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Chapter 7. Coordination Compounds

d-Metal complexes

Position of the transition metals in the periodic table and distinctive properties of the atoms and their compounds. Patterns of oxidation states, to be discussed in terms of ionisation energies and other relevant factors. Crystal field/ligand field effects to be discussed in the context of thermodynamic, structural, spectroscopic and magnetic properties; simple MO pictures for octahedral and tetrahedral coordination of a transition metal atom.

This chapter describes the chemistry of the first transition series: aqueous behaviour and redox properties; importance of the ligand in determining behaviour. Properties of the elements and simple inorganic and organic derivatives with reference to formation, structures and other physical properties, and characteristic reactions. Cross-reference to biological roles.

Overview of the heavier transition elements: major differences between the first-, second-, and third-row transition elements; redox and coordination properties; bonding behaviour, including metal-metal bonding.

There are four transition series:

1. The first transition series: Scandium (Sc) through Copper (Cu): 3d subshell is filling.

Irregularities are observed for Chromium, Cr, and Copper, Cu, because the listed electronic configurations are energetically favoured (i.e. 3d54s1 is more stable than 3d44s2, and 3d104s1 is more stable than 3d94s1 respectively.).
2. The second transition series: Yttrium (Y) through Silver (Ag): 4d subshell is filling.

Irregularities are observed for Nb which skips from 4d^25s^2 to 4d^45s^1, and Pd, which goes from 4d^85s^2 to 4d^{10}5s^1.

3. The third transition series: Lanthanum (La) to Hafnium (Hf) through Gold (Au): 5d subshell is filling.

Irregularities are observed for Pt which skips from 5d^96s^2 to 5d^{10}6s^1.

4. The fourth transition series which is incomplete:

Actinium (Ac) to element 104 through element 109: 6d subshell is filling, If elements 110 and 111 are found then this will complete this series.

**Transition Metal Electronic Configurations**

Co: [Ar] 4s^2 3d^7

Due to spin correlation energy and Hunds rule d^5 or d^{10} and f^7 or f^{14} are stable

Cr: [Ar] 3d^4 4s^2 wrong
Cr: [Ar] 3d^5 4s^1 correct
Cu: [Ar] 3d^9 4s^2 wrong
Cu: [Ar] 3d^{10} 4s^1 correct

**Electron Configuration of Metal Ions**

**Transition Metal Ions**

Electronic Configuration of Transition Metal cations
d-block and f-block elements
d orbitals are lower in energy than s orbitals
f orbitals are lower in energy than d orbitals

**Iron**

Predict the electron configuration of the Fe^{3+} and Co^{3+} ion.

E.g. Neutral atom Fe: [Ar] 3d^6 4s^2
Cation, Fe^{3+}: [Ar] 3d^5

**Cobalt**

Co: [Ar] 4s^2 3d^7
Co^{2+}: [Ar] 3d^7
Co^{3+}: [Ar] 3d^6

Even though you place 2d electrons last when you are removing you should remove from 4s first because ionization means removing electrons from the outer most or valence shell. One electron same added orbitals follow the energy order 3d 4s.

**Oxidation States of the Transition Metals**

Some oxidation states, however, are more common than others. The most common oxidation states of the first series of transition metals are given in the table below. Efforts to explain the apparent
pattern in this table ultimately fail for a combination of reasons. Some of these oxidation states are common because they are relatively stable. Others describe compounds that are not necessarily stable but which react slowly. Still others are common only from a historic perspective.

**Possible electron configurations of transition metal ions**

<table>
<thead>
<tr>
<th>Transition Metal</th>
<th>Electronic Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>[Ar]&lt;sup&gt;3d&lt;/sup&gt;&lt;sup&gt;0&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ti&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>[Ar]; Ti&lt;sup&gt;4+&lt;/sup&gt;, [Ar]&lt;sup&gt;3d&lt;/sup&gt;&lt;sup&gt;0&lt;/sup&gt;</td>
</tr>
<tr>
<td>V&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>[Ar]&lt;sup&gt;3d&lt;/sup&gt;&lt;sup&gt;3&lt;/sup&gt;; V&lt;sup&gt;3+&lt;/sup&gt;, [Ar]&lt;sup&gt;3d&lt;/sup&gt;&lt;sup&gt;2&lt;/sup&gt;; V&lt;sup&gt;4+&lt;/sup&gt;, [Ar]&lt;sup&gt;3d&lt;/sup&gt;&lt;sup&gt;1&lt;/sup&gt;; V&lt;sup&gt;5+&lt;/sup&gt;, [Ar]&lt;sup&gt;3d&lt;/sup&gt;&lt;sup&gt;0&lt;/sup&gt;</td>
</tr>
<tr>
<td>Cr&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>[Ar]&lt;sup&gt;3d&lt;/sup&gt;&lt;sup&gt;1&lt;/sup&gt;; Cr&lt;sup&gt;3+&lt;/sup&gt;, [Ar]&lt;sup&gt;3d&lt;/sup&gt;; Cr&lt;sup&gt;4+&lt;/sup&gt;, [Ar]&lt;sup&gt;3d&lt;/sup&gt;&lt;sup&gt;2&lt;/sup&gt;; Cr&lt;sup&gt;6+&lt;/sup&gt;, [Ar]</td>
</tr>
<tr>
<td>Mn&lt;sup&gt;2+&lt;/sup&gt;, [Ar]&lt;sup&gt;3d&lt;/sup&gt;&lt;sup&gt;5&lt;/sup&gt;; Mn&lt;sup&gt;4+&lt;/sup&gt;, [Ar]&lt;sup&gt;3d&lt;/sup&gt;&lt;sup&gt;3&lt;/sup&gt;; Mn&lt;sup&gt;7+&lt;/sup&gt;, [Ar] &lt;sup&gt;3d&lt;/sup&gt;&lt;sup&gt;0&lt;/sup&gt;</td>
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<tr>
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<tr>
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<td>Cu&lt;sup&gt;+&lt;/sup&gt;, [Ar]&lt;sup&gt;3d&lt;/sup&gt;&lt;sup&gt;10&lt;/sup&gt;; Cu&lt;sup&gt;2+&lt;/sup&gt;, [Ar]&lt;sup&gt;3d&lt;/sup&gt;&lt;sup&gt;9&lt;/sup&gt;</td>
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<tr>
<td>Zn&lt;sup&gt;2+&lt;/sup&gt;, [Ar]&lt;sup&gt;3d&lt;/sup&gt;&lt;sup&gt;10&lt;/sup&gt;</td>
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**Common Oxidation States of the First Series of Transition Metals**

<table>
<thead>
<tr>
<th>Transition Metal</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
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<tbody>
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<tr>
<td>Co</td>
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<td></td>
</tr>
<tr>
<td>Ni</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>10</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

One point about the oxidation states of transition metals deserves particular attention: Transition-metal ions with charges larger than +3 cannot exist in aqueous solution.

**Consider the following reaction in which manganese is oxidized from the +2 to the +7 oxidation state.**

\[
\text{Mn}^{2+}(aq) + 4 \text{H}_2\text{O}(l) \rightarrow \text{MnO}_4^-(aq) + 8 \text{H}^+(aq) + 5 \text{e}^- 
\]

When the manganese atom is oxidized, it becomes more electronegative. In the +7 oxidation state, this atom is electronegative enough to react with water to form a covalent oxide, \(\text{MnO}_4^-\).

