $+2.00$

Explain its non existance

$[Al(H_2O)_6]^{3+}$

Al : -0.12
6 O : -0.36
12 H : $+3.48$

Total : 3.00 explains it's existance.

$[Al(NH_3)_6]^{3+}$:

Al : -1.08
6 N : $+1.20$
18 H : $+2.88$

Total : 3.00 (explain its' non existance)

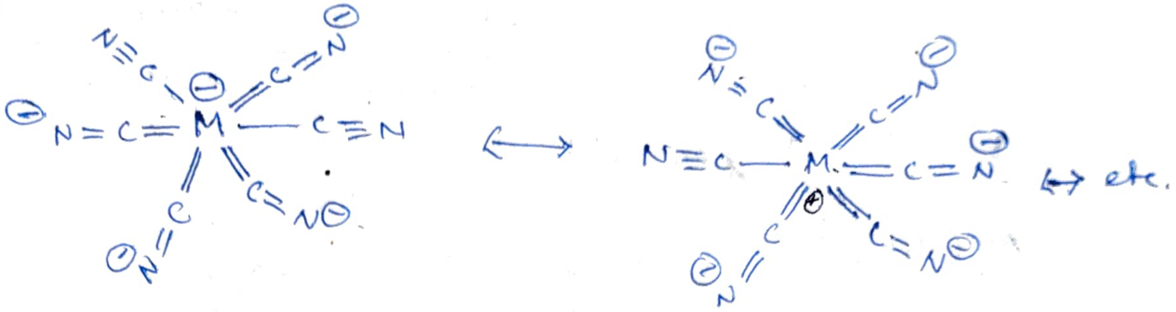
Back bonding :

There are many ligands like CO or PR_3 in which the donar atom has a low electronegativity. Though these ligands are poor electron donars, yet they form strong complexes with metals, especially in the lower oxidation states. In these cases, the electron density of the metal is reduced by backbonding or resonance involving the donation of d electrons of the metal ions to the ligand.

$$\ddot{Ni}-C\equiv O \longleftrightarrow \overset{1+}{Ni}=C=O^{\ominus}$$

Thus in carbonyls, the electron density shifts from metal to oxygen atom. This requires the use of a pure p-orbital of carbon for the acceptance of d electrons from metals, so that it is now not available for the π- bond formation with the oxygen atoms. Hence the bond order of C—O bond decreases and that of Ni—C increases.

Thus the accumulated -ve charge in cyano (or similar complexes) will be distributed to the six ligands as



The centre may actually becomes neutral / even slightly +ve, satisfies Pauling's electroneutrality principle.

✱ $M(d_\pi) \rightarrow L(p_\pi)$ / $M(d_\pi) \longrightarrow L(d_\pi)$ / $L(p_\pi) \longrightarrow M(d_\pi)$ / $L(p_\pi) \longrightarrow M(p_\pi)$

By courtesy of :

i) Advance Inorganic Chemistry
- Satyprakash, Tuli, Basu & Madan

ii) Selected topics in Inorganic Chemistry
- Malik, Tuli & Madan

iii) General & Inorganic Chemistry
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iv) Theoretical principles of Inorganic chemistry - G. S. Manku

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Theories in Co-ordination Complexes.

(VBT)

To explain the bonding in transition metal complexes, three different theories are generally proposed. These are

i) Valence Bond Theory (VBT)
ii) Crystal field Theory (CFT)
iii) Ligand Field Theory (LFT).

VALENCE BOND THEORY

The Theory was proposed and extended by Pauling and Slater in 1935, which deals with the electronic structure of central metal ion in its ground state, kind of bonding, geometry (i.e shape) and magnetic properties of the complexes. The theory based on the following assumptions–

a) The central metal atom / ion makes available a no. of ~~unpaired~~ empty s, p and d atomic orbitals equal to its co-ordination no. These vacent orbitals hybridise togather to form hybrid orbitals which are the same in no. as the AO's hybridising togather.

(b) The ligands have at least one σ- orbital containing a lone pair of electrons.

(c) Vacent hybrid orbitals of the metal atom / ion overlap with the filled σ-orbital of the ligand to form $L \xrightarrow{\sigma} M$ bond which is a co-ordinate covalent bond and shows the characteristics of both the overlapping orbitals. However, the bond has got some polarity because of the mode of its formation.

