Coordination Chemistry I: Structures and Isomers


Images from Miessler and Tarr “Inorganic Chemistry” 2011 obtained from Pearson Education, Inc.
Coordination compounds

- Term usually used in inorganic chemistry to include compounds composed of a metal atom or ion and one or more ligands
- Ligands are atoms, ions or molecules that formally donate electrons to the metal
- This definition includes compounds with metal-carbon bonds, or organometallic compounds
Coordination compounds (cont.)

- The term coordination compound comes from the coordinate covalent bond, which historically was considered to form by donation of a pair of electrons from one atom to another.
- The donors are usually the ligands, and the acceptors are the metals.
- Coordination compounds are also acid-base adducts, frequently called complexes or, if charged, complex ions.
History

- Prussian blue, aureolin and alizarin were pigments / dyes known since antiquity
- Advances in analytical methodology allowed for the determination of formulas, and theories of structure and bonding became possible
- But organic chemistry bonding theory was not adequate to account for the experimentally determined formulas of some coordination compounds
  - Hexaamminecobalt(III) chloride – only three other atoms were “allowed” to attach to cobalt
<table>
<thead>
<tr>
<th>Werner Formula (Modern Form)</th>
<th>Number of Ions Predicted</th>
<th>Blomstrand Chain Formula</th>
<th>Number of Ions Predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Co(NH}_3\text{)}_6\text{Cl}_3])</td>
<td>4</td>
<td>(\text{NH}_3\text{--Cl}) (\text{Co}\text{--NH}_3\text{--NH}_3\text{--NH}_3\text{--NH}_3\text{--Cl}) (\text{NH}_3\text{--Cl})</td>
<td>4</td>
</tr>
<tr>
<td>([\text{Co(NH}_3\text{)}_5\text{Cl}\text{)}_2\text{Cl}_2)</td>
<td>3</td>
<td>(\text{NH}_3\text{--Cl}) (\text{Co}\text{--NH}_3\text{--NH}_3\text{--NH}_3\text{--NH}_3\text{--Cl}) (\text{Cl})</td>
<td>3</td>
</tr>
<tr>
<td>([\text{Co(NH}_3\text{)}_4\text{Cl}_2\text{)}_2\text{Cl})</td>
<td>2</td>
<td>(\text{Cl}) (\text{Co}\text{--NH}_3\text{--NH}_3\text{--NH}_3\text{--NH}_3\text{--Cl}) (\text{Cl})</td>
<td>2</td>
</tr>
<tr>
<td>([\text{Co(NH}_3\text{)}_3\text{Cl}_3)</td>
<td>0</td>
<td>(\text{Cl}) (\text{Co}\text{--NH}_3\text{--NH}_3\text{--NH}_3\text{--Cl}) (\text{Cl})</td>
<td>2</td>
</tr>
</tbody>
</table>

NOTE: The italicized chlorides dissociate in solution, according to the two theories.

Jorgensen vs Werner

trans green

[cobalt(II)(ammonia)4](Cl)2

[cobalt(I)(hydrazine)(ammonia)2](hydrazine)(chlorine)4

cis violet

[cobalt(I)(hydrazine)(ammonia)2](hydrazine)(chlorine)4
Werner vs other chemists

- This complex was originally prepared by Jorgensen and Werner was able to resolve it into its two optically active forms.
- This complex does not have carbon atoms.
Primary vs secondary bonding

- Primary bonding required counterbalance ions
- Secondary bonding were that of the ligands – now known as coordination sphere

- Current practice considers the coordination sphere more important so the words primary and secondary exchanged the significance
cis - and trans - Tetramminedichlorocobalt (III), $[\text{Co(NH}_3\text{)}_4\text{Cl}_2]^+$

Trigonal prismatic (three isomers)

Octahedral (two isomers)
Tetrahedral vs square planar

* cis- and trans- Diamminedichloroplatinum(II), $[\text{PtCl}_2(\text{NH}_3)_2]$*

Tetrahedral (one isomer)

Square planar (two isomers)
Some facts

- Werner’s theory required more bonds than that commonly accepted.
- The 18-electron-rule is useful to account the number of valence electrons around the central atom.
- Pauling used his valence bond approach to explain differences in magnetic behavior by use of either 4s or 3d orbitals.
- Griffith and Orgel developed and popularized the use of ligand field theory derived from the crystal field theory of Bethe and Van Vleck.
Nomenclature

