

Bonding Theories in Coordination Compounds

Inorganic chemists tried to use the advances in organic bonding theory and the simple ideas of ionic charges to explain bonding in coordination compounds, but found that the theories were inadequate.

In a compound such as hexaamminecobalt(III) chloride, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, the early bonding theories allowed only three atoms to be attached to the cobalt (because of its “valence” of 3). By analogy with ordinary salts, such as FeCl_3 , the chlorides were assigned this role. This left the six ammonia molecules with no means of participating in bonding, and it was necessary to develop new ideas to explain the structure.

One theory, proposed first by C. W. Blomstrand (1826-1894) and developed further by S. M. Jorgensen (1837-1914), was that the nitrogens could form chains much like those of carbon (and thus could have a valence of 5) and that chloride ions attached directly to cobalt were bonded more strongly than those bonded to nitrogen.

Blomstrand's theory allowed dissociation of chlorides attached to ammonia but not of chlorides attached directly to cobalt.

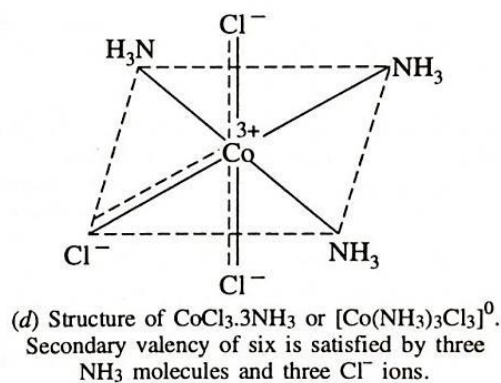
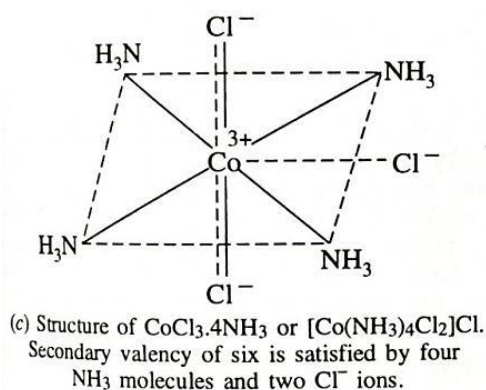
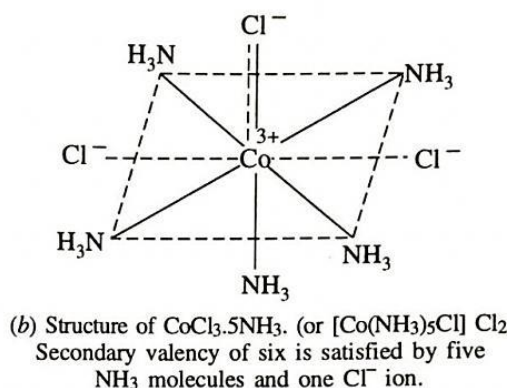
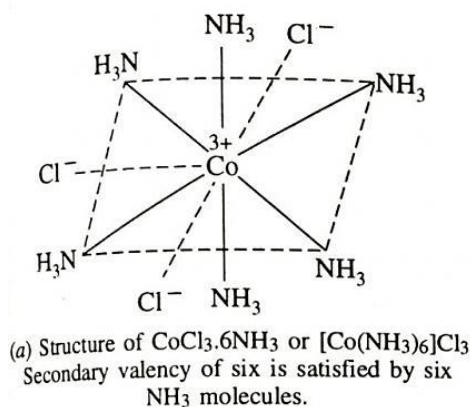
Alfred werner (1866-1919) proposed instead that all six ammonias could bond directly to the cobalt ion. Werner allowed for a looser bonding of the chloride ions; we now consider them as independent ions. The series of compounds in the following Table illustrates how both the chain theory and Werner's coordination theory predict the number of ions to be formed by a series of cobalt complexes.