(d) The non-bonding electrons of the metal atom / ion are then arranged in the metal orbitals which do not participate in forming hybrid orbitals. The arrangement of non-bonding electrons ~~p~~ takes place according to Hund's rule.

Applying the above assumptions, the VBT ~~bead~~ explained the formation of some octahedral, square planar ~~complexes~~ and tetrahedral complexes nicely. e.g

Octahedral Complexes:

This geometry is formed by considering $(n-1)d^2 ns np^3$ or $ns np^3 nd^2$ hybridisation.

In both the cases the d- orbitals that participate in bonding are of eg set i.e d_{z^2} and $d_{x^2-y^2}$ as they are projected along the axis, to get better mixing with ns and np_x, np_y and np_z respectively.

(2)

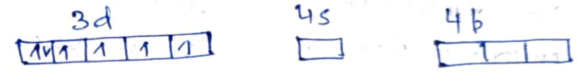
$(n-1)d^2\,ns\,np^3$ hybridisation (Inner-orbital Complex).

Pauling originally called such complex as covalent complexes as the M—L bonds are primarily co-valent in nature: According to him the electrons of $(n-1)d$ orbital of metal atom/ion are paired up to vacate two $(n-1)d$ orbital which undergoes hybridisation with one ns and three np orbitals to max 6 equivalent orbitals which are occupied by the ligand electrons to form M—L bonds.

As the d-orbitals used in the hybridisation have one quantum no. less $(n-1)$ than s orbital (ns) / p orbitals (np) have, The complexes that formed by these hybridisation are known as Inner-orbital complexes.

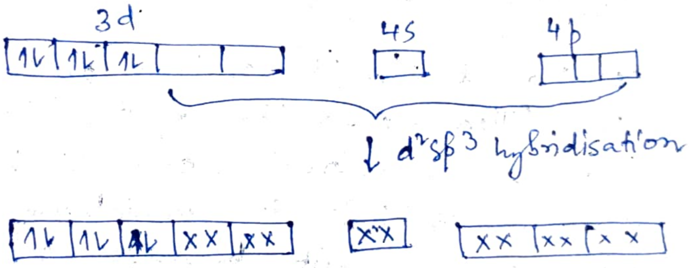
e.g $[Co(NH_3)_6]^{3+}$:

Co^{3+} (free ion) $3d^6$



to accomodate 6 pairs of $e^{\ominus}$ from ligands, the two unpair electrons first pair up to vacate two d orbitals which further undergoes d^2sp^3 hybridisation, as shown

$[Co(NH_3)_6]^{3+}$



x - denotes the electron coming from the ligand and they filled the each hybrid orbital with opposite spins.

*. The proposed diamagnetic nature of the complex (as there is no unpaired $e^{\ominus}$) was experimentally varified, supports the proposed hybridisation.

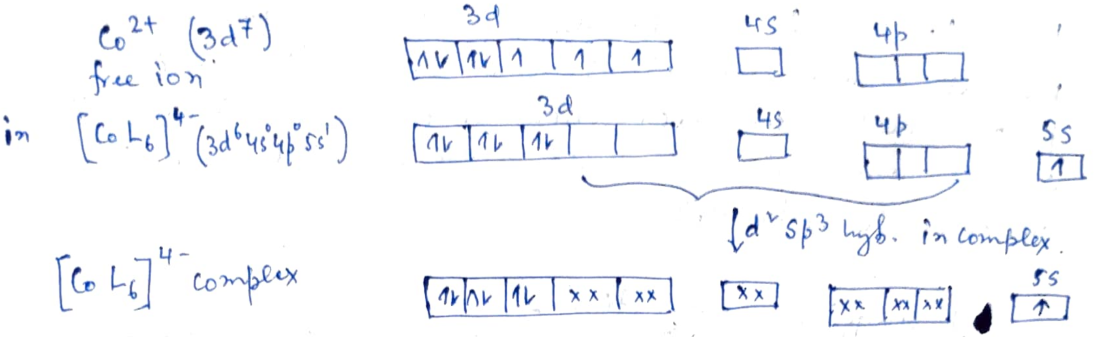
*: No. of unpaired $e^{\ominus}$ decreases during the complex formation compared to free state of the metal atom/ion. So also the spin only magnetic moment. Thus the complexes are known as spin paired or low spin complexes.

