

Course CHB-401 (B.Sc. SEM-IV)

Inorganic Chemistry

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CONTENTS

- 1. Double Salts*
- 2. Coordination or Complex Compounds*
- 3. Ligands*
- 4. Denticity of Ligands and Classification*
- 5. Werner's Theory*
- 6. Sidgwick's EAN Concept*
- 7. Valence Bond Theory*
- 8. Nomenclature of Coordination Compounds*
- 9. Isomerism*

1. DOUBLE SALTS

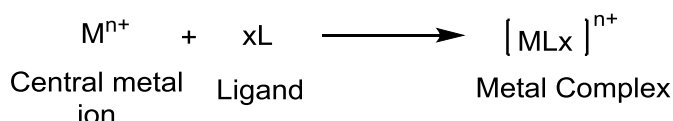
These are combination of two simpler salts and dissociate into their constituent ions in the solution.

These exist only in the crystalline states.

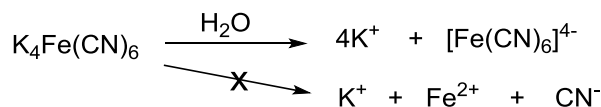
Examples: $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Carnallite)
 $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (Mohr's Salt)
 $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ (Potash Alum)
 $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ (Chrome Alum)

2. COORDINATION OR COMPLEX COMPOUNDS

These compounds do not lose their identity in the solution and also, do not give test of their constituent ions. These are formed from the combination of central metal atom or ion and electron donating groups (ligands).



Example:



3. LIGANDS (LEWIS BASES)

Molecules or ions which can donate electron pair or pairs to the central metal atom or ion in a coordination compound.

Oxygen donor ligands: H_2O , ROH , R_2O

Nitrogen donor ligands: NH_3 , RNH_2 , R_2NH , R_3N , pyridine

Halide anions: F^- , Cl^- , Br^- , I^-

σ -donor and π -acceptors: CO , CN^- , Phosphines (PR_3), NO

π -electron donor ligands: Organic molecules which do not have lone pair but have π -electrons-alkenes, alkynes, benzene

4. DENTICITY OF LIGANDS

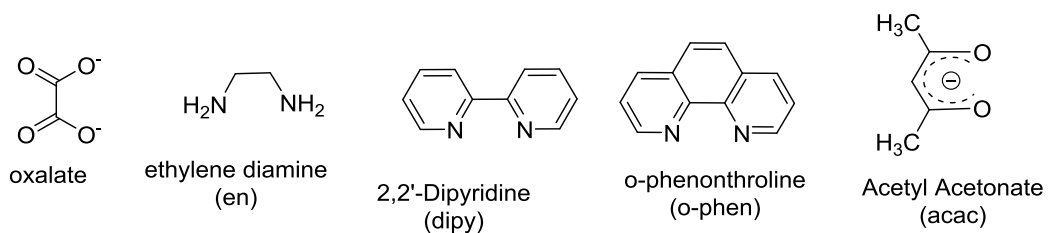
This represents number of sites in a ligand by which it can bind with metal ion in a coordination compound.

Classification of Ligands based on denticity

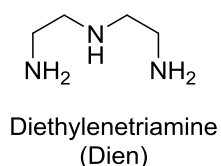
Monodentate ligand - one binding site

H₂O, NH₃, Cl⁻, CO etc.

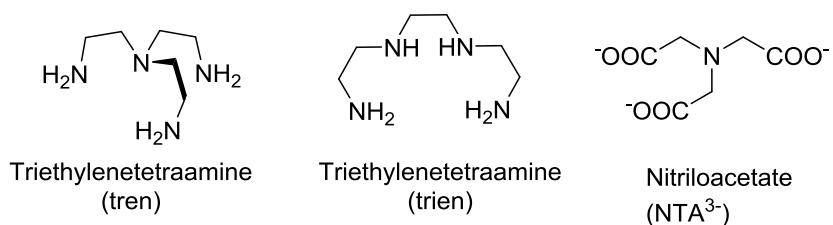
Bidentate ligand – two binding sites



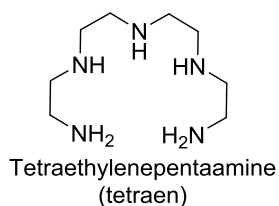
Tridentate ligand – three binding sites



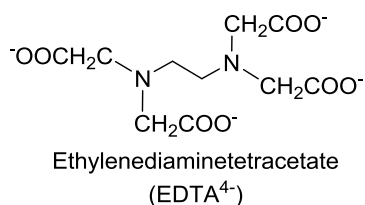
Tetradentate ligand – Four binding sites



Pentadentate ligand – Five binding sites



hexadentate ligand – Six binding sites



5. WERNER THEORY (1893)

The most successful attempt to explain the formation of coordination compounds was made by Alfred Werner in 1893. (Alfred Werner was first inorganic chemist to get Nobel Prize in 1913). The basic postulates of Werner's theory can be summarized as follows:

1. In coordination compounds, there are two types of valencies
 - (a) Primary or Principal valency : Ionizable and non-directional
 - (b) Secondary or Auxiliary valency : Nonionizable and directional
2. Primary valencies are satisfied by negative ions but secondary valencies are satisfied by either negative ions or neutral molecules.
3. The number of secondary valency is fixed for a metal.
4. The secondary valencies are oriented in the fixed positions in the space. This is related to the geometry of the coordination compound.