Werner's theory also included two kinds of chlorides. The number of chlorides attached to the cobalt (and therefore unavailable as ions) plus the number of ammonia molecules totaled six. The other chlorides were considered less firmly bound and could therefore form ions in solution.

<i>Werner Formula (Modern Form)</i>	<i>Number of Ions Predicted</i>	<i>Blomstrand Chain Formula</i>	<i>Number of Ions Predicted</i>
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	4	$\begin{array}{c} \text{NH}_3-\text{Cl} \\ \diagup \quad \diagdown \\ \text{Co}-\text{NH}_3-\text{NH}_3-\text{NH}_3-\text{NH}_3-\text{Cl} \\ \diagdown \quad \diagup \\ \text{NH}_3-\text{Cl} \end{array}$	4
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	3	$\begin{array}{c} \text{NH}_3-\text{Cl} \\ \diagup \quad \diagdown \\ \text{Co}-\text{NH}_3-\text{NH}_3-\text{NH}_3-\text{NH}_3-\text{Cl} \\ \diagdown \quad \diagup \\ \text{Cl} \end{array}$	3
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	2	$\begin{array}{c} \text{Cl} \\ \diagup \quad \diagdown \\ \text{Co}-\text{NH}_3-\text{NH}_3-\text{NH}_3-\text{NH}_3-\text{Cl} \\ \diagdown \quad \diagup \\ \text{Cl} \end{array}$	2
$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$	0	$\begin{array}{c} \text{Cl} \\ \diagup \quad \diagdown \\ \text{Co}-\text{NH}_3-\text{NH}_3-\text{NH}_3-\text{Cl} \\ \diagdown \quad \diagup \\ \text{Cl} \end{array}$	2

Postulates of Werner's Coordination Theory :

- 1- In complex compounds, the central metal atom exhibits two types of valency:
 *Primary valency, In modern terminology, the primary valency of the metallic atom in a complex compound is equal to the oxidation state (oxidation number) of that metal.
 **Secondary valency, In modern terminology the secondary valency of the metallic atom in a complex compound is equal to the coordination number of that metal.
- 2- The metal atom always tends to satisfy both of its valencies.
- 3- The secondary valencies have directional nature, since the species satisfying the secondary valency (ligands) are directed towards the fixed positions in space.



When a given ammine is treated with an aqueous solution of AgNO_3 , some Cl^- ions get precipitated as AgCl . The number of Cl^- ion precipitated is the number of Cl^- ions that are ionizable and hence are present outside the coordination sphere.

$[\text{CoCl}_3 \cdot 3\text{NH}_3]$ gives no precipitate, showing that all the three Cl^- ions are present in the coordination sphere.

<i>Molecular and structural formula of amines</i>	<i>Ionisation of ammine</i>	<i>Number of particles (ionic or molecular) as determined by cryoscopic measurements</i>	<i>Molar conductance, Λ_m (ohm⁻¹ cm²)</i>
Co (III) amines CoCl ₃ .6NH ₃ or [Co(NH ₃) ₆]Cl ₃ CoCl ₃ .5NH ₃ or [Co(NH ₃) ₅ Cl]Cl ₂ CoCl ₃ .4NH ₃ or [Co(NH ₃) ₄ Cl ₂]Cl CoCl ₃ .3NH ₃ or [Co(NH ₃) ₃ Cl ₃] ⁰ (Non-electrolyte)	$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \rightarrow [\text{Co}(\text{NH}_3)_6]^{3+} + 3\text{Cl}^-$ $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2 \rightarrow [\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+} + 2\text{Cl}^-$ $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \rightarrow [\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+ + \text{Cl}^-$ $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]^0 \rightarrow \text{No ionisation}$	4 3 2 0	390 262 102 0 ↓ Decreasing
Pt (IV) amines PtCl ₄ .6NH ₃ or [Pt(NH ₃) ₆]Cl ₄ PtCl ₄ .5NH ₃ or [Pt(NH ₃) ₅ Cl]Cl ₃ PtCl ₄ .4NH ₃ or [Pt(NH ₃) ₄ Cl ₂]Cl ₂ PtCl ₄ .3NH ₃ or [Pt(NH ₃) ₃ Cl ₃]Cl PtCl ₄ .2NH ₃ or [Pt(NH ₃) ₂ Cl ₄] ⁰ (Non-electrolyte)	$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4 \rightarrow [\text{Pt}(\text{NH}_3)_6]^{4+} + 4\text{Cl}^-$ $[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3 \rightarrow [\text{Pt}(\text{NH}_3)_5\text{Cl}]^{3+} + 3\text{Cl}^-$ $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2 \rightarrow [\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^{2+} + 2\text{Cl}^-$ $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl} \rightarrow [\text{Pt}(\text{NH}_3)_3\text{Cl}_3]^+ + \text{Cl}^-$ $[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]^0 \rightarrow \text{No ionisation}$	5 4 3 2 0	524 404 230 97 0 ↓ Decreasing