$[Co(CN)_6]^{4-}$ / $\{[Co(NO_2)_6]^{4-}\}$

Both these ions are paramagnetic corresponding to one unpaired $e^{\ominus}$. But the free ion (d^7) has three unpaired $e^{\ominus}$.

Pauling has suggested that, in order to have only one unpaired electron, ~~in eg orbitals~~ one electron of eg orbitals is forced to occupy t_{2g} orbitals and the other electron of eg set is promoted to the higher vacant 5s orbital. Then the config^n of Co^{2+} becomes $3d^6 4s^0 4p^0 5s^1$.

The formation of $[CoL_6]^{4-}$ $\{L = CN^-, NO_2^-\}$ by d^2sp^3 hybridisation has been shown as



xx - electrons ~~p~~ from the ligand L with opposite spins

The presence of unpair electron in 5s orbital is supported by the fact that since 5s orbital is of very high energy, the single electron residing in it should be unstable and hence should be easily lost. Experimentally it has been found ~~so~~ true, which supports the proposed hybridisation.

$$[CoL_6]^{4-} \xrightarrow{H_2O_2} [CoL_6]^{3-} + e$$

$ns^1 np^3 nd^2$ hybridisation (Outer-orbital Complex)

$[CoF_6]^{3-}$:

Electronic config^n of Co^{3+} ion is

Physical measurements have shown that $[CoF_6]^{3-}$ ion has paramagnetic character corresponding to the presence of four unpaired electrons in 3d-orbital. Thus d^2sp^3 hybridisation cannot predict the observed magnetic moment.

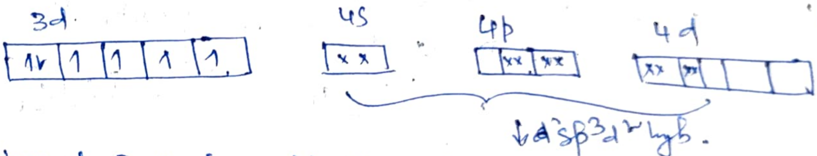
To explain its formation two suggestions have been put forward:

a) Pauling's suggestion - Pauling originally suggested that in the complex ions such as $[CoF_6]^{3-}$ ion the metal ligand bonds are primarily 'ionic' and not covalent and the d electrons in the complexe ion are, therefore, not required to pair but are allowed to remain unpaired just as they are in free Co^{3+} ion. e.g he assumed that the metal ion electrons and the ligan electrons are contained in seperated orbitals located primaril on the ligand. According to him, when electronegative lig are involved, the electrostatic bonding taxes place which does not disturb the electrons of the d-orbitals. The use of the term 'ionic' for such strongly paramagnetic compound was abandoned, when it became known that many of such paramagnetic complexes such as $Fe(acac)_3$, behave like typical covalent compounds (high volatility and high solubility in organic solvents)

b) Huggin's suggestion -

To account the paramagnetic nature of the complexes like CoF_6^{3-}. Huggin assumed that d-orbitals involved in the hybridisation to form six hybrid orbitals are not 3d but are 4d orbitals. Thus explain the paramagnetic nature ~~of~~ corresponding to four unpaired $e^{\ominus}$.

$[CoF_6]^{3-}$



xx – electron from ligand F having opposite spin.

In general, complexes which use one ns, three np and two nd orbitals to form the six sp^3d^2 hybrids are called outer-orbital complexes.

*. These complexes have magnetic moment corresponding to the no. of unpaired electron as that of free metal atom or ion.

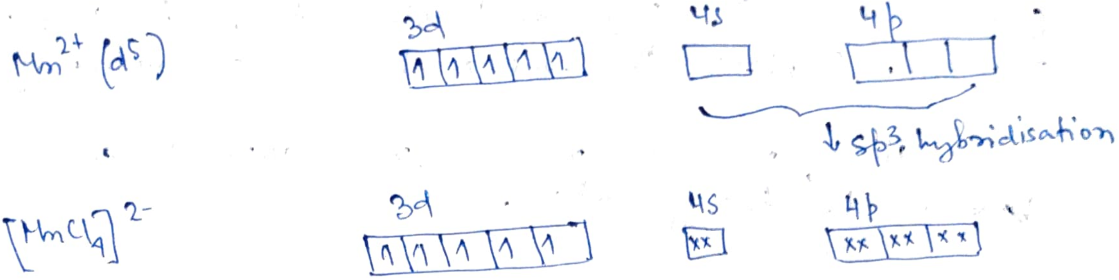
*. These complexes are known as high spin / spin free complexes.