It is useful to have a way of distinguishing between the charge on a transition-metal ion and the oxidation state of the transition metal. By convention, symbols such as \(\text{Mn}^{2+}\) refer to ions that carry a +2 charge. Symbols such as \(\text{Mn}(\text{VII})\) are used to describe compounds in which manganese is in the +7 oxidation state.
Mn(VII) is not the only example of an oxidation state powerful enough to decompose water. As soon as Mn$^{2+}$ is oxidized to Mn(IV), it reacts with water to form MnO$_2$. A similar phenomenon can be seen in the chemistry of both vanadium and chromium. Vanadium exists in aqueous solutions as the V$^{2+}$ ion. But once it is oxidized to the +4 or +5 oxidation state, it reacts with water to form the VO$^{2+}$ or VO$_2^+$ ion. The Cr$^{3+}$ ion can be found in aqueous solution. But once this ion is oxidized to Cr(VI), it reacts with water to form the CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$ ions.

Calculate the oxidation number on the transition-metal ion in the following complexes.

(a) Na$_2$Co(SCN)$_4$
(b) Ni(NH$_3$)$_6$(NO$_3$)$_2$
(c) K$_2$PtCl$_6$

Transitional Metal Complex Nomenclature

Nomenclature is similar to regular chemical compounds.

silver arsenate - AgAsO$_4$, ammonium silicate - ?, iron (III) bromide - ?, Ni(BrO$_3$)$_3$ - ?, aluminum chromate - ?, CuF$_2$ - ?, barium phosphate - ?, Au$_2$S$_3$ - ?, tin (IV) acetate - ?, potassium nitride - ?, Li$_4$C - ?, NH$_4$ClO$_2$ - ?, zinc cyanide - ?, Ca(OH)$_2$ - ?, Co$_3$(PO$_4$)$_3$ - ?, aluminum oxide - ?, mercury (I) carbonate - ?, FeCl$_2$ - ?, magnesium phosphate - ?, chlorous acid - ?, H$_3$PO$_4$ - ?, hyponitrous acid - ?, carbonic acid - ?, HBrO$_2$ - ?

But use the numbers in paraenthesis after metal name to indicate the oxidation state.

FeCl$_2$-iron (II) chloride.

**bis-2, tris-3 tetrakis- 4 to show number of ligands**

The rules for naming complex ions or compounds are as follows:

1. To name any complex ion, list first the ligands, then the central atom.
2. The ligand names are made to end in -O if they are negative (chloro, bromo, nitrito, etc.), and unless they are negative the ligand names must not end in -O. Examples of ligand names are chloro, hydroxo, cyano, aqua (for H$_2$O), ammine (for NH$_3$), and thiosulfato (for S$_2$O$_3^{2-}$).
3. Anions end in -ate and, when a Latin symbol is used for the element, the element takes the Latin name in anions but not in cations. For example, Cu(NH$_3$)$_4^{2+}$ is called the tetraamminecopper(II) ion but Cu(CN)$_6^{4-}$ is called the hexacyanocuprate(II) ion. Likewise Al(NH$_3$)$_6^{3+}$ is called the hexaamminealuminum(III) ion but Al(OH)$_4^{-}$ is called the tetrahydroxoaluminate(III) ion.
4. The number of each kind of ligand is specified by the usual Greek prefix. The ligands are named in alphabetic order. For example, Cu(Cl$_2$Br$_2$I$_2$)$^+$ is the dibromodichlorodiodocuprate(II) ion while Cu(Cl$_2$Br$_2$INH$_3$)$^+$ is the amminedibromodichloriodocuprate(I) ion.

The oxidation state of the central metal atom to which the ligands are attached must be indicated, unless it is an element which has only one known oxidation state such as sodium. The oxidation state is not always obvious; the compound GaCl$_2$ was named gallium dichloride until it was discovered to be the dimeric Ga$_2$Cl$_4$. Its renaming as digallium tetrachloride was not sufficient, since its actual structure is Ga$^+$[GaCl$_4$$^-$] and so its name really should be gallium(I) tetrachlorogallate(III) in order to indicate the oxidation states.

Example. We will name the following salts:

1. [Co(NH$_3$)$_4$Cl$_2$]Cl: dichlorotetramminecobalt(III) chloride.
2. [Co(NH$_3$)$_5$Cl]Cl$_2$: monochloropentamminecobalt(III) chloride.
3. K$_3$[Co(NO$_2$)$_5$], known as Fischer's Salt: potassium hexanitritocobaltate(III).
4. \([\text{Pt}(\text{NH}_3)_2\text{Cl}]_2[\text{PtCl}_4]\), known as Magnus' Pink Salt: di(monochlorotriammineplatinum(II)) tetrachloroplatinate(II).

5. \([\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]\), known as Magnus' Green Salt: tetrammineplatinum(II) tetrachloroplatinate(II).

6. Reinecke's Salt, \(\text{NH}_4[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]\): ammonium tetrathiocyanatodiamminechromate(III).

7. Drechsel's Chloride, \([\text{Pt}(\text{NH}_3)_6]\text{Cl}_4\): hexammineplatinum(IV) chloride.

8. Cossa's First Salt, \(\text{K}[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\): potassium trichloroammineplatinate(II).

Cossa's Second Salt, \(\text{K}[\text{Pt}(\text{NH}_3)_3\text{Cl}_5]\): potassium pentachloroammineplatinate(IV)

Correctly write the name for the following coordination compounds or ions:

- \([\text{CoI}(\text{NH}_3)_5]\text{Cl}_2\): pentaammineiodocobalt(III) chloride
- \([\text{Cu}(\text{NH}_3)_4]\text{SO}_4\) tetraamminecopper(II) sulfate
- \([\text{CrCl}(\text{en})_2(\text{H}_2\text{O})]\text{Cl}_2\): aquachlorobis(ethylenediamine)chromium(III) chloride
- \((\text{NH}_4)_2[\text{CdCl}_4]\): ammonium tetrachlorocadmate(II)
- \([\text{Na}[\text{Rh}(\text{EDTA})]\): sodium ethylenediaminetetraacetatorhodate(III)
- \([\text{Pd}(\text{en})_2][\text{CrCl}_4](\text{NH}_3)_2\text{Cl}_2\): bis(ethylenediamine)palladium(II)diamminetetrachlorochromate(III)
- \([\text{K}_3[\text{Fe}(\text{ox})(\text{ONO})_4]\): potassium tetranitritooxalatoferrate(III)
- \([\text{Sc}(\text{NC})_2(\text{NO})_4]_3[\text{Co(NCS)}_3(\text{SCN})_3]\): diisocyanotetranitrosylscandium(II) triisothiocyanatotrithiocyanatocobalt(III)
- \([\text{Au(CO)}_4]_2[\text{Au(CO)}_3(\text{OH})_3\text{Cl}\]: tetracarbonylgold(III)carbonatohydroxoaurrate(I)
- \([\text{Ag(NH}_3)_2]^+\): diamminesilver(I)
- \([\text{RuCl}_5(\text{H}_2\text{O})]_2^-\): aquapentachlororuthenate(III)
- \([\text{Fe(CN)}_6]^{4-}\): hexacyanoferrate(II)
- \([\text{Na}_4[\text{Ni(C}_2\text{O}_4)_3]\]_3\): sodiun tris(oxalato)nickelate(II)
- \([\text{Co(NH}_3)_5\text{Cl}](\text{NO}_3)_2\text{Cl}_2\): pentaamminechlorocobalt(III) nitrate
- \([\text{CrCl}_2(\text{H}_2\text{O})_4]_2^+\): tetraaquachlorochromium(III)
- \([\text{Co(H}_2\text{O})_6]^3-\): hexaaquacobalt(III) iodide

Correctly write the formula for the following coordination compounds or ions:

