## Contents

23 Notes on Transition Metals and Coordination Compounds     3
  23.1 Introduction .................................................. 3
  23.2 Formation of Metal Complexes and some of their Properties . 4
  23.3 The Geometry of Complexes .................................... 5
  23.4 The Colors of Complexes ....................................... 7
  23.5 Origin of Magnetism in 3d Octahedral Complexes ............. 9
  23.6 Complex Ion Equilibria ......................................... 10
Chapter 23

Notes on Transition Metals and Coordination Compounds

23.1 Introduction

There are several reasons for interest in transition metals. The common use of the metals like iron, copper, nickel and zinc are obvious reasons for interest in their chemistry. But there are many other important uses of these metals and their compounds.

Complex ions— that is, ions that form relatively stable arrangements with various chemical groups such as Cl\(^-\), NH\(_3\), etc. An example is [Co(NH\(_3\))\(_6\)]\(^{3+}\) which is a yellow compound.

Examples of complex formation are given below.

\[
\begin{align*}
Cu^{2+} + NH_3 & \rightarrow Cu(NH_3)^{2+} & K_1 \\
Cu(NH_3)^{2+} + NH_3 & \rightarrow Cu(NH_3)_2^{3+} & K_2 \\
Cu(NH_3)_2^{3+} + NH_3 & \rightarrow Cu(NH_3)_3^{3+} & K_3 \\
Cu(NH_3)_3^{3+} + NH_3 & \rightarrow Cu(NH_3)_4^{3+} & K_4 \\
\end{align*}
\]

where the K’s are appropriate equilibrium constants.

Some typical reactions:

\[
Cu(NH_3)_4^{3+} + 4H^+ + 4H_2O \rightarrow Cu(H_2O)_4^{3+} + 4NH_4^+ \\
\text{bright blue} \quad \text{pale blue} \quad K = \text{large}
\]

A fast reaction with an immediate color change.

\[
Co(NH_3)_6^{3+} + 6H^+ + 6H_2O \rightarrow Co(H_2O)_6^{3+} + 6NH_4^+ \\
\text{orange yellow} \quad K = \text{large}
\]

A very slow reaction with a slow color change.

We are interested in metal ion complexes for purely chemical reasons as for example ruthenium hydride complexes used to introduce H into specific places in compounds, or as a general problem in structural chemistry. We are certainly interested in complexes as they occur in biology. For example, heme complexes Fe\(^{2+}\) and is part of the active transport
of oxygen to the body. Complexes of metal ions are important in enzyme structure and provide a local symmetry, organizing the surrounding molecular framework. Complexes are also important in metal extraction between aqueous phases and organic phases in which the complex is selectively soluble. Important is the incorporation of complexing agents within membranes so that metal ions selectively penetrate the membrane passing through to a “strip” solution on the other side.\(^1\) This transport is affected by the metal-carrier (complexing agent) and driven by the concentration gradient across the selective membrane. This technique is used in the food industry for purification, in the petrochemical industry for separation, in recycling and in productions of pure chemicals.

### 23.2 Formation of Metal Complexes and some of their Properties

We find that mixtures of metal ions like Co\(^{3+}\) with ammonia and chloride ion yield stable molecular structures with remarkable properties. Among these properties are a generally octahedral geometry, a characteristic color depending on the number and types of complexing molecules, and an inherent magnetism (or lack of magnetism) and the ability in some cases to rotate the plane of polarized light (optical activity).

First let’s look at the atomic structure of cobalt. Co has an argon core and valence electrons \((3d)^7(4s)^2\) leaving three 3d holes. The Co\(^{3+}\) ion has electron configuration \((3d)^6\) and is called a d\(^6\) structure having six electrons available for bonding. The d-electron orbit is one where the orbital angular momentum has the value \(L = 2\) and there are \(2L + 1 = 5\) different orbitals. These five orbitals have five different spacial properties as shown below.

![Figure 23.1: Five 3d Orbitals and their Spacial Directions](image)

The way in which the d-electrons fill the available orbits is given by “Hund’s Rule” which states that *everything else being equal, the greatest total spin-multiplicity is lowest in energy.*

\(^1\)Virtually all the salt, NaCl, used in Japan comes from membrane separation technology.
The species complexing the central metal ion are called ligands. Cobalt forms a stable complex with a number of “ligands” one of them being \( \text{Co}[\text{Cl}^\text{3\text{\text{−}}}]_{\text{6\text{\text{−}}}} \) and in this case the ligands are the 6 chloride ions. The three dimensional structure of the complex depends on the valence electron orbits available to the ligands. In the case of \( \text{Co}[\text{Cl}^\text{3\text{\text{−}}}]_{\text{6\text{\text{−}}}} \) the structure is octahedral.

The number of bonds to the central ion is called the \textit{coordination number} and in this cobalt example the coordination number is 6.

Ligands forming one bond to the central ion, as in the case of \( \text{Co}[\text{Cl}^\text{3\text{\text{−}}}]_{\text{6\text{\text{−}}}} \), are called \textit{monodentate} ligands. Oxalic acid, which forms a complex with iron \( \text{Fe}([\text{C}_2\text{O}_4]^\text{3\text{\text{−}}}]_{\text{3\text{\text{−}}}} \), forms two bonds per ligand and is called a \textit{bidentate} ligand complex.

In a crude way we can say that the structure of the complex is determined by the number of d-electrons in the central metal ion. These metal ion valence electrons fill up the available orbits (3d-orbits in the case of transitions elements) according to Hund’s rule.