Tetrahedral Complexes (sp^3 hybridisation)

Vacant ns and three np orbital of metal atom / ion undergoes hybridisation to form 4 sp^3 hybrid orbital which accomodate 4 pair of ligand to form tetrahedral geometry.

Thus tetrahedral complexes does not involve the metal d orbital in bonding. Hence the no. of unpaired electron in complex metal ion remain same as that of free metal ion and so the magnetic moment (spin only) e.g $[MnCl_4]^{2-}$

The configⁿ and hybridisation scheme shown below.



xx – electron pair of Cl^- with opposite spin.

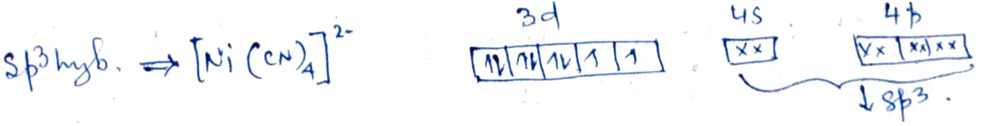
The structure shows the presence of 5 unpaired electron. Experiments also found that this ion is paramagnetic corresponding to five unpaired electron. ($\mu_s = 5.92$ B.M; $\mu_{exp} = 5.95$ B.M).

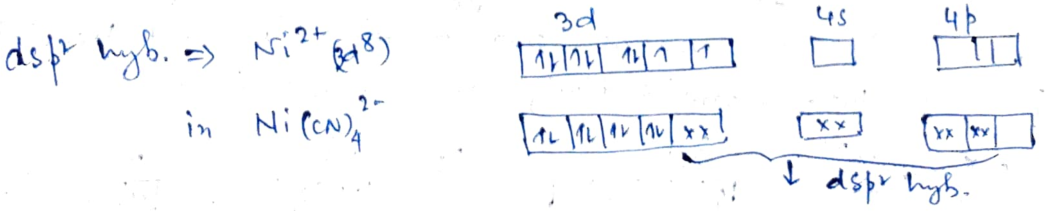
Square Planar Complexes [$(n-1)d_{x^2-y^2}$. ns . np^2 hybridisation] or ns, np^2 $nd_{x^2-y^2}$ hybridisation.

In the formation of 4 dsp^2 or sp^2d hybrid orbitals, $d_{x^2-y^2}$ orbital should be ~~of lower energy shell than the~~ is taken and p_x and p_y should be taken as the lobes are projected along x- and y- axis.

. The formation of square planar complexes by VBT can be explained by considering the complexes such as $[Ni(CN)_4^{2-}]$ and $[Cu(NH_3)_4]^{2+}$.

a). $[Ni(CN)_4]^{2-}$ – Since in the complex, CN of metal ion is 4, it can be explained by either sp^3 hybridisator or dsp^2 hybridisation as.





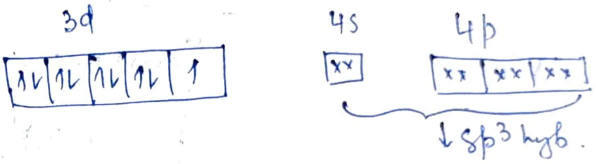
(6) Th

If The complex is tetrahedral, than it shows the magne moment, corresponds to 2 unpaired $e^{\ominus}$. On the otherha if it is square planar, then it has no magnetic mome (i.e diamagnetic). Experiment shows that it has no mag moment, supports the square planar geometry of $[Ni(CN)_4$

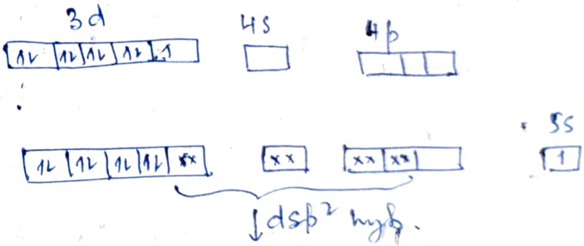
Thus, magnetic moment measurement can distinguish ~~between~~ the two geometries.

b) $[Cu(NH_3)_4]^{2+}$ – By The same line of argument we can not ~~distin~~ predict the str. of $[Cu(NH_3)_4]^{2+}$ as both the tetrahedral and square planar geometry gives same no. of unpaired electrons*. This can be shown below.
*($n=1$, found experimentally)

$[Cu(NH_3)_4]^{2+}$
tetrahedral



$[Cu(NH_3)_4]^{2+} \Rightarrow Cu^{2+} (3d^9)$
Sq. planar
In $[Cu(NH_3)_4]^{2+}$



However, physical measurements have indicated the non-existance of tetrahedral geometry.