- Potassium hexafluorocobaltate (III): \(\text{K}_3[\text{CoF}_6]\)
- tetraamminechloronitrocobalt(III) chloride : \([\text{CoClNO}_2(\text{NH}_3)_4]\text{Cl}\)
- tris(ethylenediamine)nickel(II) sulfate : \([\text{Ni(en)}_3]\text{SO}_4\)
- tetramminedichloroplatinum(IV) tetrachloroplatinate(II) : \([\text{PtCl}_2(\text{NH}_3)_4][\text{PtCl}_4]\)
- tris(ethylenediamine)cobalt(II) nitrate : \([\text{Co(en)}_3](\text{NO}_3)_2\)
- cobalt(II) hexanitrocobaltate(III) : \(\text{Co}_3[\text{Co(NO)}_2)_6]\_2\)
- ammineaquadicarbonylidyanoion(III) : \([\text{Fe(CN)}_2(\text{NH}_3)(\text{H}_2\text{O})(\text{CO})_2]^+\)
- Sodium tetracyanoosmium(III) : \(\text{Na}[\text{Os(CN)}_4]\)
- Tris(ethylenediamine)nickel(II) tetraoxomanganate(II) : \([\text{Ni(en)}_3)_3[\text{MnO}_3]\)
- Hexaamminezinc(II) tris(oxalato)chromate(III) : \([\text{Zn(NH}_3)_6]\_3[\text{Cr(ox)}_3]_2\)
- tris(oxalato)vanadate(II) : \([\text{V(ox)}_3]^{3+}\)
- sodium dihydroxodinitritomercurate(II) : \(\text{Na}_2[\text{Hg(OH)}_2(\text{ONO})_2]\)
- ammonium tetrabromocobaltate(II) : \((\text{NH}_4)_2[\text{AuBr}_4]\)
- Potassium ethylenediaminetetraacetatorhodate(II) \(\text{K}_2[\text{Fe(EDTA)}]\)
- diaquabis(ethylenediamine)iridium(III) chloride : \([\text{Ir(H}_2\text{O})_2(\text{en})_2]\text{Cl}_3\)

The Eta(η) System of Nomenclature
In the early days of organometallic chemistry, the simple distinction between s- and p-bonded ligands was enough to specify the structures of complexes e.g. pentacarbonyl(s-methyl) manganese, MnMe(CO)$_5$

tricarbonyl(p-cyclopentadienyl) manganese,

and even to differentiate between two complexes containing the same ligand, but attached in a different way.

e.g. pentacarbonyl(s-allyl) manganese, Mn(CH$_2$CH=CH$_2$)(CO)$_5$

tetraacarbonyl (p-allyl)manganese,

As more complex ligands were described, Cotton proposed that the mode of attachment of the donor ligand be described by denoting the number of atoms (together with positions if necessary) attached to the metal atom by $h^n$. This formalism contained no implications regarding the type of bonding.

e.g. pentacarbonyl (h$^1$-methyl) manganese, MnMe(CO)$_5$

pentacarbonyl (h$^1$-allyl) manganese, Mn(CH$_2$CH=CH$_2$)(CO)$_5$

tetraacarbonyl (h$^3$-allyl) manganese, Mn(C$_3$H$_5$)(CO)$_4$

tricarbonyl (h$^5$-cyclopentadienyl) manganese, Mn(C$_5$H$_5$)(CO)$_3$

The two isomers of Os(CO)$_3$(C$_8$H$_8$) could be distinguished:

As a consequence with unsaturated ligands it became necessary to specify the number of carbon atoms which interact with the metal centre. The prefix $h^n$ before the ligand formula implies bonding to $n$ carbons, while $m_k$ indicates a ligand bridging $k$ metal atoms. Individual numbers of ligand atoms might be required to describe more complicated structures:
7.1 Constitution
Ions of d-block elements are excellent Lewis acids (electron pair acceptors). They form coordinate covalent bonds with molecules or ions that can act as Lewis bases (electron pair donors). Complexes formed in this way participate in many biological reactions (e.g., hemoglobin, vitamin B12) and are important in other ways as well (e.g., catalysis, dyes, solar energy conversion).

A transition metal complex consists of a central metal atom or ion surrounded by a set of ligands which have one or more atoms bearing lone-pairs of electrons. These "donor" atom are bound electrostatically and covalently to the metal ion. In non-transition metal complexes such as Na\(^{+}\)(aq), which can be approximately formulated as \([\text{Na}(\text{H}_2\text{O})_6]^{+}\), or \([\text{Ca}(\text{EDTA})]^{n+}\), the binding is largely electrostatic, while in transition metal complexes there is significant covalency.

**Representative ligands and nomenclature**

**Ligand Types**

Examples of common ligands:

**Monodentate Ligands**
Halide ions, \(\text{H}_2\text{O}\), \(\text{OH}^-\), \(\text{O}^{2-}\), \(\text{SH}^-\), \(\text{S}^{2-}\), \(\text{NH}_3\), \(\text{NR}_3\), \(\text{NC}_5\text{H}_5\) (pyridene), \(\text{PR}_3\), \(\text{AsR}_3\), \(\text{CO}\)

**Ambidentate**
The following are ambidentate - they can bond via either end, or bridge: \(\text{CN}^-\), \(\text{SCN}^-\)

**linkage isomerism**
Some ambidentate ligands can bind differently in complexes with the same molecular formula. This is called "linkage isomerism". For example, nitrite can bind either through nitrogen or oxygen:

\[
[\text{Co(NH}_3)_5(\text{ONO})]^{2+} \text{ (the red "nitrito" complex)}
\]

\[
[\text{Co(NH}_3)_5(\text{NO}_2)]^{3+} \text{ (the yellow "nitro" complex)}
\]

(Replacement of one \(\text{NH}_3\) in \([\text{Co(NH}_3)_6]^{3+}\) by \(\text{NO}_2^-\) in a cold solution yields the kinetically favoured nitrito complex, i.e. in the intimate substitution mechanism, an oxygen binds to the cobalt first. If the solution is then heated, the nitrito complex rearranges to the thermodynamically favoured nitro complex i.e. the cobalt - nitrogen bond is presumably stronger than the cobalt - oxygen bond.)

**Bidentate Ligands**
Tridentate Ligands

Ethylenediamine (en)
Bis(diphenylphosphino)ethane (dphos)
Bipyridyl (bpy)
Phenanthroline (phen)
Acetylacetonate (acac)
Acetate (ac)
Oxalate (ox)

Terpyridyl (terpy)
Bisethylenetriamine (tris)
Polydentate Ligands
The structures below are examples of two important tetradentate and one hexadentate ligand.

The Chelate Effect
Polydentate ligands which are flexible enough so that two or more of their "donor" atoms can wrap around and bind to the same metal are called chelating ligands. Their complexes are stabilized by two effects which are basically entropy related:

1. Consider this reaction:
   \[ \text{Co(NH}_3\text{)}_6^{2+} + 3 \text{en} \iff [\text{Co(en)}_3]^{2+} + 6\text{NH}_3 \]
Both the reactant and the product complexes contain 6 cobalt-nitrogen bonds (the only ones broken
in this reaction, so the enthalpy should be very small. On the other hand, there are four molecules to the left and 7 to the right, so there is greater potential for disorder to the right. Number of particles on right is 7 compared to 4 in left. Therefore the driving force, that is the dominant factor in $D_G$, is the very positive entropy change.

2. If one end of a bidentate ligand becomes detached from the metal ion, there is a strong probability that it will re-attach itself before the other end becomes separated if the chain connecting the two ends is quite short. If the chain is long, the loose end can drift far from the metal ion and the probability of reattachment is diminished. The optimum ring size in chelate complexes is found to be four or five members (including the metal ion). This too can be related to entropy, but it is in the nature of a kinetic effect since it has to do with order/disorder in the reaction intermediate.