Werner used compounds with four or six ligands in developing his theories, with the shapes of the coordination compounds established by the synthesis of isomers. For example, he was able to synthesize only two isomers of the $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ ion. The possible structures with six ligands are octahedral, trigonal prismatic, trigonal antiprismatic, and hexagonal (either planar or pyramidal).

Werner's synthesis and separation of optical isomers proved the octahedral shape conclusively, because none of other six-coordinate geometries could have similar optical activity.

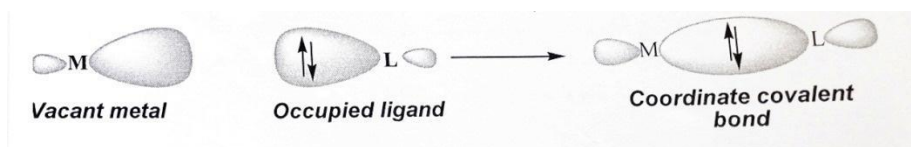
In a similar way, other experiments were consistent with square-planar Pt(II) compounds, with the four ligands at the corners of a square. Only two isomers are found for $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.

Valence Bond Theory (VBT)

The valence bond theory, originally proposed by Pauling in the 1930s, uses the hybridization ideas. This theory deals with the electronic structure of the central metal ion in its ground state, kind of bonding, geometry and magnetic properties of the complexes.

Assumptions of valence bond theory

- 1- The central metal atom or ion makes available a number of empty s, p, and d atomic orbitals equal to its coordination number. These vacant orbitals hybridize together to form hybrid orbitals which are the same in number as the atomic orbitals hybridizing together. These hybrid orbitals are vacant, equivalent in energy and have definite geometry.
- 2- The ligands have at least one σ -orbital containing a lone pair of electrons.
- 3- Vacant hybrid orbitals of the metal atom or ion overlap with the filled orbitals of the ligands to form ligand \rightarrow metal bond.
- 4- The non-bonding electrons of the metal atom or ion are then rearranged in the metal orbitals (pure d, s or p orbitals) which do not participate in forming the hybrid orbitals.