Again Sq. planar structure with above a scheme of hybridisation has not got any support (i.e excitation of 3d e to 5s orbital) as it happens in the case of Co^{2+} ion in inner-orbital octahedral complex.

[Co^{2+} is strongly reducing while Cu^{2+} does not exhibit such property]

It is now suggested by Huggin that it has square planar shape corresponding to sp^2d hybridisation [$4s, (4p)^2$ 4d - hybridisation] is shown below

$[Cu[NH_3)_4]^{2+}$

actual str. is distorted octahedral geometry

The no. of Unpaired electrons in a given complex.

The no. of unpaired electrons (n) present in a given complex ion depends on the geometry of the complex ion and the type of hybridisation undergone by the central metal atom or ion. The relation between the no. of unpaired electrons and geometries of the complex ions are given below –

Config. of the central metal atom/ion	no. of unpaired electron			
	Inner-orbital Octahedral complexes	Outer-orbital Octahedral complexes	Tetrahedral complexes	Square planar complexes
d^1	1	1	1	1
d^2	2	2	2	2
d^3	3	3	3	3
d^4	2	4	4	4
d^5	1	5	5	3
d^6	0	4	4	2
d^7	1	3	3	1
d^8	0	2	2	0
d^9	1	1	1	1

Limitations of VBT :

i) a) Octahedral (both inner & outer orbital), tetrahedral and square. planar complexes of d^1, d^2, d^3 and d^9 ions have the same no. of unpaired electrons and hence can not be distinguished from each other on the basis of the no of unpaired electrons.

b) Similarly, Outerorbital and tetrahedral complexes of all the ions viz. $d^1 - d^9$ which have the same no. of unpaired electrons can not be distinguished from each other.

ii) VBT fails to explain the finer details of magnetic properties including the magnitude of the orbital contribution to the magnetic moments. e.g although both tetrahedral (sp^3 hybridisation) and outer orbital octahedral (sp^3d^2) complexes of Co^{2+} (d^7) have three unpaired $e^{\ominus}$, to which expected μ value is 3.87 BM. But the tetrahedral complexes generally have μ value in the range of 4.4 – 4.8 BM, while the octahedral complexes have μ value in the range 4.7 – 5.2 BM.

iii) VBT can not interpret the spectra (colour) of the complexes

iv) VBT does not give any detailed information about the magnetic properties of the complexes. In perticular it can not explain the temperature dependent paramagnetism of the complexes.

v) VBT can not account for the relative stabilities for different shapes and different co-ordination nos. in metal complexes e.g it can not satisfactorily explain as to why Co(+2) forms both O_h & T_d complexes while Ni(+2) rarely forms tetrahedral complexes. Fe^{3+} forms both T_d & O_h complex while Cr^{3+} gives only octahedral complexes.

vi) VBT can not explain as to why Cu^{+2} forms only one distorted octahedral complexes even when all the six ligands are identical.

vii) The theory cannot account for the relative rates of reactions of analogous metal complexes e.g. $[Mn(phen)_3]^{2+}$ dissociates instantly in acidic aq. solution while $[Fe(phen)_3]^{2+}$ dissociates at a slow rate. It does not explain

The mechanism of the complexes.

viii) VBT fails to distinguish the geometry by only magnetic moments. e.g $[Ni(CN)_4]^{2-}$ in tetrahedral & sq. planar form contains one unpaired $e^{\ominus}$.

ix) VBT neglects the excited states of the complexes. Hence, no thermodynamic properties can be predicted.

X) Too much stress is given to metal ion whereas the ligands field is ignored.

Problems:

① Show that all octahedral complexes of Ni^{2+} must be outer-orbital complexes.

② The magnetic moment of $[MnBr_4]^{2-}$ is 5.9 B.M. What is the geometry of this complex ions?