**Coordination number, Isomerism and chirality**

**Coordination Numbers and Geometries (geometrical Isomerism)**

There are a number of possible "defined" geometries for transition metal complexes, together with an infinite range of "in between" cases. Only the most important: octahedral, tetrahedral, and square-planar are covered in this section of the course.

**Coordination Number 6**

**Octahedral**

At least three different cobalt(III) complexes can be isolated when CoCl$_2$ is dissolved in aqueous ammonia and then oxidized by air to the +3 oxidation state. A fourth complex can be made by slightly different techniques. These complexes have different colors and different empirical formulas.

\[
\begin{align*}
\text{CoCl}_3 \cdot 6\ \text{NH}_3 & \quad \text{orange-yellow} \\
\text{CoCl}_3 \cdot 5\ \text{NH}_3 \cdot \text{H}_2\text{O} & \quad \text{red} \\
\text{CoCl}_3 \cdot 5\ \text{NH}_3 & \quad \text{purple} \\
\text{CoCl}_3 \cdot 4\ \text{NH}_3 & \quad \text{green}
\end{align*}
\]
Werner explained these observations by suggesting that transition-metal ions such as the Co\(^{3+}\) ion have a **primary valence** and a **secondary valence**. The primary valence is the number of negative ions needed to satisfy the charge on the metal ion. In each of the cobalt(III) complexes previously described, three Cl- ions are needed to satisfy the primary valence of the Co\(^{3+}\) ion.

The principal geometry for six-coordination is octahedral. (Another, which is much much rarer is trigonal-prismatic.) There are a couple of important types of isomerism, and a number of lesser significance. All are relevant only to complexes which are kinetically inert, that is, not subject to ligand exchange processes which will thwart attempts to physically separate the isomers.

**Geometrical Isomerism - cis/trans and fac/mer.** These are the named types, but there can be others for more complicated sets of ligands:

- **cis and trans**-[Co(NH\(_3\)\(_4\))Cl\(_2\)]\(^{+}\)
- **fac and mer**-Co(NH\(_3\)\(_3\))Cl\(_3\)
**Geometric Isomers of ML₆ Complexes**

Coordination Number 4

Tetrahedral

The tetrahedral geometry is never favoured over the octahedral on the basis of crystal field stabilization energy (CFSE - see below). At best, for d⁰, d⁵ or d¹⁰, the CFSE will be zero for both geometries. The tetrahedral geometry is therefore only found if the ligands are bulky. In addition, tetrahedral complexes are always *labile*, that is subject to the ligands exchanging, either with the solvent or other dissolved ligands, or exchanging positions. For this reason, optical isomers of tetrahedral transition metal complexes cannot be isolated.

**Square-planar**

Square-planar complexes exist only when the CFSE (see below) favours this geometry over the alternatives. Most such complexes are formed with d⁸ ions such as Pd²⁺, Pt²⁺, Ni²⁺ (sometimes), Rh⁺, Ir⁺ and Au³⁺. Most square-planar complex ions are inert so *cis/trans* isomers can be separated:
Preparation of Cis/trans square planar complexes

Using either $[\text{PtCl}_4]^{2-}$ or $[\text{Pt}(	ext{NH}_3)_4]^{2+}$ as metal containing starting materials, the synthesis of cis and trans isomers of $[\text{Pt}(	ext{NH}_3)(\text{NO}_2)\text{Cl}_2]^{-}$, be accomplished given that the substituent trans effects are in the order $\text{NO}_2^- > \text{Cl}^- > \text{NH}_3$ and following following synthetic route.

Square Planar Substitution: The Trans Effect

• when the ligand, T, trans to the leaving group in square planar complexes effects the rate of substitution
• If T is a strong $\sigma$ donor or $\pi$ acceptor, the rate of substitution is dramatically increased
• why?
  – if T contributes a lot of e- density (is a good $\sigma$ donor) the metal has less ability to accept electron density from X (the leaving ligand)
  – if T is a good $\pi$ acceptor, e- density on the metal is decreased and nucleophilic attack by Y is encouraged

Trans Effect Strengths

• Trans effect is more pronounced for $\sigma$ donor as follows: $\text{OH}^- < \text{NH}_3 < \text{Cl}^- < \text{Br}^- < \text{CN}^- < \text{CO}, \text{CH}_3^- < \text{I}^- < \text{PR}_3$
• Trans effect is more pronounced for a $\pi$ acceptor as follows: $\text{Br}^- < \text{Cl}^- < \text{NCS}^- < \text{NO}_2^- < \text{CN}^- < \text{CO}$

Geometrical Isomerism

Most square-planar complex ions are inert so cis/trans isomers can be separated.

Optical isomerism - $\Delta/\Lambda$
Complexes with two or three chelating ligands can show optical activity. The molecules can exist in two forms which are mirror images of each other. Such isomers, if separated, have the property of rotating the plane of polarization of polarized light.

Notice that the molecules can be approximated to a propeller shape. If the propeller is "right-handed", that is, it would tend to pull away from you if you rotated it clockwise, then the molecule is the \( \Delta \)-isomer. If the propeller would tend to move towards you when rotated clockwise, then it is the \( \Lambda \)-isomer.

Complexes with only two chelate rings and two identical monodentate ligands in \textit{cis} positions could also be isolated as \( \Delta \) or \( \Lambda \)-isomers. The \textit{trans} isomer has mirror symmetry and is therefore not optically active. Complexes with a single chelate ring and four identical monodentate also have mirror symmetry. Make sure you can recognize or draw diagrams which illustrate this!

**Bonding and electronic structure**

**Crystal-field theory**

**Bonding Theories**

**Ligand Field Theory: Transition Metal Complexes**

It uses "outer orbital" \( sp^3d^2 \) and "inner orbital" \( d^2sp^3 \) hybridization to explain the formation of compounds.

\[
\begin{array}{cccccccc}
& 3d & 4s & 4p & 4d \\
Co^{2+} & \uparrow \downarrow & \uparrow & \uparrow & \uparrow & & & \\
CoF_6^{3-} & \uparrow \downarrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\
\end{array}
\]

Outer orbital hybridization (also called high spin) see the \( d_{x^2-y^2} \) and \( d_{xy} \) orbitals, so only the \( d_{xz} \), \( d_{yz} \), and \( d_{yz} \) orbitals are available.
The figure above illustrates inner orbital hybridization (also called low spin).

The theories included under the general heading Ligand Field Theory directly address the two main properties of transition metal complexes: colour and para/diamagnetism. The theories also give insight into the relative stability of one coordination geometry relative to another, and the properties of inertness and lability which qualify the ease of ligand exchange. This course considers only crystal field theory, where only electrostatic effects are considered. Treatment of the more sophisticated molecular orbital theory of transition metal complexes: ligand field theory.

Crystal Field Theory

The d-orbitals are degenerate in the absence of an electrical field (or in a spherically symmetric electric field), that is, for example, in the case of a bare gas phase atom. Their energies are split in ligand fields, i.e. when surrounded by a group of ligands.

Octahedral

The orbitals are split into two groups: a set consisting of \( d_{xy}, d_{xz}, \) and \( d_{yz} \) stabilized by \( 2/5 \Delta_0 \), known by their symmetry classification as the \( t_{2g} \) set, and a set consisting of the \( d_{x^2-y^2} \) and \( d_{z^2} \), known as the \( e_g \) set, destabilized by \( 3/5 \Delta_0 \) where \( \Delta_0 \) is the gap between the two sets.