In complex ML_6 with coordination number 6 (coordination number is another name of secondary valency), there are three possible arrangements of ligand (L) around metal (M) namely a planar hexagon, a trigonal prism and an octahedron (Fig. 1)

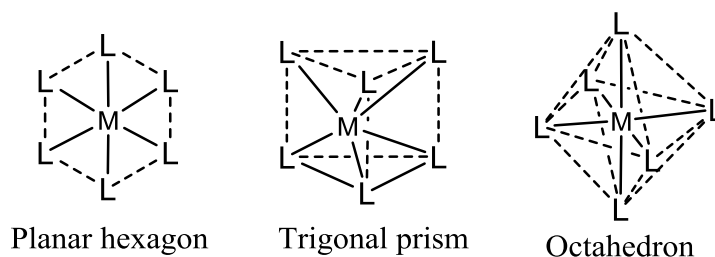


Fig.1: Possible arrangements of L around M in ML_6

Werner find out how many isomeric forms of a complex can be prepared in the laboratory and he compared this with the theoretical number for each of the possible shape or geometry (Table 1).

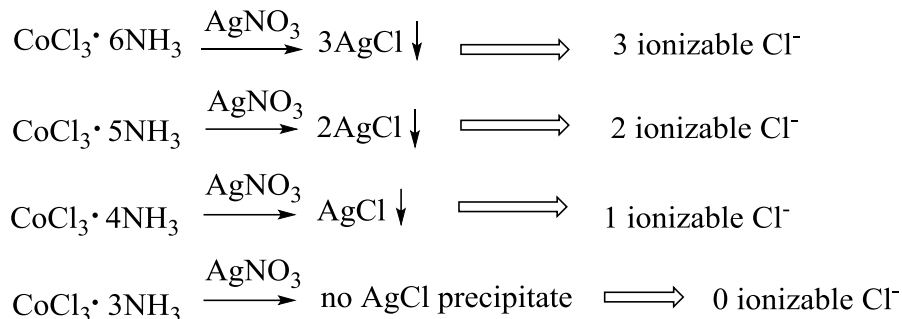
Table 1: Number of isomers predicted and experimentally found

Complex	Planar hexagon	Trigonal prism	Octahedron	Experimental
ML_6	1	1	1	1
ML_5L'	1	1	1	1
$ML_4L'_2$	3	3	2	2
$ML_3L'_3$	3	3	2	2

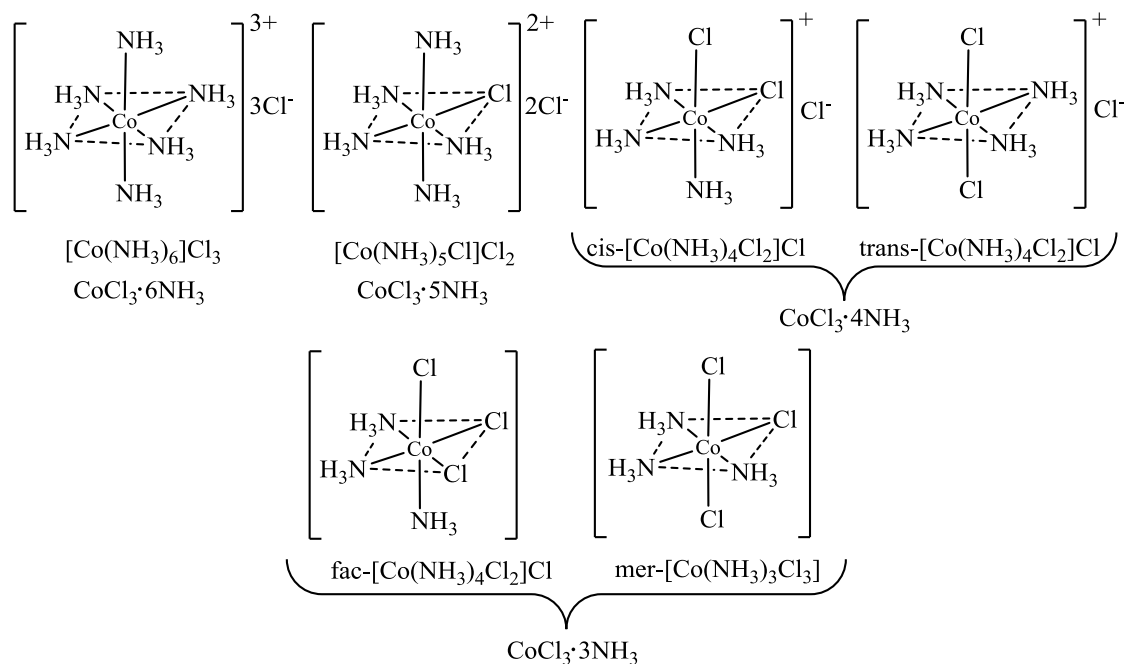
These results strongly suggested the shape or geometry of ML_6 is octahedral. However, this was not absolute proof of shape since correct experimental condition for preparing all isomers may not have been found.

Interpretation of Werner's Theory with Example

Werner synthesized a series of compounds with varied $\text{CoCl}_3:\text{NH}_3$ ratio and deduced the structures on the basis of experimental observations.



We can write formulae and structures of these complexes as:



Verification of Werner's Theory

Later experiments on molar conductivity measurement showed that structure proposed by Werner were correct and were in agreement with following:

Complex	Ionizable Cl^-	Total Charges	Molar Conductance ($\text{mol}^{-1}\text{ohm}^{-1}\text{cm}^2$)
$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$	3	6	~432
$[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$	2	4	~262
$[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$	1	2	~100
$[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$	0	0	0

The molar conductivity of cobalt complexes are comparable with known simple ionic compounds:

Complex	Total Charges	Molar Conductance ($\text{mol}^{-1}\text{ohm}^{-1}\text{cm}^2$)
$\text{NaCl} \longrightarrow \text{Na}^+ \text{Cl}^-$	2	~120
$\text{BaCl}_2 \longrightarrow \text{Ba}^{2+} 2\text{Cl}^-$	4	~260
$\text{LaCl}_3 \longrightarrow \text{La}^{3+} 3\text{Cl}^-$	6	~393.5

Similarly, Werner was able to predict the shapes/geometries of $[\text{Pt}^{\text{II}}(\text{NH}_3)_2\text{Cl}_2]$ and $[\text{Pd}^{\text{II}}(\text{NH}_3)_2\text{Cl}_2]$ as **square planar** because he isolated two different isomers.

