CYL120 (INORGANIC)  Prof. A. K. Ganguli

Organic:
Prof Nalin Pant
Minor I & II

J D Singh

(i) Transition metal complexes: Crystal field theory, basic concepts, crystal field effects in linear (ML2), tetrahedral, square planar (ML4) and octahedral geometry (ML6), pairing energies, weak field and strong field case, crystal field stabilization energy, factors affecting magnitude of 10Dq, high and low spin complexes, evidences for crystal field stabilization, tetragonal distortions from octahedral geometry, electronic spectra and magnetism.

(ii) Organometallics: EAN rule, metal carbonyls – synthesis, bonding and structure, metalloccenes – synthesis and properties, Homogeneous and heterogeneous catalysis.

(iii) Bioinorganic chemistry: Metalloporphyrins, metalloproteins, hemoglobin and myoglobin – structure and function.


(all lectures till from September 19 to October 17, 2012)
MS-709, TEL: 1511; email: ashok@chemistry.iitd.ac.in

October 18 to Nov 16: Prof J D Singh

Quiz (October)

Major Exam: AKG & JDS (inorganic)
1. Transition metal complexes – **REVISION** of Nomenclature, Isomerism and valence bond theory 1

2. **CRYSTAL FIELD Theory** 7
   Magnetic / optical properties of complexes
   Structural distortion in metal complexes

3. Introduction to Inorganic Solids 2
Books Recommended

1. James E. HuHeey

Inorganic chemistry

2. F. A. Cotton, G. Willkinsion and P. L. Gaus


3. Shriver and Atkins : Inorganic Chemistry

( my part)

Quiz (10 marks; 30 min)

Major (20 marks; 1 hr)
Why Study Inorganic Chemistry??

Intellectual Pursuit

Practical Impact

1. Eight out top ten chemicals are Inorganic. (H$_2$SO$_4$) *max tonnage*

2. Inorganic Materials

   (Semi conductors, Light guides on linear optical materials, superconductors)  GaAs, KTaO$_3$, LiNbO$_3$, YBa$_2$Cu$_3$O$_7$

*Dupont, Monsanto, Dow Chemicals, Hercules, Baeyer, Unilever – Top Chemical Companies*
ATOMIC ORBITALS

s

p

d

f
\[ H\psi = E\psi \quad \text{Schrodinger's equation} \]

\[ \Psi = R(r) \Theta(\theta, \varphi) \]

\[ n = 1, 2, 3, \ldots \]

\[ l = 0 \text{ to } n-1 \quad \text{Quantum numbers} \]

For \( n = 1, l = 0 \)  
1s sub shell

For \( n = 2, l = 0, 1 \)

\( l = 0 \)  
2s sub shell

\( l = 1 \)  
2p sub shell

\[ M_l = -l \text{ to } +l. \]

Example \( Y_{-1}^1(\theta, \phi) = \frac{1}{2} \left( \frac{\sqrt{3}}{\sqrt{2\pi}} \right) (\sin \theta) e^{-i\phi}. \)

\[ M_l = -1, l = 1 \]
\[ \Psi_{p_x}(r) = \frac{x}{r} R'(r) \]
\[ \Psi_{p_y}(r) = \frac{y}{r} R'(r) \]
\[ \Psi_{p_z}(r) = \frac{z}{r} R'(r) \]
Transition Metal Complexes

Transition Metal?

Elements having partial filled ‘d’ or ‘f’ shell in any of their commonly occurring oxidation states.

Fe, Co, Ni, Cu, Ag, Au etc

d - block transition metals.

f - block (inner) transition metals (Lanthanides and actinides)

*Metals, variable oxidation states, hard, high melting point*
Transition metal complexes / Coordination Compounds

A central atom, ion surrounded by anions or neutral molecules, which are Lewis bases and may be monoatomic or polyatomic, neutral or anionic (ligands) are coordination compounds.

Ligand: Lewis base bonded (coordinated) to a metal ion in a coordination compound.