For configurations \( d^4 \) to \( d^7 \), there are two ways in which the electrons can be placed into the \( t_{2g} \) and \( e_g \) orbitals which depend on the magnitude of \( \Delta_0 \). In the weak field case (also called high spin of spin free), the electrons are distributed one at a time, with parallel spins before pairing as if the d-orbitals were still degenerate. In the strong field case (also known as low spin or spin paired), the electrons first fill the \( t_{2g} \) set. For configurations \( d^1 \) to \( d^3 \) and \( d^8 \) to \( d^{10} \) there is no difference.

In the diagram above, the arrangements for \( d^7 \) are shown as an example. The configurations would be written \( t_{2g}^5 e_g^2 \) for the weak field case and \( t_{2g}^6 e_g^1 \) for the strong field case.

A configuration has an associated crystal field stabilization energy (CSFE) calculated by taking a contribution of \(-2/5\Delta_0\) for each \( t_{2g} \) electron and \(+3/5\Delta_0\) for each \( e_g \) electron. Thus for the two possible
d⁷ cases shown, the CFSE is

for the weak field case:  \[ 5(-2/5 \Delta_o) + 2(+3/5 \Delta_o) = -4/5 \Delta_o \]

for the strong field case:  \[ 6(-2/5 \Delta_o) + 1(+3/5 \Delta_o) = -9/5 \Delta_o \]

A particular complex ion will adopt a configuration depending on the balance between the CSFE, which is always negative or zero, and the pairing energy which is always positive.

As an example consider the complex \([\text{Fe(H}_2\text{O)}_6]^{2+}\). Iron has a d₀ configuration, the value of \(\Delta_o\) is 10,400 cm⁻¹ and the pairing energy is 17600 cm⁻¹. (1 kJ mol⁻¹ = 349.76 cm⁻¹.) We must compare the total of the CFSE and the pairing energy for the two possible configurations.

CFSE (high spin) = \[ 4 \times -2/5 \times 10400 + 2 \times 3/5 \times 10400 = -4160\text{cm}^{-1} \] (-11.89 kJ mol⁻¹)
Pairing energy (1 pair) = \[ 1 \times 17600 = 17600\text{cm}^{-1} \] (50.32 kJ mol⁻¹)
Total = +13440 cm⁻¹ (38.43 kJ mol⁻¹)

CFSE (low spin) = \[ 6 \times -2/5 \times 10400 = -24960 \text{cm}^{-1} \] (-71.36 kJ mol⁻¹)
Pairing energy (3 pairs) = \[ 3 \times 17600 = 52800 \text{cm}^{-1} \] (151.0 kJ mol⁻¹)
Total = +27840 cm⁻¹ (79.60 kJ mole⁻¹)

The high spin configuration is about 41 kJ mol⁻¹ more stable than the low spin configuration, so it is preferred. This is in accordance with the experimental observation of the paramagnetism of \([\text{Fe(H}_2\text{O)}_6]^{2+}\). (Note that it looks as if both configurations are unstable, but remember that what happens to the d-electron energies is only part of the picture. The ligands are held to the central ion (in crystal field theory) by electrostatic attractions which provide a substantial exothermic contribution to the total heat of formation.

**Tetrahedral complexes**
The orbital splitting is the inverse of octahedral. The lower group of two orbitals, known as the e set, are stabilized by $3/5\Delta_T$ and the upper group of three, known as the t$_2$ set, are destabilized by $2/5\Delta_T$ where $\Delta_T$ would equal $4/9\Delta_o$ if the metal ion and ligands were the same.

Note that there are no known complexes where $\Delta_T$ is great enough to cause spin pairing.

Tetrahedral 4-coordination is never favoured over octahedral 6-coordination by the CFSE, and because there are only four metal - ligand bonds vs six for octahedral, it is also disfavoured on electrostatic (or covalent) grounds. Tetrahedral is found where there is zero CFSE difference i.e. d$^0$, d$^5$ (high spin O$_h$), and d$^{10}$, and where bulky ligands preclude 6-coordination.

**Square-planar complexes**

The orbitals are split into four sets. From the lowest in energy: $d_{xz}$ and $d_{yz}$ (known as e$_1$), $d_x^2$ (a$_1$), $d_{xy}$ (b$_2$) and $d_{x^2-y^2}$ (b$_1$). The gap between the b$_1$ and b$_2$ sets is the only gap of importance and would be equivalent to $\Delta_o$ if the metal ion and ligands were the same.

This geometry is favoured if the value of $\Delta_o$ is sufficiently high and if the configuration is d$^8$. This includes some Ni$^{2+}$ complexes and many 4-coordinate complexes of Pd$^{2+}$, Pt$^{2+}$, Rh$^+$, Ir$^+$, and Au$^{3+}$.

**Some generalizations about Ligand Field Splittings and Spectra**

The actual value of $\Delta$ depends on both the metal ion and the nature of the ligands:

- The splitting increases with the metal ion oxidation state. For example, it roughly doubles going from II to III.
- The splitting increases by 30 - 50% per period down a group.
- Tetrahedral splitting would be $4/9$ of the octahedral value if the ligands and metal ion were the same. Of course, generally only the octahedral or tetrahedral complex can actually be prepared for a particular combination, so a direct comparison is rarely feasible.

**Spectrochemical Series**

It is possible to arrange representative ligands in an order of increasing field strength called the spectrochemical series:

$$\Gamma^- < Br^- < -SCN^- < Cl^- < F^- < OH^- < C_2O_4^{2-} < H_2O < -NCS^- < py < NH_3 < en < bipy < o\text{-phen} < NO_2^- < CN^- < CO$$

In comparing groups of similar ligands, for example the halogens, it is possible to rationalize the order. (The negative charge on F$^-$ is more localized that that on the larger Cl$^-$ and so on, so it has a larger effect on the metal ion.) In general, ligands e.g. CN$^-$ or CO which are capable of $\pi$-bonding to the metal appear high in the series. Molecular orbital theory (called ligand field theory for transition metal complexes) is required to explain this in more detail.

These effects have been placed on a semi-quantitative basis by Jorgensen who assigned a factor $g$ to a sampling of metal ions and a factor $f$ to a sampling of ligands such that:

$$\Delta_o \approx g \times f \times 1000 \text{ cm}^{-1}$$

<table>
<thead>
<tr>
<th>Ligand</th>
<th>f - Factor</th>
<th>Metal Ion</th>
<th>g - Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br$^-$</td>
<td>0.72</td>
<td>Mn(II)</td>
<td>8.0</td>
</tr>
</tbody>
</table>
Molecular Orbital Theory (Ligand Field Theory)
The variety of molecular orbital theory applied to transition metal complexes is called ligand field bond theory.

Magnetic Properties (Section 7.4)

- Molecules or ions containing no unpaired electrons are diamagnetic. A sample of such a compound is very very weakly repelled out of a magnetic field. Compounds containing unpaired electrons will be attracted into a magnetic field very weakly if the electrons are acting independently. Such compounds are paramagnetic.
- A substance, usually a metal e.g. iron or nickel with unpaired electrons acting in a concerted way will be strongly attracted into a magnetic field. Such materials are ferromagnetic.
- (Some substances have unpaired electrons (that is one electron per orbital) which are nevertheless organized with their spins oriented in opposite directions in approximately equal numbers. They are called anti-ferromagnetic.)