Coordination number of the central metal atom/ion	Type of hybridisation undergone by the central metal atom/ion	Geometry of the complex	Examples of complexes
2	$sp(4s, 4p_x)$	Linear or diagonal	$[\text{CuCl}_2]^-$, $[\text{Cu}(\text{NH}_3)_2]^+$ etc.
3	$sp^2(4s, 4p_x, 4p_y)$	Trigonal planar or equilateral triangular	$\left[\text{Cu}^+ \left(\text{S}=\text{C} \begin{array}{c} \text{NH}-\text{CH}_2 \\ \\ \text{NH}-\text{CH}_2 \end{array} \right)_3 \right]^+$, $[\text{Cu}^+\text{Cl}(\text{tu})_2]^0$ (distorted trigonal planar) etc.
4	$dsp^2(3d_{x^2-y^2}, 4s, 4p_x, 4p_y)$	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{PdCl}_4]^{2-}$
4	$sp^2d(4s, 4p_x, 4p_y, 4d_{x^2-y^2})$	Square planar	$[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{Pt}(\text{NH}_3)_4]^{2+}$ etc.
4	$sp^3(4s, 4p_x, 4p_y, 4p_z)$	Tetrahedral	$[\text{NiCl}_4]^{2-}$, $[\text{Cu}(\text{CN})_4]^{3-}$, $\text{Ni}(\text{CO})_4$ etc.
5	$dsp^3(3d_{z^2}, 4s, 4p_x, 4p_y, 4p_z)$	Trigonal bipyramidal	$\text{Fe}(\text{CO})_5$, $[\text{CuCl}_5]^{3-}$, $[\text{Ni}^{2+}(\text{triars}) \text{Br}_2]^0$
5	$dsp^3(3d_{x^2-y^2}, 3d_{z^2}, 4s, 4p_x, 4p_y, 4p_z)$	Square pyramidal	$[\text{Co}^{2+}(\text{triars}) \text{I}_2]^0$, $[\text{Ni}(\text{CN})_5]^{3-}$ etc.
6	$d^2sp^3(3d_{x^2-y^2}, 3d_{z^2}, 4s, 4p_x, 4p_y, 4p_z)$	Inner-orbital octahedral	$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{3-}$ etc.
6	$sp^3d^2(4s, 4p_x, 4p_y, 4p_z, 4d_{x^2-y^2}, 4d_{z^2})$	Outer-orbital octahedral	$[\text{Fe}^+(\text{NO}^+)(\text{H}_2\text{O})_5]^{2+}$, $[\text{CoF}_6]^{3-}$ etc.

Geometry of 6-coordinated complex ion

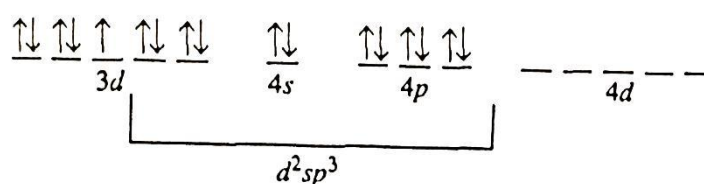
In all these complex ions the coordination number of the central metal atom or ion is six and hence these complex ions have octahedral geometry. This octahedral geometry arises due to d^2sp^3 or sp^3d^2 hybridization of the central metal atom or ion. The number of unpaired electrons, measured by the magnetic behavior of compounds, determines which d orbitals are used.

Octahedral complexes in which the central atom is d^2sp^3 hybridized called inner-orbital octahedral complexes while the octahedral complexes in which the central atom is sp^3d^2 hybridized are called outer-orbital octahedral complexes.

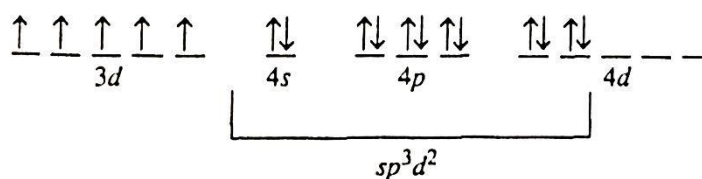
Fe(III) has five unpaired electrons as an isolated ion, one in each of the 3d orbitals. In octahedral coordination compounds, it may have either one or five unpaired electrons. In complexes with one unpaired electron, the ligand electrons force the metal d electrons to pair up and leave two 3d orbitals available for hybridization and bonding.

In complexes with five unpaired electrons, the ligands do not bond strongly enough to force pairing of 3d electrons. Pauling proposed that the 4d orbitals could be used for bonding in such cases.