LIMITATIONS

1. Werner's theory is purely based on experimental observations. He did not give any theoretical basis of secondary valency.
2. The geometries of complexes were predicted on the basis of number of isolated isomers. However, it is not essential that all isomers could be prepared and isolated.
3. Secondary valency is also satisfy by positive ions e.g. NO^+
4. It does not explain color, magnetic and thermodynamic properties of the coordination compounds.

6. SIDGWICK'S EFFECTIVE ATOMIC NUMBER (EAN) CONCEPT

At the time of development of Werner's theory, the theory of electronic structure of metal was unknown. To explain the Werner theory in electronic concept, Sidgwick introduced the idea of a coordinate bond. According to him, secondary valency proposed by Werner is special form of covalent bond in which bonding electrons are furnished by a donor and accepted by an acceptor. Once bond is formed it is not different from the covalent bond. For example in $[\text{Co}(\text{NH}_3)_6]^{3+}$, Co^{3+} accepts 12 electrons from six NH_3 molecules.

Sidgwick also introduced the concept of effective atomic number (EAN). *According to EAN rule, when forming a complex, ligands are added until the total number of electrons on the metal ion plus electrons donated by ligands becomes the same as the number of electrons in the next inert gas.*

$\text{EAN} = [\text{Atomic number} - \text{electrons lost in cation formation} + \text{electrons gained by coordination}]$

OR

$\text{EAN} = [\text{Atomic number} + \text{electrons gained in anion formation} + \text{electrons gained by coordination}]$

Examples

KMnO_4 EAN of Mn = $25 - 7 + 8 = 26$

$\text{K}_4[\text{Fe}(\text{CN})_6]$ EAN of Fe = $26 - 2 + 12 = 36$

$\text{K}_3[\text{Fe}(\text{CN})_6]$ EAN of Fe = $26 - 3 + 12 = 35$

$[\text{Ni}(\text{CO})_4]$ EAN of Ni = $28 - 0 + 8 = 36$

$[\text{V}(\text{CO})_6]^-$ EAN of V = $23 + 1 + 12 = 36$

$[\text{V}(\text{CO})_5]^{3-}$ EAN of V = $23 + 3 + 10 = 36$

LIMITATIONS

1. Although this rule is invariably obeyed by binary metal carbonyl complexes (exception $\text{V}(\text{CO})_6$) and a number of complexes, there are large number of exceptions.
2. This rule unable to explain geometrical shapes of complexes.
3. This does not help to interpret the magnetic, spectral and thermodynamic behavior of complexes
4. According to this rule many electron pairs are accepted by metal ion which would result accumulation of negative charge on the metal. This is a serious problem and is against the electropositive nature of the metals.

7. VALENCE BOND THEORY (VBT)

Pauling in 1931 was able to predict the geometries of many metal complexes on the assumption that hybrid orbitals are involved in the formation of coordination complexes. The main features of VBT are:

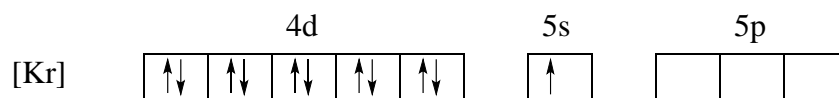
1. Each ligand is assumed to donate a pair of electron to the metal ion to form a coordinate covalent M–L bond.
2. The central metal ion makes available a number of hybrid orbitals (equal to coordination number) for the formation of M–L bond.
3. A σ –bond arises from the overlap of a vacant metal hybrid orbital and a filled orbital of ligand.
4. In addition to σ –bond, there is possibility of π –bond formation by overlap of filled d-orbital of metal with vacant orbital of ligand.

Coordination Number	Geometry	Hybridization	Examples
2	Linear	$sp(sp_z)$	$[Ag(NH_3)_2]^+$
3	Trigonal planar	$sp^2(sp_xp_y)$	$[Ag(PR_3)_3]$
4	Tetrahedral	$sp^3(sp_xp_y p_z)$	$[Ni(CO)_4]$
		$sd^3(sd_{xy}d_{yz}d_{xz})$	$[MnO_4]^-$
	Square Planar	$dsp^2(d_{x^2-y^2}sp_xp_y)$	$[Ni(CN)_4]^{2-}$
5	Trigonal bipyramidal	$sp^3d(sp_xp_y p_z d_{z^2})$	$[CuCl_5]^{3-}$
	Square pyramidal	$sp^3d(sp_xp_y p_z d_{x^2-y^2})$	$[VO(acac)_2]$
6	Octahedral (outer orbital complex)	$sp^3d^2(sp_xp_y p_z d_{x^2-y^2}d_{z^2})$	$[Cu(H_2O)_6]^{2+}$
	Octahedral (inner orbital complex)	$d^2sp^3(d_{x^2-y^2}d_{z^2}sp_xp_y p_z)$	$[Fe(CN)_6]^{4-}$

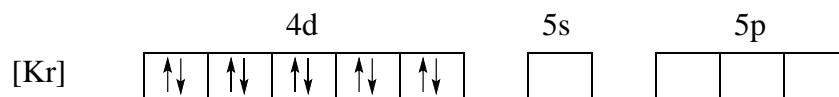
Let's consider few examples to explain their geometries:



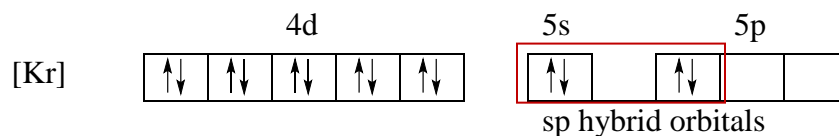
Ground state electronic configuration of ⁴⁷Ag is [Kr]4d¹⁰4s¹



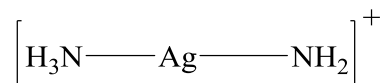
Since, Ag is in 1+ oxidation state in the complex, ground state electronic configuration of Ag⁺ is



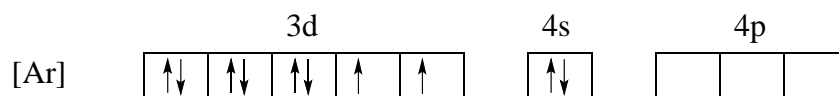
Two electron pairs from two NH₃ molecules will be accommodated in the sp hybrid orbitals as shown below:



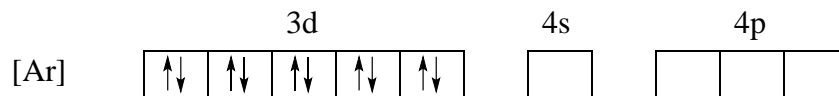
Accordingly, geometry will be linear.



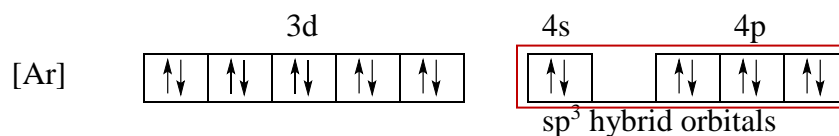
Ground state electronic configuration of ²⁸Ni is [Ar]3d⁸4s²



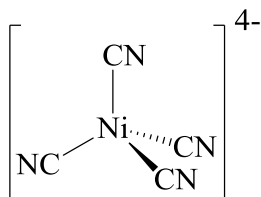
Since, Ni is in zero oxidation state in the complex ion, the above electronic configuration will be same for complex also. CN⁻ is ligand in the complex and it has tendency to pair the unpaired of electrons in the metal ion. Accordingly, excited state electronic configuration will be



Four electron pairs from 4 CN⁻ ligands will be accommodated in the sp³ hybrid orbitals as shown below:



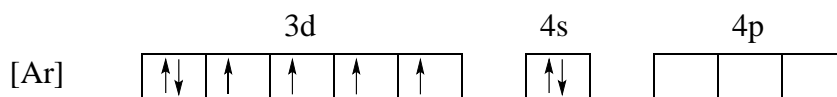
Accordingly, geometry will be tetrahedral. Complex is diamagnetic because does not contain unpaired electron.



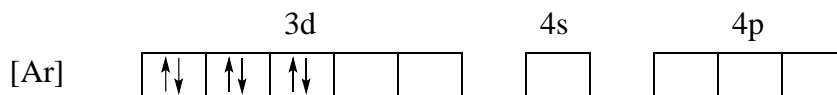
(Note: In general carbon and nitrogen donor ligands have tendency to pair the unpaired electrons but oxygen and halogen donor ligands do not)



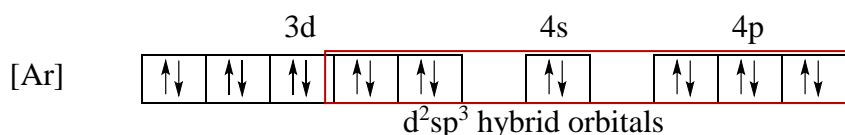
Ground state electronic configuration of ²⁶Fe is [Ar]3d⁶4s²



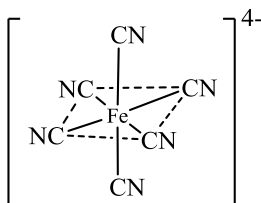
Since, Fe is in 2+ oxidation state in the complex ion and CN⁻ is ligand, excited state electronic configuration will be



Six electron pairs from 6 CN⁻ ligands will be accommodated in the d²sp³ hybrid orbitals as shown below:

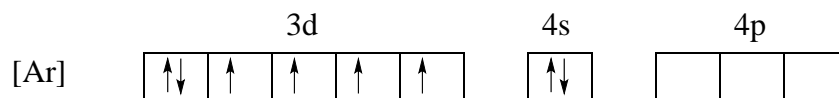


Accordingly, geometry will be octahedral (inner orbital complex because inner shell d-orbitals involved in the bonding). Complex is diamagnetic because does not contain unpaired electron.