A paramagnetic substance is characterised experimentally by its (molar) magnetic susceptibility, $\chi_m$. This is measured by suspending a sample of the compound under a sensitive balance between the poles of a powerful electro-magnet, but above the regions where the field is strongest. The weight of the sample is measured with the field off, and then with the field turned, on which pulls the paramagnetic sample downwards. From the weight increase $\chi_m$ can be determined (usually by comparison with a known standard).
The magnetic moment of the substance is given by the Curie Law:

\[ \mu = 2.54(\chi_{m-corr}T)^{1/2} \] (in units of Bohr magnetons - don't ask!)

where \( \chi_{m-corr} \) is the molar magnetic susceptibility corrected for the diamagnetic contribution of all the paired electrons, and \( T \) is the temperature (K). The theoretical magnetic moment for the case where the electron spin is the main contributor is given by the formula:

\[ \mu = 2(S(S+1))^{1/2} \]

where \( S \) is \( \frac{1}{2}n \) where \( n \) is the number of unpaired electrons in the molecule or ion. (There is also a component of the magnetic moment generated by the orbital motion of the electrons, but this is often negligible for lighter transition metal ions.) The following table gives the possible values of \( \mu \) for 1 to 5 unpaired electrons:

<table>
<thead>
<tr>
<th>( n )</th>
<th>( S )</th>
<th>( \mu )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/2</td>
<td>1.73</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>2.83</td>
</tr>
<tr>
<td>3</td>
<td>3/2</td>
<td>3.87</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>4.90</td>
</tr>
<tr>
<td>5</td>
<td>5/2</td>
<td>5.92</td>
</tr>
</tbody>
</table>

Even a rather approximate measurement of the magnetic moment of a complex can allow the assignment of geometry and, in the case of an octahedral species, a discrimination between the high or low spin configuration.

**Examples**

Consider the complexes \([\text{Ni(CN)}_4]^{2-}\) and \([\text{NiCl}_4]^{2-}\). The former is observed to be diamagnetic, and the latter is paramagnetic. What are their structures?

- Work out the oxidation state and d-configuration of the nickel in both complexes. You have to know that chloride and cyanide are anions (both -1) and that neutral nickel has 10 valence electrons. This leads to the conclusion that both complexes contain \( \text{Ni}^{2+} \), a \( d^8 \) ion.
- Choose the possible geometries and draw the configurations. Both compounds contain four ligands so the only likely geometries are square-planar or tetrahedral. Remember, square-planar is normally spin paired and tetrahedral is always spin free. The diagrams below show the configurations:
Clearly, $[\text{Ni(CN)}_4]^{2-}$ fits the square-planar geometry, and $[\text{NiCl}_4]^{2-}$ fits the tetrahedral geometry. This makes sense because it requires a strong field ligand such as CN$^-$ to produce the spin paired configuration which stabilizes the square-planar geometry for a lighter transition metal like nickel (relative to the spin free tetrahedral equivalent that is).

The complex $[\text{Fe(CN)}_6]^{4-}$ is diamagnetic while $[\text{Fe(H}_2\text{O)}_6]^{2+}$ is paramagnetic. Why?

- Work out the oxidation state and the d-electron configuration of the iron in both complexes. You have to know that cyanide has a charge of -1 and water is neutral and that neutral iron has 8 valence electrons. This leads to the conclusion that both complexes contain Fe$^{2+}$, a d$^6$ ion.
- There are six ligands in both complexes, so they are virtually certainly both octahedral. Therefore the only possible difference must be weak field vs strong field. The two configurations are illustrated below.

  ![Diagram showing square-planar and tetrahedral geometries](image)

  **Square Planar**

- The strong field configuration has no unpaired electrons, so it goes with the cyanide complex. The weak field configuration has four unpaired electrons.

**Electronic Absorption Spectroscopy**  Chapter 13

This is quite a complex topic which is not covered in any real detail in Chem 281. The 481 text is rather not too detailed to be very useful. The d-d transitions in complex ions correspond to absorptions which are often, though not always, the cause for their colour. The position of absorption peaks in the spectra allow the direct measurement of □. This is particularly straightforward for ions with a d$^1$ or d$^{10}$ configurations.
Some complexes, usually very intensely coloured, owe their colour to charge-transfer transitions which involve the excitation of an electron from a molecular orbital largely centered on the metal to one largely centered on the ligands or *vice versa*. Such transitions often result in a big dipole change for the molecule which is a factor which is associated with a highly probable transition and hence an intense color.

**Selection Rules for d-d Transitions and Colour Intensity** *(Section 13.5)*

- **The Laporte Rule.** In a molecule or ion possessing a centre of symmetry, transitions are not allowed between orbitals of the same type, for example d to d. The geometries affected by this rule include octahedral and square-planar depending on the ligands and isomers involved. The rule never applies to tetrahedral complexes.

  In cases where the rule applies, the colours of the complexes are usually relatively pale. The reason transitions are observed at all is because the symmetry centre is transiently destroyed by vibrations of the molecules or ions. As examples, consider \([\text{Cu(H}_2\text{O)}_6]^{2+}\) which is a rather pale blue colour vs \([\text{Cu(NH}_3)_4]^{2+}\) which is an intense dark blue.

- **Spin Allowed - Spin Forbidden** Transitions which would require an electron to change its spin are *strongly* forbidden. Consider the case of the high spin d⁵ complex \([\text{Mn(H}_2\text{O)}_6]^{2+}\). This complex is sometimes very pale pink due to the presence of very small amounts of impurities. Finally, bear in mind that allowed and Laporte forbidden transitions can occur outside the visible region of the spectrum if the crystal field splitting is very large. This can happen with strong field ligands such as CN⁻ or CO.

  **7.5 The electronic structures of four-coordinate complexes**

  1. **Four-Coordinate Complexes -- two structural types**

- Tetrahedral structures -- *common for ions with filled d subshells*, e.g., Zn²⁺ as in Zn(OH)₄²⁻
- tetrahedral: no geometric isomers

\[
\begin{array}{c}
\text{OH} \\
\text{HO} \\
\text{Zn} \\
\text{OH}
\end{array}
\]

- Square Planar structures -- common for d^8 metal ions (Ni^{2+}, Pd^{2+}, Pt^{2+}) and for Cu^{2+} e.g.,

\[
\begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Pt} \\
\text{Cl}
\end{array} \quad \begin{array}{c}
\text{H}_3\text{N} \\
\text{H}_3\text{N} \\
\text{Cu} \\
\text{NH}_3
\end{array} \quad \begin{array}{c}
\text{Cl} \\
\text{Cl} \\
\text{Cl} \\
\text{Cl}
\end{array} \quad \begin{array}{c}
\text{H}_3\text{N} \\
\text{H}_3\text{N} \\
\text{NH}_3 \\
\text{NH}_3
\end{array}
\]

Geometric Isomers of ML_4 square planar complexes: cis and trans isomers

**Ligand-field theory**

**Reactions of complexes**

**Stability of Coordination Compounds**

When the term stability is applied to coordination compounds (metal complexes) there can be two interpretations, *thermodynamic* or *kinetic* stability. Thermodynamic stability refers to the change in energy on going from reactants to products, i.e., G for the reaction. Recall that \( \Delta G = \Delta H - T\Delta S = -RT \ln K \), where \( \Delta H \) is the enthalpy, \( \Delta S \) the entropy and K is the equilibrium constant for the reaction. Kinetic stability refers to reactivity, generally ligand substitution. Substitution occurs extremely rapidly in some cases and extremely slowly in others. Complexes of the former type are referred to as labile and those of the latter type inert. Sometimes these two types of stability parallel one another, but often they do not, *vide infra*.