- Organic and some inorganic ligands are frequently named using older trivial names rather than IUPAC names, although IUPAC names are preferred.
- Ligands can be **monodentated** (one point of attachment), **ambidentated** (two mutually exclusive points of attachment), **bidentated** (two points of attachment), **tridentated**, etc.
- Bidentated and multidentated ligands usually are called **chelating ligands** because they can form rings.
<table>
<thead>
<tr>
<th>Common Name</th>
<th>IUPAC Name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>hydrido</td>
<td>hydrido</td>
<td>$H^-$</td>
</tr>
<tr>
<td>nitrido</td>
<td>nitrido</td>
<td>$N_3^-$</td>
</tr>
<tr>
<td>azido</td>
<td>azido</td>
<td>$N_3^-$</td>
</tr>
<tr>
<td>oxo</td>
<td>oxido</td>
<td>$O^{2-}$</td>
</tr>
<tr>
<td>cyano</td>
<td>cyano</td>
<td>$CN^-$</td>
</tr>
<tr>
<td>thiocyanato-S</td>
<td>thiocyanato-S (S-bonded)</td>
<td>$SCN^-$</td>
</tr>
<tr>
<td>isothiocyanato</td>
<td>thiocyanato-N (N-bonded)</td>
<td>$NCS^-$</td>
</tr>
<tr>
<td>hydroxo</td>
<td>hydroxo</td>
<td>$OH^-$</td>
</tr>
<tr>
<td>aqua</td>
<td>aqua</td>
<td>$H_2O$</td>
</tr>
<tr>
<td>carbonyl</td>
<td>carbonyl</td>
<td>CO</td>
</tr>
<tr>
<td>Chelating Points</td>
<td>Common Name</td>
<td>IUPAC Name</td>
</tr>
<tr>
<td>-----------------</td>
<td>-------------</td>
<td>------------</td>
</tr>
<tr>
<td>monodentate</td>
<td>ammine, methylamine</td>
<td>ammine, methylamine</td>
</tr>
<tr>
<td>bidentate</td>
<td>ethylenediamine</td>
<td>1,2-ethanediamine</td>
</tr>
<tr>
<td>tridentate</td>
<td>diethylenetriamine</td>
<td>2,2′-diaminodiethylamine or 1,4,7-triazaheptane</td>
</tr>
<tr>
<td>tetradentate</td>
<td>triethylenetetraamine</td>
<td>1,4,7,10-tetraazadecane</td>
</tr>
<tr>
<td></td>
<td>β, β′, β″-triaminotriethylamine</td>
<td>β, β′, β″-tris(2-aminoethyl)amine</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pentadentate</td>
<td>tetraethylenepentamine</td>
<td>1,4,7,10,13-pentaazatridecanes</td>
</tr>
<tr>
<td>hexadentate</td>
<td>ethylenediaminetetraacetate</td>
<td>1,2-ethanediyl (dinitrilo) tetraacetate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Common Name</td>
<td>IUPAC Name</td>
<td>Abbreviation</td>
</tr>
<tr>
<td>---------------------------</td>
<td>-----------------------</td>
<td>--------------</td>
</tr>
<tr>
<td>acetylacetonato</td>
<td>2,4-pentanediono</td>
<td>acac</td>
</tr>
<tr>
<td>2,2’-bipyridine</td>
<td>2,2’-bipyridyl</td>
<td>bipy</td>
</tr>
<tr>
<td>1,10-phenanthroline, o-phenanthroline</td>
<td>1,10-diaminophenanthrene</td>
<td>phen, o-phen</td>
</tr>
<tr>
<td>oxalato</td>
<td>oxalato</td>
<td>ox</td>
</tr>
</tbody>
</table>
Nomenclature rules

- Positive ion comes first, then the negative ion
  - Potassium hexacyanoferrate(III)

- Ion negativo se escribe primero, luego el positivo
  - Hexacianoferrato(III) de potasio
Nomenclature rules

- Inner coordination sphere is enclosed in square brackets in the formula, the metal is written first in the formula but last in the name
  - Hexamminecobalt(III) chloride, \([\text{Co(NH}_3\text{)}_6]\text{Cl}_3\)

- La esfera de coordinación interna se coloca en “brackets”, el metal se escribe primero en la fórmula, pero último en el nombre
  - Cloruro de hexaaminocobalto(III), \([\text{Co(NH}_3\text{)}_6]\text{Cl}_3\)
Nomenclature rules

• The number of ligands is given with prefixes
• If the ligand name is complicated or it includes a prefix, the second prefix is used (the one ending with “is”)

Dichlorobis(ethylenediamine)cobalt(III)
Tris(bipyridine)iron(III)

Diclorobis(etilendiamina)cobalto(III)
Tris(bipiridina)hierro(III)
Nomenclature rules

- Ligands are named in alphabetical order, according to the name of the ligand, not the prefix
- Earlier rule gave anionic ligands first, then neutral ligands

- Tetraamminedichlorocobalt(III)
- Amminebromochloromethylamineplatinum(II)
Nomenclature rules

- Anionic ligands are given an o suffix
  - Chloro
  - Bromo
  - Sulfato
- Neutral ligands retain their usual name
- Coordinated water is called aqua
- Coordinated ammonia is called ammine
Nomenclature rules

- Two systems exist for designating the charge or oxidation number: Stock system (oxidation number of metal ion as a Roman numeral) and Ewing-Basset system (charge of coordination sphere as a “normal” numeral).
- Ewing-Basset is used in Chemical Abstracts.
- In either case, if the charge is negative, the suffix –ate (–ato in Spanish) is used.