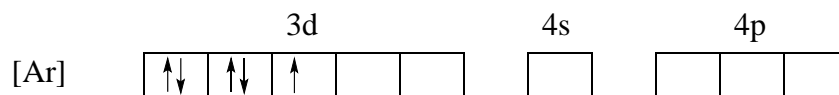


[Fe(CN)₆]³⁻

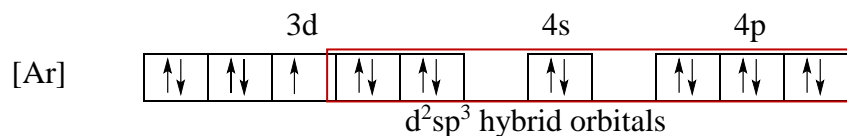
Ground state electronic configuration of ²⁶Fe is [Ar]3d⁶4s²



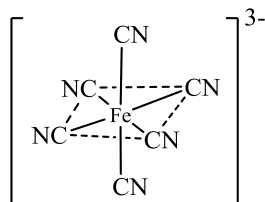
Since, Fe is in 3+ oxidation state in the complex ion and CN⁻ is ligand, excited state electronic configuration will be



Six electron pairs from 6 CN⁻ ligands will be accommodated in the d²sp³ hybrid orbitals as shown below:

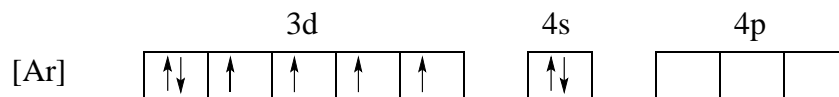


Accordingly, geometry will be octahedral. Complex is paramagnetic because it contains one unpaired electron.

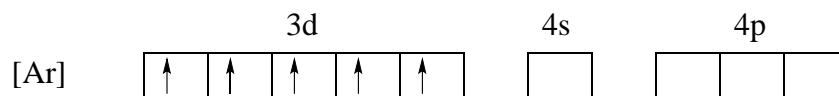


[FeF₆]³⁻

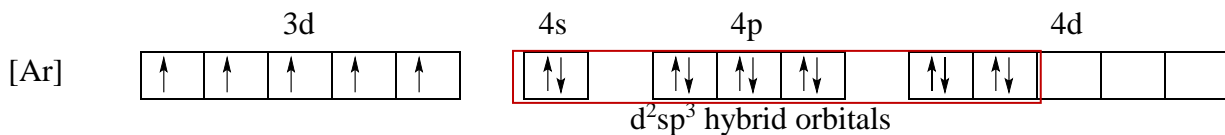
Ground state electronic configuration of ²⁶Fe is [Ar]3d⁶4s²



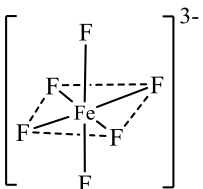
Since, Fe is in 3+ oxidation state in the complex ion and F⁻ is ligand, excited state electronic configuration will be



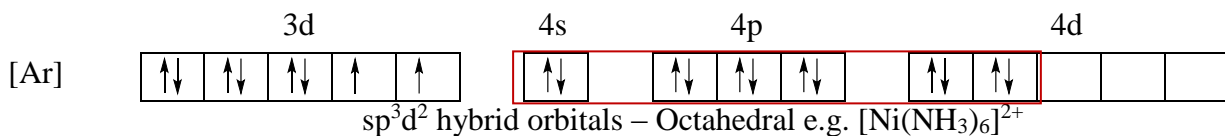
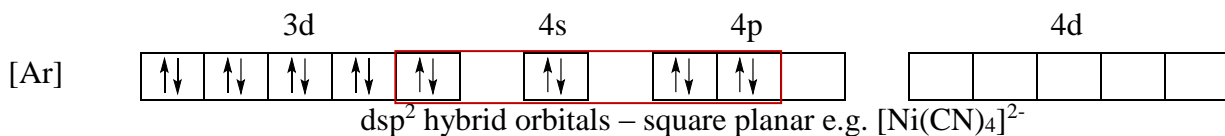
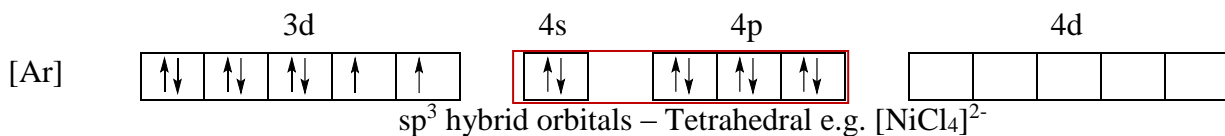
Six electron pairs from 6 F⁻ ligands will be accommodated in the sp³d² hybrid orbitals as shown below:



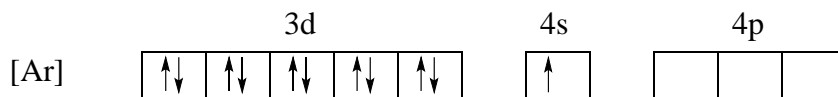
Accordingly, geometry will be octahedral (outer orbital complex because outer shell d-orbitals involved in the bonding). Complex is paramagnetic because it contains five unpaired electron.



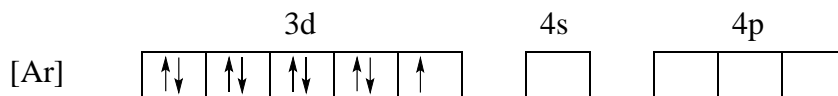
Ni²⁺ ion can adopt any of the following configurations:



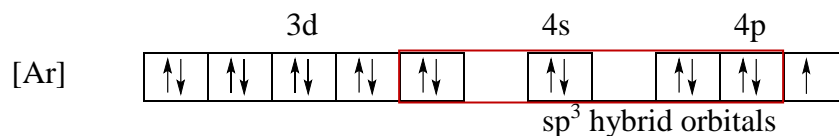
V.B. Theory failed to explain the geometry of [Cu(NH₃)₄]²⁺. Ground state electronic configuration of ²⁹Cu is [Ar]3d¹⁰4s¹



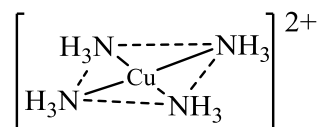
Cu is in 2+ oxidation state in the complex ion, the excited state electronic configuration will be



The observed geometry for this complex is square planar and hence hybridization would be dsp^2 . This was explained by promotion of one unpaired electron from 3d orbital to higher energy 4p orbital leaving one 3d orbital vacant which is participated in the hybridization. Four electron pairs from 4 NH_3 ligands will be then accommodated in the dsp^2 hybrid orbitals as shown below:



Accordingly, geometry will be square planar. Complex is paramagnetic because it contains one unpaired of electron.