Thermodynamic stability often refers to the energetics and associated equilibrium constant for the reaction of an aquated metal ion with some other ligand (other than water).
The overall equilibrium constant expression for this reaction, generally referred to as $\beta_4$, is defined in the usual fashion as

$$\beta_4 = \frac{[\text{Cu(NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4}.$$ 

Note that overall equilibrium constants are designated as $\beta$’s and values for individual (step-wise) reactions as $K$’s. For simplicity the water molecules associated with the Cu$^{2+}$ have been deleted. This reaction can be described as four individual reactions with individual step-wise equilibrium constants $K_1, K_2,..., K_4$, i.e.,

1. $[\text{Cu(OH}_2)_4]^{2+} + \text{NH}_3 \rightleftharpoons [\text{Cu(OH}_2)_3(\text{NH}_3)]^{2+} + \text{H}_2\text{O}$ \hspace{1cm} log $K_1 = 4.22$
2. $[\text{Cu(OH}_2)_3(\text{NH}_3)]^{2+} + \text{NH}_3 \rightleftharpoons [\text{Cu(OH}_2)_2(\text{NH}_3)_2]^{2+} + \text{H}_2\text{O}$ \hspace{1cm} log $K_2 = 3.50$
3. $[\text{Cu(OH}_2)_2(\text{NH}_3)_2]^{2+} + \text{NH}_3 \rightleftharpoons [\text{Cu(OH}_2)(\text{NH}_3)_3]^{2+} + \text{H}_2\text{O}$ \hspace{1cm} log $K_3 = 2.92$
4. $[\text{Cu(OH}_2)(\text{NH}_3)_3]^{2+} + \text{NH}_3 \rightleftharpoons [\text{Cu(NH}_3)_4]^{2+} + \text{H}_2\text{O}$ \hspace{1cm} log $K_4 = 2.18$

The decrease in successive step-wise constants is invariably observed and is due to several factors including statistics (number of replaceable positions), and increased steric interactions between the new ligands. Overall equilibrium $\beta$ values from 1 to 4 can be defined as $K_1, K_1K_2, K_1K_2K_3$, and $K_1K_2K_3K_4$. The speciation of copper(II) as a function of free ammonia concentration is shown in the Figure.

Equilibrium constants defined as shown above are termed formation constants or stability constants. Those for the reverse reaction are instability or dissociation constants. There can be some confusion here because in certain areas of chemistry and biology the term “stability constant” actually is defined as the dissociation constant.

**Chelate effect**

The stability of the complex of a metal ion with a bidentate ligand such as ethylenediamine (en) is invariably significantly greater than the complex of the same ion.
with two monodentate ligands of comparable donor ability, i.e., for example two ammonia molecule. The is illustrated by the following data:

\[
[Cu(OH_2)_2]^{2+} + \text{en} \rightleftharpoons [Cu(OH_2)_2(\text{en})]^2+ + 2\text{H}_2\text{O} \quad \log K_1 = 10.6
\]
\[
\Delta H = -54 \text{ kJ mol}^{-1}, \quad \Delta S = 23 \text{ J K}^{-1}\text{mol}^{-1}
\]

\[
[Cu(OH_2)_2]^{2+} + 2\text{NH}_3 \rightleftharpoons [Cu(OH_2)_2(\text{NH}_3)_2]^{2+} + 2\text{H}_2\text{O} \quad \log \beta_2 = 7.7
\]
\[
\Delta H = -46 \text{ kJ mol}^{-1}, \quad \Delta S = -8.4 \text{ J K}^{-1}\text{mol}^{-1}
\]

This greater stability for complexes of chelate complexes is termed the chelate effect. Its origin is primarily in the differences in entropy between chelate and non-chelate complex reactions. The formation of chelate complexes results in greater disorder because of the formation of a larger number of free particles in the products whereas there is no change in the number of particles in the formation of comparable nonchelate complexes. Ligand exchange is a good way to examine kinetic stability without complications from changes in \(\Delta H\) for the reaction. Water exchange rates have been determined for a wide range of metal ions and oxidation states. A selection of these is given in the Table. Although the absolute rate of exchange will differ for other ligands the values in the table can be used to gauge the relative reactivity of two metal ions or two different oxidation states of the same metal.

**Reaction Mechanisms**
There are several observations/conclusions that can be made from these data but before stating some of these some comments concerning the mechanism of these reactions are in order.

There are two limiting mechanisms for substitution reactions of coordination complexes, associative, which corresponds to the \(\text{SN}2\) reaction in organic chemistry, and dissociative, which corresponds to the \(\text{SN}1\) reaction in organic chemistry.

**Substitution Reactions**

Ligand exchange is a category of substitution reaction.

\[
[Cu(OH_2)_4]^{2+} + n\text{NH}_3 = [Cu(OH_2)_{4-n}(\text{NH}_3)_n]^{2+}
\]

- **Associative (A)** (2 steps)
  
  \[
  \text{ML}_nX + Y \rightarrow \text{ML}_nXY \rightarrow \text{ML}_nY + X
  \]

- **Dissociative (D)** (2 steps)
  
  \[
  \text{ML}_nX + Y \rightarrow \text{ML}_n + X + Y \rightarrow \text{ML}_nY + X
  \]

- **Interchange** (1 continuous process)
  
  \[
  \text{ML}_nX + Y \rightarrow Y-\text{ML}_n--X \rightarrow \text{ML}_nY + X
  \]

**Associative (A) vs Dissociative (D) Reactions**

- Ligand substitution reactions are either associative or dissociative

**Associative (A):** reaction intermediate has higher coordination number than reactants or products. Rates depend on the entering group. Substitution of square planar complexes is almost always \(A_n\) mechanisms
**Dissociative (D):** reaction intermediate has lower coordination number than reactants or products. Octahedral complexes and smaller metal centers show a rate that depend on leaving group.

**Associative Reactions**
In the limiting case of an associative reaction the entering ligand begins to interact with the metal as the bond to the departing ligand (leaving group) lengthens. In order for the entering ligand to bond to the metal there must be a vacant (preferably) or partially vacant orbital that is accessible to the entering ligand. In an octahedral complex only the $t_{2g}$ d orbitals are accessible as the eg orbitals and the n+1 s and p orbitals are blocked by the presence of the original six ligands. Associative processes are more likely for larger metal ions than for smaller so that they are more important early in a transition series and for heavier members of a family.

**Dissociative Reactions**
In the limiting case the dissociative process involves the formation of a five-coordinate intermediate as a result of complete bond dissociation to the departing ligand (leaving group). The five-coordinate intermediate then reacts with the new ligand (entering group) to reform a six-coordinate complex.

There are many subtleties to mechanisms of substitution of coordination complexes including simultaneous reaction by both pathways, but in the limit the associative mechanism is a second order reaction, first order in both complex and entering group (L), i.e., rate = k[complex][L]. Dissociative processes are first order in complex only since the entering group is not involved in the rate limiting step, which is bond cleavage between the metal ion and the leaving group. The rate law is then rate = k[complex].