Monodentate, bidentate

Coordination compounds on dissolution give rise to complex ions (complexes)

\[
[\text{Retains the identity in solution}] \\
[Cr(NH}_3\text{)}_6\text{]}\text{Cl}_3 \rightarrow [Cr(NH}_3\text{)}_6\text{]}^{3+} + 3\text{Cl}^{-} \\
\text{Coordination compound} \quad \text{Complex ion}
\]
How Complexes differ from Double salts??

Double salts on dissolution in water lose their identity

\[ \text{K}_2\text{SO}_4.\text{Al}_2(\text{SO}_4)_3.24\text{H}_2\text{O} \text{ (Alum)} \rightarrow \text{K}^+, \text{Al}^{3+}, \text{SO}^{2-} \]

Dissolve in water

No complex ion

Complex ions don’t lose their identity on dissolution

\[ \text{[Co(NH}_3\text{)_6]Cl}_3 \rightarrow \text{[Co(NH}_3\text{)_6]^{3+} + 3Cl}^- \]

S. M. Jorgensen (1837 – 1914) Synthesized many transition metal complexes

A. Werner (1866 - 1919) 1st Nobel prize in Inorganic chemistry (1913) : Werner
CoCl₃ – NH₃ Complexes

<table>
<thead>
<tr>
<th>compound</th>
<th>Colour</th>
<th>Moles of AgCl</th>
<th>Werner’s formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCl₃·6NH₃</td>
<td>Yellow</td>
<td>3</td>
<td>[Co(NH₃)₆]Cl₃</td>
</tr>
<tr>
<td>CoCl₃·5NH₃</td>
<td>Purple</td>
<td>2</td>
<td>[Co(NH₃)₅Cl]Cl₂</td>
</tr>
<tr>
<td>CoCl₃·4NH₃</td>
<td>Green</td>
<td>1</td>
<td>[Co(NH₃)₄Cl₂]Cl</td>
</tr>
</tbody>
</table>

Werner’s main Study

Primary Valencies

\[ [\text{Co(NH}_3\text{)₆}]\text{Cl}_3 + 3\text{AgNO}_3 \rightarrow 3\text{AgCl} \downarrow + \text{Co(NH}_3\text{)₆}^{3+} \]

Secondary Valencies

Normally fixed for a particular ion and oxidation state.
**[Mn(H_2O)_6]SO_4**

Octahedral complex

- Coordination number is 6 (secondary valency)
- Mn^{2+} Central metal ion (lewis acid)
- H_2O Ligand (Lewis base)

Electrostatic interaction

Covalent bond
Types of Ligands

Monodentate ligands

Donate one pair of electrons to a central metal ion.

- e.g. Cl\(^-\), Br\(^-\), I\(^-\), NH\(_3\), H\(_2\)O

Bidentate ligands

They have two donor atoms

- Ethylenediamine (en)

\[
\text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2
\]

- Dimethyl glycol (glyme)

\[
\text{CH}_3\text{O} - \text{CH}_2 - \text{CH}_2 - \text{OCH}_3
\]

- Oxalate ion (oxalato)

\[
\text{COO}^- \\
\text{COO}^-
\]
More Examples

Glycinato (gly)

\[
\text{NH}_2 - \text{CH}_2 - \text{COO}^-
\]

bidentate

Iminodiacetato (imda)

\[
-\text{OOC} - \text{CH}_2 - \text{NH} - \text{CH}_2 - \text{COO}^-
\]

tridentate

Triethylenetetramine (tren)

\[
\begin{align*}
\text{NH}_2 & - \text{CH}_2 - \text{CH}_2 - \text{NH} - \text{CH}_2 \\
\text{NH}_2 & - \text{CH}_2 - \text{CH}_2 - \text{NH} - \text{CH}_2
\end{align*}
\]

tetradentate

Ethylenediamine tetraacetate (edta)

\[
\begin{align*}
-\text{OOC} - \text{CH}_2 & \\
\text{N} & - \text{CH}_2 - \text{CH}_2 - \text{N} \\
-\text{OOC} - \text{CH}_2 & \\
\text{CH}_2 & - \text{COO}^-
\end{align*}
\]

hexadentate
**Ambidentate Ligands**

- Nitro
- Thiocyanato
- Isothiocyanato

**Organic Ligands**

- 2, 2’-Bipyridine (bpy)
- 1,10 – Phenanthroline (phen)
Alkyl groups as ligands

CH₃ (methyl), CH₃CH₂ (ethyl), C₆H₅ (Phenyl)