For a d^5 metal ion:
Inner orbital



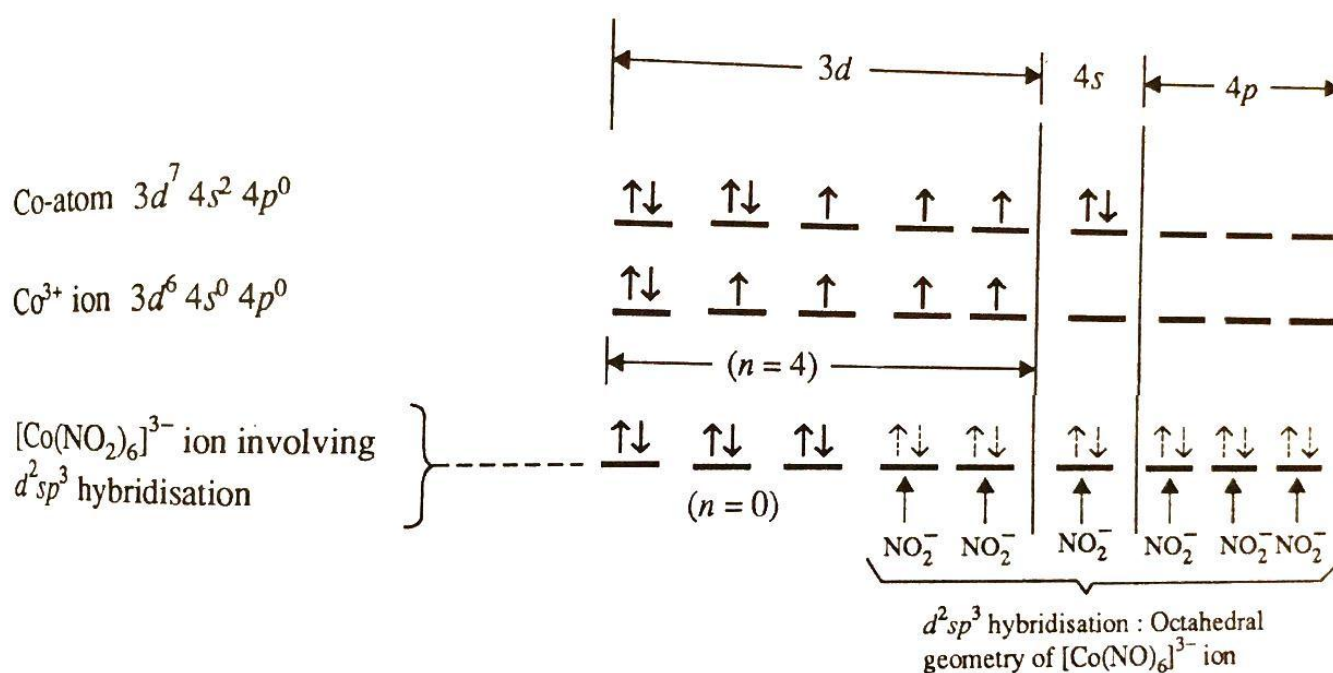
For a d^5 metal ion:
Outer orbital



d^2sp^3 Hybridization in Inner Orbital Octahedral Complexes

This type of hybridization takes place in those octahedral complexes which contain strong ligands. The ligand electrons force the metal d electrons to pair up and leave two 3d orbitals available for hybridization and bonding. Two (n-1) d-orbitals, one ns and three np orbitals combine together and form six d^2sp^3 hybrid orbitals.

Examples: $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{NO}_2)_6]^{3-}$



sp^3d^2 Hybridization In Outer Orbital Octahedral Complexes

This type of hybridization takes place in those octahedral complexes which contain weak ligands. Weak ligands do not bond strongly enough to force pairing of the 3d electrons. Pauling proposed that the 4d orbitals could be used for bonding in such cases.