LIMITATIONS

1. It cannot predict whether a coordination compound will be tetrahedral or square planar e.g. $[Cu(NH_3)_4]^{2+}$ is a planar complex but V.B. theory failed here to interpret the structure.
2. It is also failed to predict whether a complex is inner orbital complex or outer orbital complex.
3. It does not predict any distortion in symmetrical complexes (John-Teller distortions).
4. It does not attempt to explain the color of the complexes.
5. It cannot explain the temperature dependent paramagnetism of the complexes.

8. NOMENCLATURE OF COORDINATION COMPOUNDS

The basic rules of nomenclature are:

1. Name the cation first and then anion with space.

2. Naming of complex portion

(a) Number of Ligands: use di, tri, tetra, penta, hexa OR if necessary then bis, tris, tetrakis etc.

(b) Naming of Ligands:

- In alphabetical order, regardless of their charges.
- Anions end in 'o'. This replaces the final 'e' when the anion ends with '-ide', '-ate' or '-ite' as '-ido', '-ato', or '-ito' (2005 IUPAC recommendations). Formerly, '-ide' was changed to '-o' (e.g. chloride as chloro and cyanide as cyano etc)

F ⁻	Flourido	CH ₃ COO ⁻	Acetato	O ₂ ⁻	Superoxido
Cl ⁻	Chlorido	H ⁻	Hydrido	SCN ⁻	Thiocyanato-S
Br ⁻	Bromido	OH ⁻	Hydroxido	NCS ⁻	Thiocyanato-N
I ⁻	Iodido	O ²⁻	Oxido	NO ₂ ⁻	Nitrito-O
CN ⁻	Cyanido	O ₂ ²⁻	Peroxido	NO ₂ ⁻	Nitrito-N

- Neutral ligands as such except

NH ₃	ammine	CO	carbonyl
H ₂ O	aqua	NO	nitrosyl

- NO⁺ nitrosylium

(c) If complex is anionic, Latin name of metal will end with 'ate'. Otherwise metal will named as such if complex is cation or neutral.

Metal	Latin name changed to	Metal	Latin name changed to
Fe	ferrate	Cr	chromate
Cu	cuprate	Ni	nickelate
Ag	argentate	Co	cobaltate
Au	aurate	Al	Aluminate

(d) Oxidation state of metal will be written in Roman numeral in small bracket: (0), (I), (II), (III) etc

(e) Bridging complex: Bridging ligands are separated by ‘ μ ’ for one bridging ligand or ‘di- μ ’ for two bridging ligands or ‘tri- μ ’ for three bridging ligands.

(f) For optical isomers use Δ or Λ and geometrical isomers cis- or trans- and fac- (facial) or mer- (meridional)

Examples

$K_4[Fe(CN)_6]$	potassium hexacyanidoferrate(II)
$[CoCl(NH_3)_5]SO_4$	pentaamminechloridocobalt(III) sulfate
$[Cu(H_2O)_6]^{2+}$	hexaaquacopper(II)
$K_2[CuBr_4]$	potassium tetrabromidocuprate(II)
$K_2[Hg(SCN)_4]$	potassium tetrathiocyanato-Smercurate(II)
$K_2[Zn(NCS)_4]$	potassium tetrathiocyanato-Nzincate(II)
$[Co(NH_3)_6]Cl_3$	hexaamminecobalt(III) chloride
$[Pt(NH_3)_4] [PtCl_4]$	tetraammineplatinum(II) Tetrachloridoplatinate(II)
$[PtCl_2(NH_3)_2]$	<i>cis</i> - and <i>trans</i> -diamminedichloridoplatinum(II),
$[(NH_3)_4Co(OH)(NH_2)Co(NH_3)_4]Cl_4$	μ -amido- μ -hydroxidobis[(tetramminecobalt(III))] chloride
$[(NH_3)_3Co(OH)_3Co(NH_3)_3]^{3+}$	tri- μ -hydroxidobis[(triamminecobalt(III))]
$[(NH_3)_5Co-O_2-Co(NH_3)_5](NO_3)_5$	μ -superoxidobis[(pentaamminecobalt(III))] nitrate
$[Ru(PPh_3)_3Cl_3]$	<i>mer</i> - and <i>fac</i> -trichlorotris(triphenylphosphine)ruthenium(III)
$Mn_2(CO)_{10}$	bis(pentacarbonylmanganese) (Mn–Mn)

9. ISOMERISM

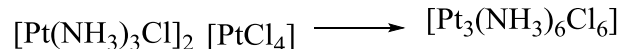
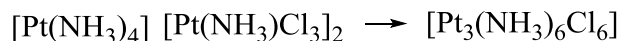
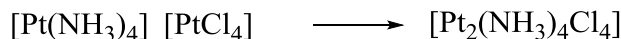
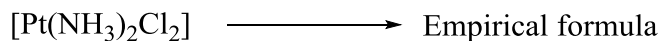
Compounds having same molecular formula but different structural arrangements called isomers and this phenomenon known as isomerism. Because of complicated formulae of coordination compounds many types of bonds and shapes are possible and therefore, these compounds show many types of isomerism.