Macrocyclic ligands

Porphyrin

tetradentate
Nomenclature of Transition metal Compounds

A. Writing the name of the complex compound

1. Designation of ligands

(a) Anionic ligands end with ‘o’

\[ \text{NO}_2^- \quad \text{nitro}, \quad \text{CN}^- \quad \text{cyano} \]
\[ \text{Cl}^- \quad \text{chloro,} \quad \text{NO}_3^- \quad \text{nitrato} \]

(b) Organic ligands retained their names

Pyridine (py) or ethylenediamine (en)

alkyl groups: methyl, phenyl

(c) Special names

\[ \text{H}_2\text{O} \quad \text{(aqua),} \quad \text{NO} \quad \text{(nitrosyl),} \quad \text{CO} \quad \text{(carbonyl),} \quad \text{NH}_3 \quad \text{(ammine)} \]
2. Designation of metal

(a) Cationic and neutral complexes end in the english name followed by the oxidation state of the metal in brackets.

   e.g. nickel(II) or iron(II).

(b) Anionic complexes have the latin name of the metal

   ferrate( ), Stannate ( )
   Cuprate ( ) , Argentate ( )

3. Numerical prefixes

(a) For two similar ligands di or bis
(b) three similar ligands tri or tris
(c) four similar ligands tetra or tetrakis etc.
3. Order of listing

The ligands are to be written in alphabetical order (irrespective of charge)

eg. $[\text{CoCl}_2(\text{NH}_4)]^+ \text{Cl}^-$

dichlorotetraamminecobalt(III) chloride. wrong

tetraamminedichlorocobalt(III) chloride. right

A. Writing the formulae of the complex compound

1. First central metal atom, then anionic ligands and then neutral ligands $(\text{Cl}^-,\text{NH}_3)$

$[\text{Co} (\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ wrong $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$ correct
Examples

1. \([\text{Co} \,(\text{NO}_2)_6]\) \, \text{Cl}_3
   
   hexanitro cobalt (III) chloride

2. \([\text{Cu(NH}_3)_4]\)\,\text{SO}_4
   
   tetra amminecopper(II)sulphate

3. \([\text{CuCl}_2(\text{py})_2]\)
   
   bis pyrridinedichlorocopper(II)
   dichloro \, \text{dipyridine copper (II)}
   dichloro bis (pyridine) copper (II)

4. cis-\([\text{Pt(NH}_3)_2\text{Cl}_2]\)
   
   cis-diamminedichloroplatinum(II)
Geometry of complexes

Coordination No. 2  (linear)

[NC---Ag---CN]

CH₃----Hg-----CH₃

Coordination no. 4  (large ligands)

(a) Square planar

Mainly d⁸ systems

Cl

Pt

Cl

Cl

Cl

(b) Tetra hedral

\[ \text{Cl} \]

\[ \text{Cl} \]

\[ \text{Cl} \]

\[ \text{Cl} \]
[Ni (CN)₅]²⁻ shows both structures (little energy difference)

[CuCl₅]³⁺ TBP structure

NbCl₅ TBP structure

Biologically important molecules

Haemoglobin, Oxomyoglobin
Coordination no. 6

$\text{ML}_6$ octahedral complex

Most important from $d^1$ to $d^9$

\[ \text{e.g. } [\text{Cr(NH}_3_6]^3+ , \ [\text{Fe(CN)}_6]^3- \]

Higher coordination possible with large cations and small anions

\[ \text{e.g. } [\text{ZrF}_7]^{3-} , \ [\text{TaCl}_4(\text{PR}_3)_3] \]

$\text{Square antiprism}$

$\text{[Nd(OH}_2)_9]^{3+} , \ [\text{ReH}_9]^2- , \ [\text{Ce(NO}_3)_6]^{2-} \]

$\text{Icosahedron}$
Isomerism

Stereoisomerism
- Geometrical
  (Same frame work but different spatial arrangement of the ligands)
- Optical
  (non-superimposable mirror images)