Examples: $[\text{FeF}_6]^{3-}$ and $[\text{CoF}_6]^{3-}$

Geometry of 4-coordinated complex ions

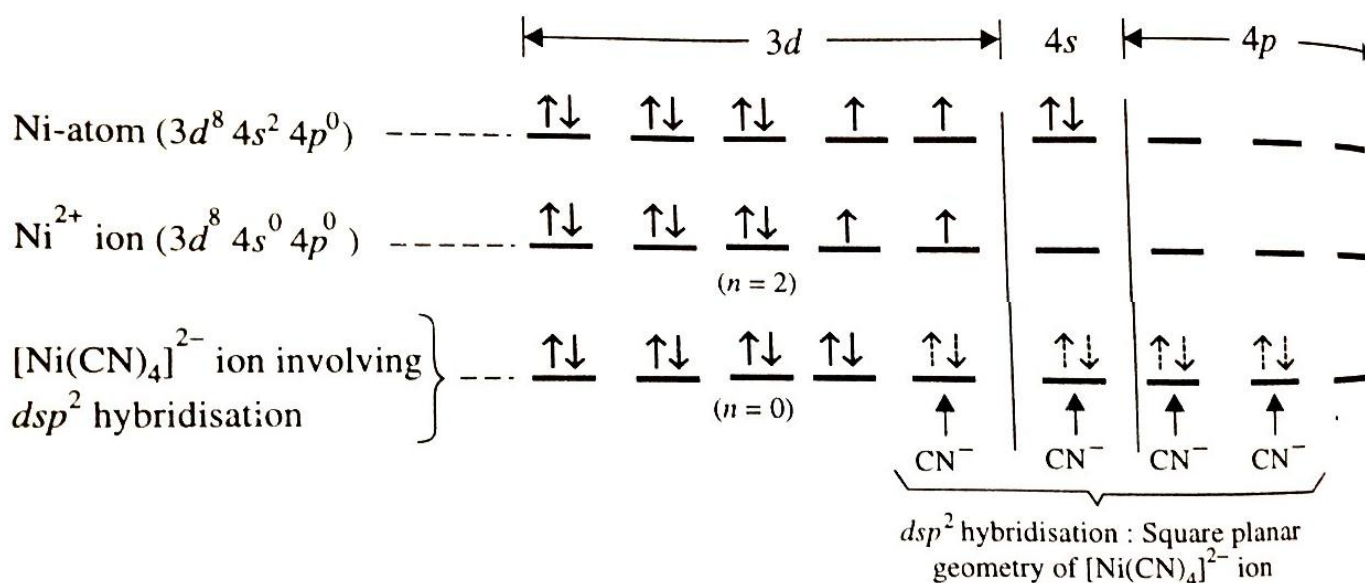
In these complex ions the coordination number of the central atom or ion is four. Such complex ions may have either square planar or tetrahedral geometry, depending on whether the central atom or ion is dsp^2 or sp^3 hybridized.

Square Planar Complex Ions



In this complex ion, since the coordination number of Ni^{2+} ion is 4, the given complex ion may be square planar or tetrahedral in shape. In order to decide whether the given complex ion is square planar or tetrahedral, we take the help of magnetic property of complex ion.

Experimentally it has been shown that $[\text{Ni}(\text{CN})_4]^{2-}$ ion has no unpaired electron ($n = 0$) and hence is diamagnetic. This magnetic property confirms the fact that this complex ion has square planar geometry with $n = 0$ and not tetrahedral geometry with $n = 2$. For getting this geometry, Ni^{2+} ion should be dsp^2 hybridized. In this hybridization, due to the energy made available by the approach of four CN^- ions (ligands), the two unpaired 3d-electrons are paired up, thereby, making one of the 3d orbitals empty. This empty 3d orbital is used in dsp^2 hybridization. This hybridization makes all the electrons paired ($n = 0$).