③ Using VBT for $[Ag(NH_3)_2]^+$ and $[Ag(CN)_2]^-$ ions, predict type of hybridisation involved, geometry of the ions and magnetic moment.

④ Discuss the geometry of $[HgI_3]^-$ ion on the basis of valence bond theory.

⑤ What is the difference between inner-orbital octahedral complexes and outer-orbital octahedral complexes.

⑥ On the basis of VBT, answer the following questions for the four-co-ordinated complex compounds or ions.

$[Ni(dmg)_2]$, $[NiCl_4]^{2-}$, $[Ni(CO)_4]^0$, $[Cu(NH_3)_4]^{2+}$, $[Cu(CN)_4]^{2-}$, $[MnX_4]^{2-}$ (X = halide ions), $[CoX_4]^{2-}$ [$X = Cl^-, Br^-, I^-, NCS^-$] $[Zn(CN)_4]^{2-}$, $[Zn(NH_3)_4]^{2+}$, $[ZnCl_2(NH_3)_2]$

i) What is the oxidation state of the central metal atom/ion.

ii) What type of hybridisation is involved

iii) What is the geometry and magnetic behaviour of the complex ion/compounds?

iv) Calculate the $\mu_{\text{spin only}}$ value?

⑦ On the basis of VBT, predict the no. of unpaired electrons in $[NiCl_4]^{2-}$, $[Ni(CN)_4]^{2-}$ & $[Cu(NH_3)_4]^{2+}$ ions.

(14) a

⑧ On the basis of VBT, explain the following.

i) $[NiCl_4]^{2-}$ & $[Ni(CO)_4]$ both are tetrahedral but differ in their magnetic properties.

ii) A square planar complex of divalent metal having the outer config^n as $ns^1 (n-1) d^{10}$ is not oxidised.

⑨ Find out the value of $\mu_{\text{spin only}}$ expected for Td & square planar complexes of Ni^{2+} and Co^{2+} ions.

⑩ Draw the str. of $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$. write the hybridisation.

⑪ On the basis of VBT answer the following questions for the six-coordinated complex ions,

$[Ti(bpy)_3]^-$, $[V(H_2O)_6]^{3+}$, $[Cr(CN)_6]^{3-}$, $[CrL_6]^{3-}$ ($L = NH_3, H_2O$)
$[Mn(CN)_6]^{4-}$, $[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$,
$[Co(NH_3)_6]^{3+}$, $[CoL_6]^{3-}$ ($L = CN^-, NO_2^-$), $[Ir(NH_3)_6]^{3+}$, $[PtX_6]^{2-}$

i) what type of hybridisation is involved

ii) whether the given complex ion is inner orbital / outer orbital complex

iii) what is the magnetic behaviour of the complex ion

iv) Calculate $\mu_{\text{spin only}}$ value?

$[MnF_6]^{4-}$, $[MnF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$, $[FeF_6]^{3-}$, $[CoF_6]^{3-}$,
$[NiL_6]^{2+}$ ($L = NH_3, H_2O$), $[Fe^+(H_2O)(NO^+)]^{2+}$.

⑫ Magnetic moment value of ring compd is 3.89 B.M. Calculate the no. of unpaired electron.

⑬ which of the following geometries can Ag(III) diamagnetic complexes have: inner orbital octahedral, outer orbital octahedral, tetrahedral, square planar?

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calculate magnetic moment in each case.

14) a) The two d-orbitals used in d^2sp^3 hybridisation are d_{z^2} and $d_{x^2-y^2}$ orbitals.

b) $[Fe(CN)_6]^{4-}$ ion is a low spin complex while $[Fe(H_2O)_6]^{3+}$ ion is a high spin complex - explain by VBT.

c) $[Co(NH_3)_6]^{2+}$ and $[Co(NO_2)_6]^{4-}$ ions are easily oxidisable

d) $Fe(CO)_5$ is diamagnetic bipyramidal (dsp^3) and not diamagneti sq. pyramidal (d^2sp^2).

By Courtsey of :

i) Advanced Inorganic Chemistry - Satyaprakash, Tuli, Basu & Madan

ii) Selected Topics in Inorganic Chemistry - Malik, Tuli, Madan

iii) Theoretical principles of Inorganic Chemistry - G.S. Manku.