Structural Isomerism
- Ionization
- Hydrate
- Coordination
- Linkage
- Polymerization
- Ligand isomer
Geometrical Isomers (coordination no. 4)

Square planar

All are optically inactive

Cis/ trans isomers can be isolated

I

II

Cis/ trans isomers can be isolated

Cl

Pt

Cl

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Cl

Pt

NH₃

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NH₃

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Excess NH₃

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Excess NH₃

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Geometrical Isomerism in Octahedral complexes

MA$_3$B$_3$

Facial

MA$_2$B$_4$

cis

e.g. [Co Cl$_2$(NH$_3$)$_4$]$^+$

RuCl$_3$(H$_2$O)$_3$

Co(NO$_2$)$_3$(NH$_3$)$_3$

Meridonal

trans
Optical isomerism

Optical isomers differ only in the direction in which they rotate the plane of the plane polarized light (enantiomers).

Absence of optical activity (superimposable mirror images)

1. Presence of a mirror plane.
2. Presence of a centre of symmetry.

[CoCl₂(NH₃)₄]⁺ Optically inactive
Non superimposable mirror images.  (Optically active)

trans

Not optically active
Bonding Concept  

(Rationalise structure)

Bonding in coordination compounds

Sidgwick (1927)

- Extended the Lewis theory
- Sharing of ‘e’ pair donated by an atom (donor).

Effective atomic Number (EAN)

M accepts electron pairs and converted into inert gas configuration.

e.g.  \([\text{Co(NO}_2\text{)}_6]^{3-}\)  \(\text{Co} \quad (Z = 27)\)

\(\text{Co}^{3+} = 24\text{e}\)

\(6(\text{NO}_2^-) = 6*2\text{e} = 12\text{e}\)

----------------------

TOTAL = 36\text{e}  \quad \text{Atomic no. of Krypton (Kr)}
Chemical Bonding

G. N. Lewis  (1916)

Bonding between atoms $\rightarrow$ Sharing of $e^-$'s

\[
\begin{align*}
\text{H} & \quad \text{C} & \quad \text{H} \\
\text{H} & \quad \text{H} & \quad \text{H}
\end{align*}
\]

Lewis diagram

Structure ??

Bond angles ??

Concept of hybridization

Valence bond Theory

(Pauling – Slater, 1930’s)

Linus Pauling – N.L. (twice)

“Nature of the chemical bond”
Valence bond Theory
(Pauling) —— Complexes

1. Metal ion must make available a number of orbitals equal to the coordination number for accommodating the electrons from the ligands.

2. Use of the hybrid orbitals by the metal ion.
   - Maximum & fruitful overlap with ligand orbitals
   - Directionality

Note: Hybrid orbitals are not s, p or d orbitals but have a mixed character.
Why Hybridisation?

CH$_4$  Four bonds

C  1s$^2$  2s$^2$  2p$^2$

Promotion of one s electron

1s$^2$  2s$^2$  2p$_x^1$  2p$_y^1$  2p$_y^1$

Results in three mutually perpendicular bonds.

But

CH$_4$ is Tetrahedral

All $\angle$HCH are equal
Successes of V. B. T.

1. Simple structure and Magnetic properties are nicely explained.

2. Accounts for low spin square planer and high tetrahedral complex.

3. Low spin inner – orbital and high spin orbital complexes.

Failures

1. Cannot predict 4 – coordination

— square planer or tetrahedrals

\[ \text{[Cu(NH}_3\text{)}_4]^2+ \] (planar)

VB \[ \text{[Zn(NH}_3\text{)}_4]^2+ \] (tetrahedral)

VB \[ \text[Cu}^2+= 3d^9 \]

But by experiments there is no evidence of unpaired e\textsuperscript{−} in orbital: e. s. r spectroscopy
2. VBT does not predict any distortion in the symmetrical complexes. [ideal — octahedra, tetrahedra]

   Au, Cu(II), Ti(III) complexes are distiorted among many more.

3. VBT neglects the exited states of the complexes.

   —no thermodynamic properties can be predicted

4. It does not explain the colour (spectra) of complexes.

5. Does not explain the temperature variation of magnetic properties of complexes.