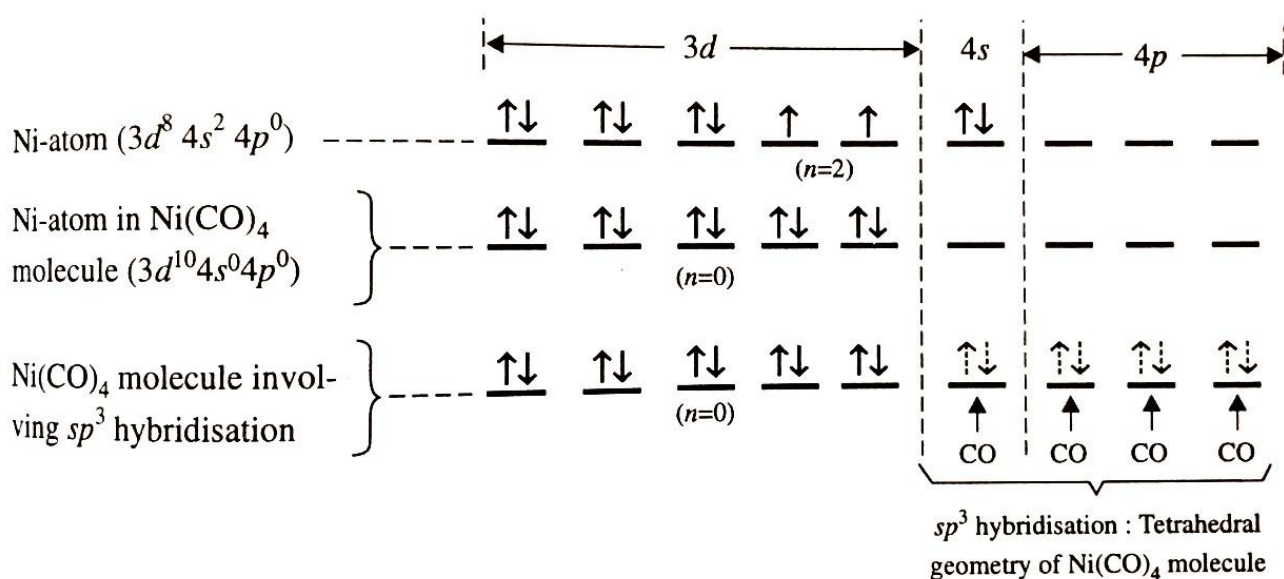


Tetrahedral Complex ion

[Ni(CO)₄] molecule

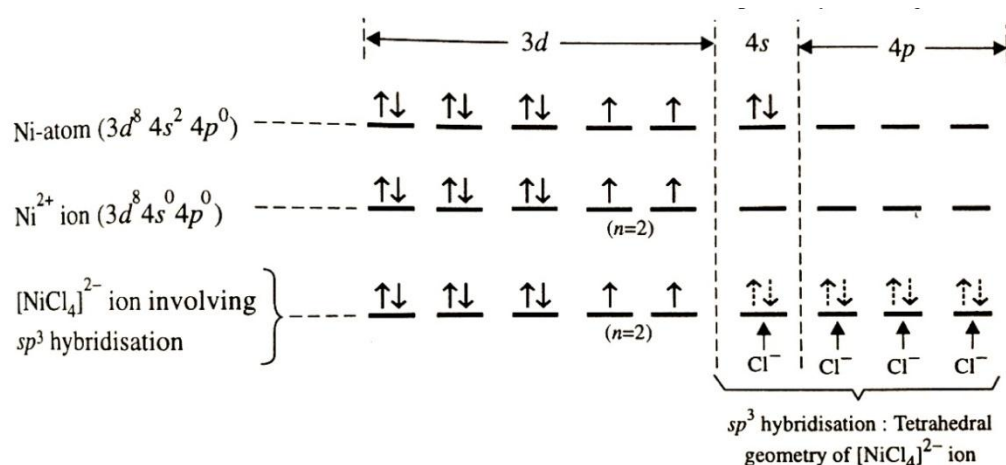
In this complex compound Ni is in zero oxidation state and its valence-shell configuration as $3d^8 4s^2$. This compound has tetrahedral geometry which arises due to sp^3 hybridization of Ni atom.