### 7.8 Rates and mechanisms of ligand substitution

**Rate constants** for water exchange

<table>
<thead>
<tr>
<th>Complex</th>
<th>Rate Constant (k/s^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[ML₆(OH₂)]^n⁺</td>
<td></td>
</tr>
<tr>
<td>[Ti(OH₂)₆]^3⁺</td>
<td>1.8 x 10^5</td>
</tr>
<tr>
<td>[V(OH₂)₆]^{2⁺}</td>
<td>8.7 x 10^1</td>
</tr>
<tr>
<td>[Cr(OH₂)₆]^{3⁺}</td>
<td>2.4 x 10^6</td>
</tr>
<tr>
<td>[Mn(OH₂)₆]^{2⁺}</td>
<td>2.1 x 10^7</td>
</tr>
<tr>
<td>[Fe(OH₂)₆]^{2⁺}</td>
<td>4.4 x 10^6</td>
</tr>
<tr>
<td>[Cr(OH₂)₆]^{3⁺}</td>
<td>1.2 x 10^2</td>
</tr>
<tr>
<td>[Ru(OH₂)₆]^{2⁺}</td>
<td>3.5 x 10^6</td>
</tr>
<tr>
<td>[Co(OH₂)₆]^{2⁺}</td>
<td>3.2 x 10^6</td>
</tr>
<tr>
<td>[Ni(OH₂)₆]^{2⁺}</td>
<td>3.2 x 10^4</td>
</tr>
<tr>
<td>[Pd(OH₂)₄]^{2⁺}</td>
<td>5.6 x 10^2</td>
</tr>
<tr>
<td>[Pt(OH₂)₄]^{2⁺}</td>
<td>3.9 x 10^4</td>
</tr>
<tr>
<td>[Cu(OH₂)₄]^{2⁺}</td>
<td>&gt;10^7</td>
</tr>
<tr>
<td>[Zn(OH₂)₄]^{2⁺}</td>
<td>&gt;10^7</td>
</tr>
<tr>
<td>[Cr(NH₃)₆OH₂]^{3⁺}</td>
<td>5.2 x 10^5</td>
</tr>
<tr>
<td>[Co(NH₃)₆OH₂]^{3⁺}</td>
<td>5.7 x 10^6</td>
</tr>
<tr>
<td>[Rh(NH₃)₆OH₂]^{3⁺}</td>
<td>8.4 x 10^6</td>
</tr>
<tr>
<td>[Ir(NH₃)₆OH₂]^{3⁺}</td>
<td>6.1 x 10^8</td>
</tr>
</tbody>
</table>

*aAll rate constants are expressed as first order rate constants for
comparative purposes even though some reactions are associative.

(1) An increase in oxidation state for the metal reduces the rate of exchange although there are obvious exceptions to this as indicated by the data for V(II) and V(III), and the exchange rate for Ti(III) appears very large compared to those of other trivalent ions (and even some divalent ions). The reason for this is that there is a large degree of associative character to reactions of the larger elements in a transition series and the activation energy for these reactions is directly related to the occupancy of the t\(_{2g}\) orbitals. Ti(III) has only one t\(_{2g}\) electron and V(III) only two, whereas V(II) has three t\(_{2g}\) electrons.

(2) The fact that water exchange occurs more rapidly in [Rh(NH\(_3\))\(_5\)OH\(_2\)]\(^{3+}\) than in the corresponding Co(III) complex is attributed to a change in mechanism for the larger rhodium complex. There are two reasons for this. First, the much smaller Co\(^{3+}\) ion (0.53 a) can only react by a dissociative process, whereas the t\(_{2g}\) orbitals of the larger rhodium ion (0.67 a, Ir\(^{3+}\) = 0.73 a) are accessible to the entering group. Also bond strengths increase on going to heavier members of a family so that dissociative processes are necessarily slower.

(3) The much slower substitution of V(II) relative to the other first-row, divalent elements is also related to the absence of any eg electrons. In the crystal field model the presence of eg electrons means that there are increased electron-electron repulsions with ligand electron pairs and therefore longer and weaker bonds. In the molecular orbital model the eg orbitals are antibonding with respect to the metal-ligand interaction and the presence of electrons in these orbitals reduces the bond order for the metal-ligand interaction. This point is also dramatically illustrated for the Fe(II)/Ru(II) and Ni(II)/Pd(II) complexes. The Fe(II), which is high spin, has two eg electrons, whereas the Ru(II) complex is low-spin and therefore has no eg electrons. Spin pairing in the Ru(II) complex is a result of the increased strength of its interaction with the six ligands, which also contributes to its decreased reactivity. The Ni(II) complex also has two eg electrons, whereas the four-coordinate, planar Pd(II) complex, like all planar d\(^8\) complexes is diamagnetic. Clearly there are multiple effects here, but the absence of antibonding electrons and the greater metal-ligand bond strength are important contributors to the much lower reactivity of the Pd complex. Note that the reactivity of the Pt analog is still lower.

In the introduction it was indicated that thermodynamic stability and kinetic stability often parallel one another but that sometimes they do not. A vivid illustration of a case where they do not parallel one another is illustrated by the formation constant and ligand exchange rate constant for [Ni(CN)\(_4\)]\(^{2-}\). The second order rate constant for CN\(^-\) exchange is >5 x 10\(^5\) M\(^{-1}\) s\(^{-1}\). However the complex is very stable since

\[
\beta_4 = \frac{[Ni(CN)]_4^{2-}}{[Ni(OH_2)]_6^{2+}[CN^-]^4} = 1.3 \times 10^{30}.
\]

The high rate of ligand exchange is not so surprising when one considers that both axial positions in the square-planar complex are accessible and that salts of the squarepyramidal complex [Ni(CN)\(_5\)]\(^3-\) have been crystallized (and structurally characterized by x-ray diffraction).

**Coordination equilibria**
Rates and mechanisms of ligand substitution

Recommended Questions Shriver and Atkins - Chapter 7:

**Exercises**

7.1, 7.2  You should be able to do these.
7.3  Only the common geometry, octahedral, was covered.
7.4  You should be able to draw them, but do not worry about the naming.
7.5  You should be able to do this.
7.6  Don't bother.
7.7  You should be able to draw structures from their names...
7.8  ...but don't worry about naming them yourself. Can you draw them, though?
7.9  You should be able to do this.
7.10 - 7.14  These are all good questions.
7.15  Not difficult, if you think about it.
7.16 - 7.19  Not covered.
7.20  You should be able to do this.
7.21  Not covered.
7.22  Covered, but in the following section of the notes.
7.23  You should be able to do this.
7.24 - 7.29  Not covered

**Problems**

7.1 - 7.10  These questions are beyond the scope of Chem 241.
7.11  You could take a shot at this one. NO$_2^-$ is ambidentate.
    You should be able to do this question.

Recommended Questions from Cotton, Wilkinson and Gaus - Chapter 23:

"Study Questions"

"A. Review"

1  You should know the answer to the first part and be able to figure out the second from your familiarity of the periodic table.
2  You should be able to answer this.
<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>3, 4</td>
<td>You should be able to answer these.</td>
</tr>
<tr>
<td>5</td>
<td>Not covered, but if you look up the answer it might help you remember the splitting for the square-planar geometry.</td>
</tr>
<tr>
<td>6</td>
<td>Although ligand field theory (M.O.) was not covered, you should know what it is as opposed to crystal field theory.</td>
</tr>
<tr>
<td>7</td>
<td>You must be able to answer this.</td>
</tr>
<tr>
<td>8</td>
<td>You might be able to tackle this though no examples were worked in lectures.</td>
</tr>
<tr>
<td>9</td>
<td>You should be able to answer this.</td>
</tr>
<tr>
<td>10</td>
<td>Not covered.</td>
</tr>
<tr>
<td>11</td>
<td>You should be able to answer this.</td>
</tr>
<tr>
<td>12</td>
<td>A bit of a trick question, but you should be able to get the answer.</td>
</tr>
<tr>
<td>13</td>
<td>You should be able to answer this.</td>
</tr>
<tr>
<td>14, 15</td>
<td>Not covered.</td>
</tr>
<tr>
<td>16</td>
<td>You should be able to do this (LFSE (\equiv) CFSE)</td>
</tr>
</tbody>
</table>

**"B. Additional Questions"**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 3</td>
<td>Beyond the scope of Chem 481.</td>
</tr>
<tr>
<td>4, 5</td>
<td>You should be able to answer these</td>
</tr>
<tr>
<td>6</td>
<td>A bit of a trick question - the answer is simpler than you might think!</td>
</tr>
<tr>
<td>7, 8</td>
<td>You should be able to do these with some &quot;educated guesses&quot;.</td>
</tr>
<tr>
<td>9 - 12</td>
<td>Not covered.</td>
</tr>
</tbody>
</table>