A. STRUCTURAL ISOMERISM

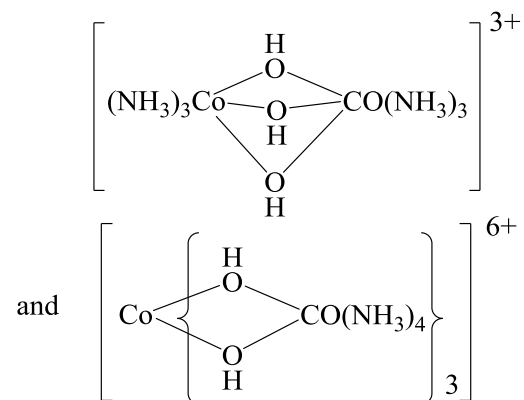
They differ in connectivity of ligands. These are various types:

(I) **Polymerization Isomerism**: These isomers have same empirical formula but different molecular weights.

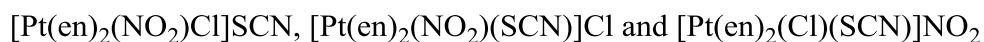
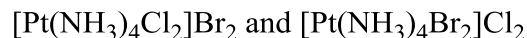
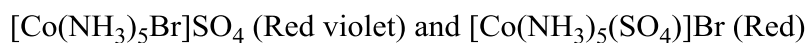
e.g. (1)



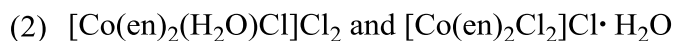
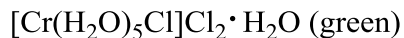
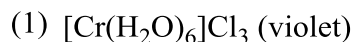
(2)



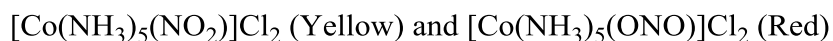
(II) Ionization Isomerism: This is due to exchange of ligands between the complex ion and ions outside it. These isomers give different ions in the solution.



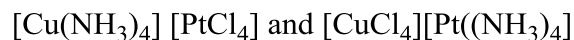
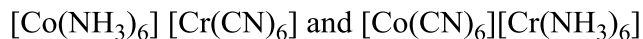
(III) Hydrate Isomerism: This is a special kind of ionization isomerism in which H_2O molecule replaces other ligands.



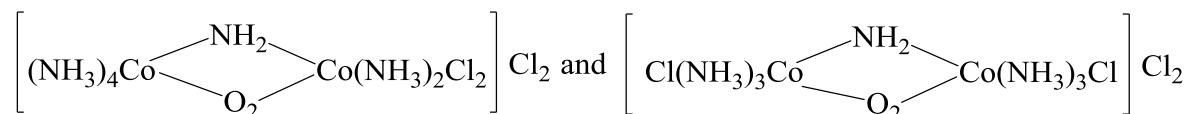
(IV) Linkage Isomerism: This occurs when there is an ambidentate ligand in the complex.



(V) Coordination Isomerism: This occurs because of ligand exchange between cation and anion complexes.



(VI) Coordination Position Isomerism: This occurs because of ligand interchange between different metal nuclei of a polynuclear complex.



B. STEREOISOMERISM

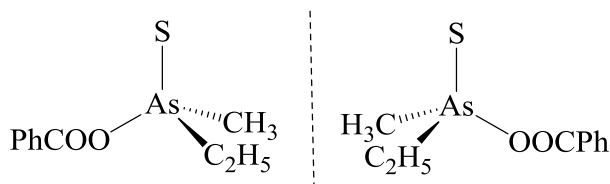
This occurs because of different orientations of ligands in the space. There are two types of stereoisomerism (i) Geometrical Isomerism and (ii) Optical Isomerism.

Stereoisomerism in Complexes with Coordination Number 4: Two principal geometries are possible for complexes with C.N. 4: Tetrahedral and Square Planar

Tetrahedral Complexes

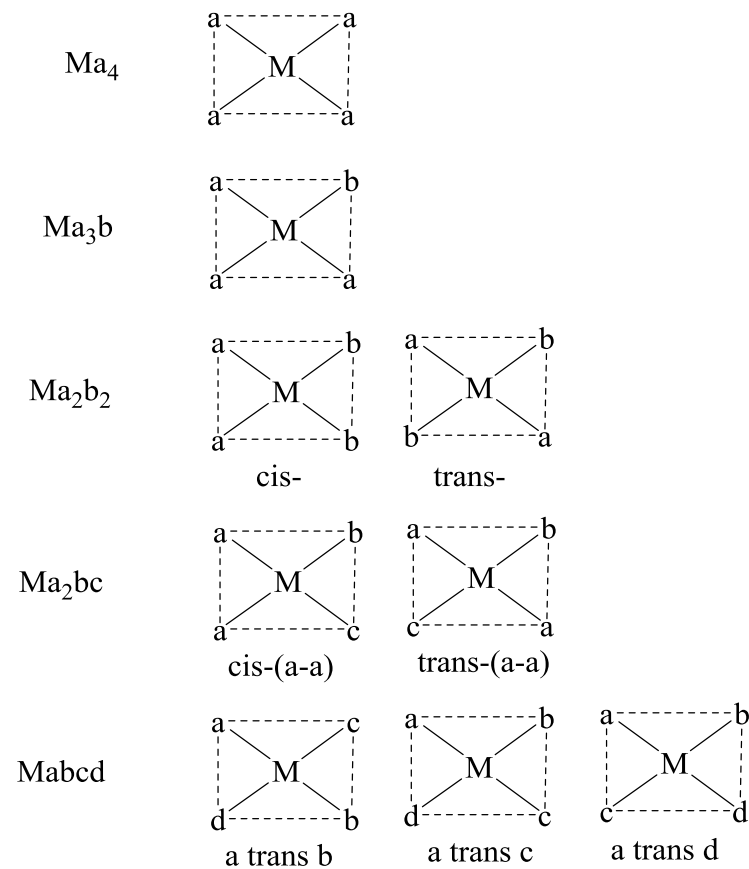
- Geometrical isomerism: This is not possible because all four ligands are adjacent to each other.
- Optical Isomerism: If plane of symmetry and center of symmetry are absent then complex may be optically active.