The magnetic studies of $Ni(CO)_4$ have indicated that this molecule is diamagnetic ($n = 0$), showing that the two $4s$ electrons are forced to pair up with $3d$ orbitals. This results in sp^3 hybridization and $Ni(CO)_4$ molecule has tetrahedral structure.



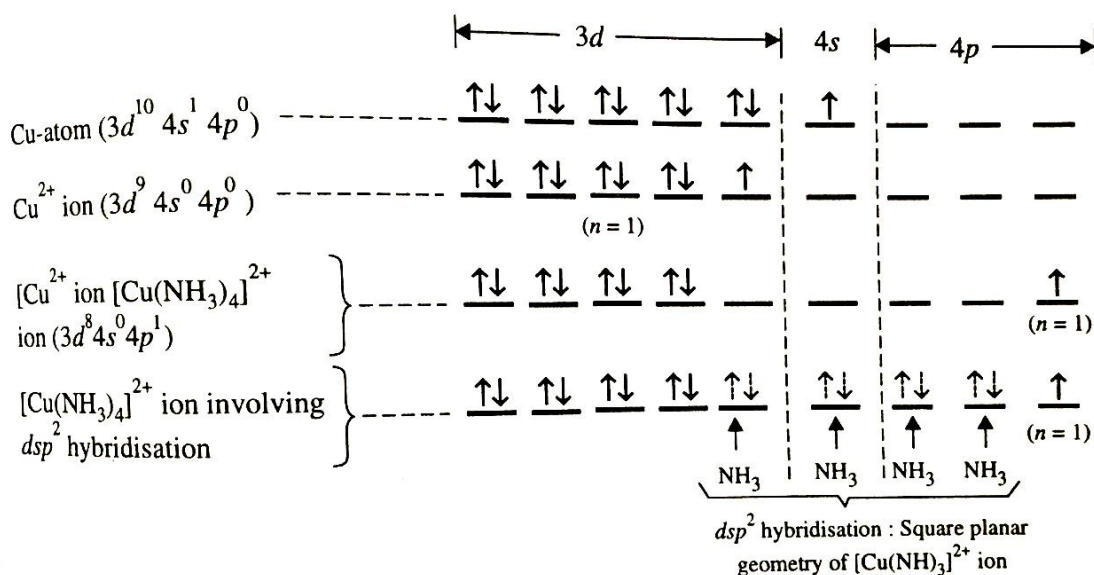
[NiCl₄]²⁻ ion

This complex ion has Ni^{2+} ion whose valence-shell configuration as $3d^8 4s^0$. Magnetic measurements reveal that the given ion is paramagnetic and has two unpaired electrons ($n = 2$). This is possible only when this ion is formed by sp^3 hybridization and has tetrahedral geometry.



Limitation of VBT

1- VBT does not predict the exact geometry of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion.



As an evident from the Figures that in both the geometries, $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion has one unpaired electron ($n = 1$). In square planar geometry, the unpaired electron resides in 4p orbital while in tetrahedral geometry this electron is present in 3d orbital.

The magnetic property of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion cannot be helpful in deciding as to what is the exact geometry of the complex ion. However, physical measurement have indicated that the tetrahedral geometry is not possible.

Now if the square planar geometry for $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion is supposed to be correct, the unpaired electron present in the higher energy 4p orbital (dsp^2 hybridization)

should be expected to be easily lost ($[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion should be easily oxidized to $[\text{Cu}(\text{NH}_3)_4]^{3+}$ ion by losing the unpaired electron residing in 4p orbital). However experiments have shown that this oxidation does not occur.

- 2- VBT cannot interpret the spectra (color) of the complexes.
- 3- This Theory does not predict or explain the magnetic behaviours of complexes. This theory only predict the number of unpaired electrons.