- Tetrachloroplatinate(II) or tetrachloroplatinate (2-) for the \([\text{PtCl}_4]^{2-}\) ion.
- Tetraammineplatinum(II) or tetraammineplatinum (2+) for the \([\text{Pt(NH}_3)_4]^{2+}\) ion.
Nomenclature rules

- Cis and trans designate adjacent and opposite geometric locations (as in organic chemistry)

\[ \text{cis} \quad \text{trans} \]
Nomenclature rules

- Bridging ligands between two metal ions have the prefix $\mu$-
as in $\mu$-amido-$\mu$-hydroxobis(tetraamminecobalt) (4+)
Nomenclature rules

- When the complex is negatively charged, the names for some metals are derived from the sources of their symbols

- Tetrachloroferrate(III) for the $[\text{FeCl}_4]^{-}$ ion

- Tetacloroferrato(III) para el ión $[\text{FeCl}_4]^{-}$

<table>
<thead>
<tr>
<th>Metal</th>
<th>Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>iron (Fe)</td>
<td>ferrate</td>
</tr>
<tr>
<td>silver (Ag)</td>
<td>argentate</td>
</tr>
<tr>
<td>lead (Pb)</td>
<td>stannate</td>
</tr>
<tr>
<td>tin (Sn)</td>
<td>aurate</td>
</tr>
<tr>
<td>gold (Au)</td>
<td></td>
</tr>
</tbody>
</table>
Isomerism

- The variety of coordination numbers in coordination compounds provides with a large number of isomers, the number of which increases with coordination number.

- Our discussion will be limited to isomers with the same ligands arranged in different geometries; types are:
  - Hydrate or solvent isomerism
  - Ionization isomerism
  - Coordination isomerism
  - Linkage (or ambidentate) isomerism
  - Stereoisomerism
Stereoisomerism

- cis/trans isomers
- Chiral isomers
- Different conformation of chelate rings
- Other isomers that differ only in the geometry of attachment to the metal atom
fac/mer Isomerism in 6-coordinate complexes

- Ligands can occupy the face of the octahedron or a meridian line.

\[
\text{Facial: } [\text{Co(NH}_3\text{)}_3\text{Cl}_3]
\]

\[
\text{Meridional: } [\text{Co(dien)}_2]^{3+}
\]
Stereoisomerism

α
No coplanar rings

β
Two coplanar rings

trans
Three coplanar rings
Isomerism – combination of chelate rings – propellers – $\Delta$ and $\Lambda$ isomers
Multiple $\Delta$ and $\Lambda$ rings and ring conformation

- Ligands such as EDTA will form multiple rings

- Chelate rings can also adopt different conformations (designated $\delta$ and $\lambda$) - we will not focus on them
Constitutional isomerism

- Hydrate (or solvent) isomerism
  \[\text{[Co(NH}_3\text{)}_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2 \text{ and } \text{[Co(NH}_3\text{)}_4\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}\]

- Ionization isomerism
  \[\text{[Co(NH}_3\text{)}_4(\text{H}_2\text{O})\text{Cl}]\text{Br}_2 \text{ and } \text{[Co(NH}_3\text{)}_4\text{Br}_2]\text{Cl} \cdot \text{H}_2\text{O}\]

- Coordination isomerism
  \[\text{[Co(en)}_3\text{][Cr(CN)}_6\text{]} \text{ and } \text{[Cr(en)}_3\text{][Co(CN)}_6\text{]}\]

- Linkage (ambidentate) isomerism
  Ligands such as NCS\(^-\) or NO\(_2^-\) which have two attachment points
Experimental separation and identification of isomers

- Geometric isomers are separated with fractional crystallization
- Chiral isomers requires chiral counterions
  - Best identification method, when crystallization allows it, is X-ray diffraction
  - Measurement of optical activity is useful for assigning absolute configuration to chiral isomers
Coordination number and structures

- Overall shape of a coordination compound is the product of several factors:
  - Number of bonds
  - VSEPR considerations
  - Occupancy of d orbitals
  - Steric interference
  - Crystal packing effects
Coordination number and structures

- Coordination number 1 is rare, except in ion pairs in gas phase
- Coordination number 2 is also rare, [Ag(NH3)2]+, [CuCl2]- and Hg(CN)2 are well-known examples with a d10 metal ion and are linear
- Coordination number 3 is likely with d10 metal ions, with a trigonal-planar structure being the most common
Coordination number and structures

- Coordination number 4 results in a tetrahedral or square-planar structure; tetrahedral is most common
- Square-planar structures, when not imposed by a planar ligand, occur for d8 metal ions
Coordination number and structures

- Coordination number 5 can result in trigonal bipyramid, square pyramid and pentagonal plane (extremely rare).
- The energy difference is small and structures can interconvert.
Coordination number and structures

- Coordination number 6 is the most common, with octahedral geometry the most common.
- Other structures are trigonal prismatic and antiprismatic.
- A regular octahedron can be distorted to tetragonal structures.

![Diagram](https://via.placeholder.com/150)

Elongated  Compressed  (a)  (b)
Coordination number and structures

- Coordination number 7 and higher are not common