Optical isomerism is possible only in those tetrahedral complexes in which central metal atom is bonded with four different ligands and such complex called as asymmetric.



Square Planar Complexes

Geometrical Isomerism

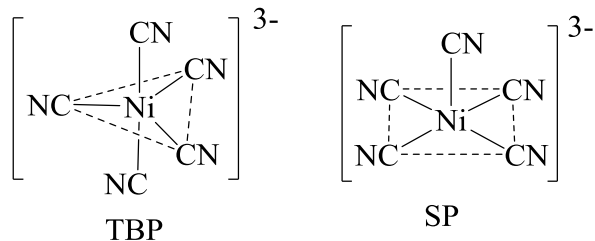


a,b,c and d = monodentate ligand

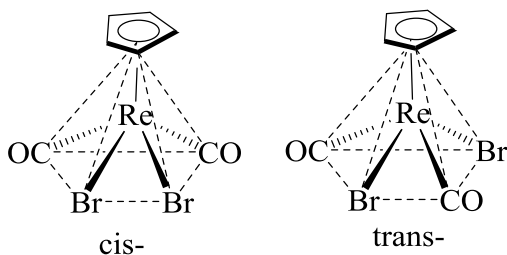
Optical Isomerism: Optically inactive because of plane of symmetry (molecular plane)

Stereoisomerism in Complexes with Coordination Number 5

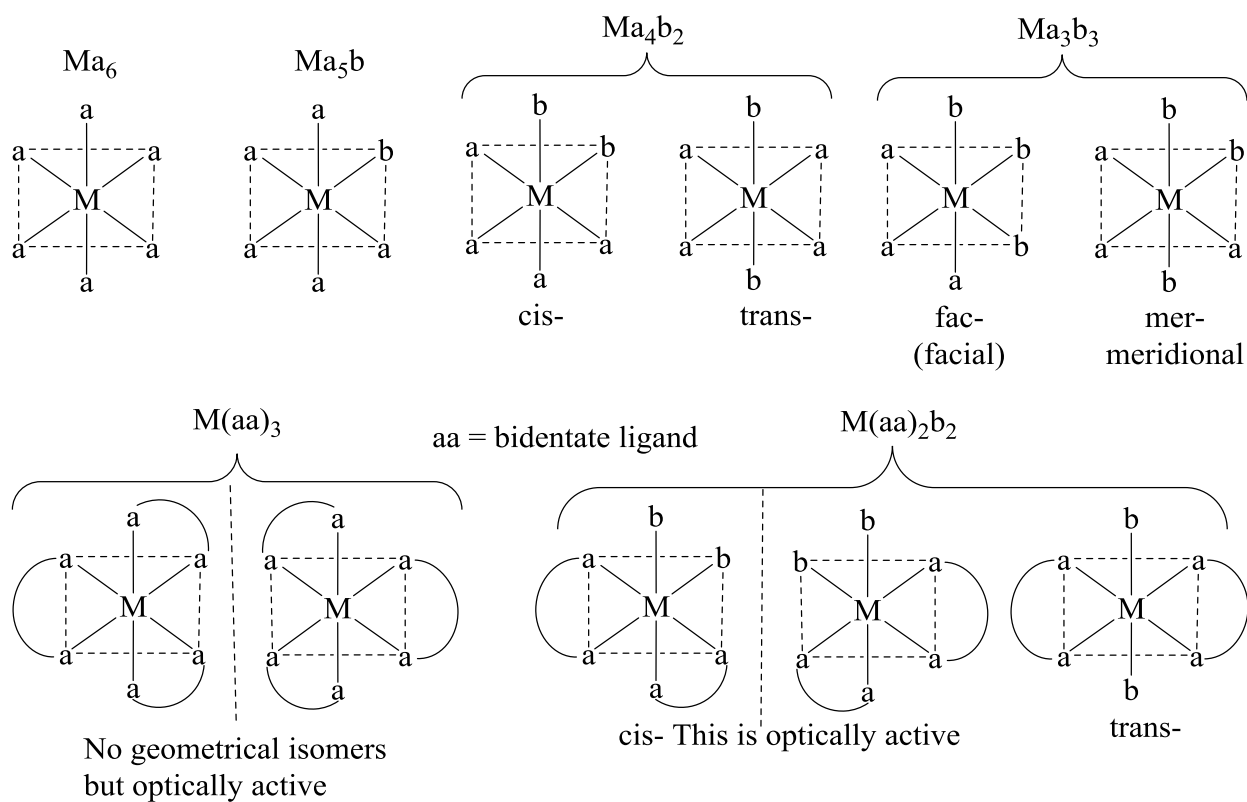
The complexes with coordination number 5 are less common but recently interest has been increased rapidly. Regular and distorted trigonal bipyramidal (TBP) and square pyramidal (SP) geometries are shown by these complexes. The energy difference between TBP and SP is very small. Hence, one geometry easily converted to another which gives the condition of polytopal isomerism. For example $[\text{Ni}(\text{CN})_5]^{3-}$ can adopt either TBP or SP geometry.



Cis- and trans-isomerism is also possible.



Stereoisomerism in Complexes with Coordination Number 6: Geometrical and optical Isomerism



Further Reading:

1. Concise Inorganic Chemistry, J.D. Lee
2. Inorganic Chemistry, J.E. Huheey, E.A. Keiter and R.L. Keiter,