\section*{23.3 The Geometry of Complexes}

The geometry of molecules is determined by the organization of valence electrons. Thus, tetrahedral carbon, typified by methane \( \text{CH}_4 \), has the configuration \( sp^3 \) mixing three differently oriented p-orbits with s-orbits to achieve its observed shape. In the case of the 3d electrons in the transition elements the complex ion geometry is also determined by the available electron orbits. In the most simple minded way if we place one of the 3d-orbits from the figure above so that the lobes are pointing towards the corners of a square then we can have an orbit pointing above and below the plane of the square. This provides six geometrical bonding sites and gives an octahedral geometry. The state of affairs is more complex than this, but we can see that the 3d orbits contain the elements of octahedral geometry.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig23_2.png}
\caption{An Octahedral Complex}
\end{figure}
Figure 23.3: A Trans Isomer of Cobalt Complex $trans - [Co(NH_3)_4Cl_2]^+$

Figure 23.4: A Cis Isomer of Cobalt Complex $cis - [Co(NH_3)_4Cl_2]^+$
23.4 The Colors of Complexes

In the case of the transition metal complexes the d-energy levels have characteristic “crystal field” splittings caused by the ligands. We can understand this by thinking of the ligands (F\textsuperscript{−} for example) as charges surrounding the metal ion. The electric field from these ligand charges will split the d-energy levels of the metal ion. Some ligand provide a strong splitting and others a weak splitting. The degree of this splitting and the number of electrons filling the d-orbits determines the color (and magnetism) of the complex.

The absorption of light excites an electron from the “ground” configuration to a higher level as shown in the figure below.

From the wavelength of the absorbed light we can estimate the d-level splitting (separation).

using the equation \( h\nu = \frac{h}{\lambda} = \Delta E = (E_2 - E_1) \).

We have a rough understanding of the fundamental processes that occur when light interacts with matter. If we have a beam of white light incident on a metal complex for example, it may absorb a specific wavelength (frequency) from the beam leaving the rest of the wavelengths to pass through the material. Since the complex has removed one color (wavelength) it stands to reason that the material will appear as the complimentary color. We can use the color wheel below to estimate the absorbed wavelengths from the color of the complex.
Figure 23.6: Typical d-electron excitation

Figure 23.7: Color Wheel
### Colors of Some Complexes

<table>
<thead>
<tr>
<th>complex</th>
<th>color</th>
<th>total spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(CN)$_6^{3-}$</td>
<td>pale yellow</td>
<td>0</td>
</tr>
<tr>
<td>Co(NH$_3$)$_6^{3+}$</td>
<td>yellow</td>
<td>0</td>
</tr>
<tr>
<td>Co(SCN)$_4^{2-}$</td>
<td>blue</td>
<td>3/2</td>
</tr>
<tr>
<td>Fe(CN)$_6^{3-}$</td>
<td>red</td>
<td>1/2</td>
</tr>
<tr>
<td>Fe(H$_2$O)$_6^{3+}$</td>
<td>pale violet</td>
<td>5/2</td>
</tr>
</tbody>
</table>

#### 23.5 Origin of Magnetism in 3d Octahedral Complexes

In metal complexes the valence electrons fill the available energy levels according to the Pauli principle, building up the electronic structure as in any molecule. In these cases the d-orbitals are the last filled and give rise to magnetic properties. The electron population of energy levels also obeys Hund’s rule which states that everything being equal the greatest number of unpaired electrons in degenerate\(^2\) orbitals will be the configuration of lowest energy. Depending whether these levels are widely separated or closely spaced and on the number of electrons, the complex will be diamagnetic (no net electron magnetism) or paramagnetic (net electron magnetism). The following figure shows the case for four 3d electrons in a strong field splitting with total spin \(S = 1\).

---

\(^2\)Orbital degeneracy means orbital of equal energy.
CHAPTER 23. NOTES ON TRANSITION METALS AND COORDINATION COMPOUNDS

The next figure shows the case for four 3d electrons in a weak field splitting with total spin $S = 2$.

![Diagram: Weak field Splitting Octahedral Complex 3d^4]

Figure 23.9: Weak field Splitting Octahedral Complex 3d^4

Both complexes are paramagnetic, but one of them has a greater magnetism than the other.

23.6 Complex Ion Equilibria

Complex ions undergo many-step dissociations and these are treated in the usual way in chemical equilibrium calculations. As an example consider the dissociation of the silver ammonia complex, $\text{Ag} (\text{NH}_3)_2^{+3}$. The complex dissociates in two steps.

$$\text{Ag}(\text{NH}_3)^+_2 \rightarrow \text{Ag}(\text{NH}_3)^+ + \text{NH}_3 \quad K_{d1} = 1.2 \times 10^{-4}$$

$$\text{Ag}(\text{NH}_3)^+ \rightarrow \text{Ag}^+ + \text{NH}_3 \quad K_{d1} = 5 \times 10^{-4}$$

It is convenient to write the following overall equilibrium constant expression

$$K_{\text{instability}} = K_1 \times K_2 = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^{+3}]} = 6 \times 10^{-8}$$

Suppose that we have a solution 0.1 mole $\text{AgNO}_3$ in 1 liter of 1.0M $\text{NH}_3$. What are the concentrations of all the species in solution? Silver nitrate completely dissociates so that $[\text{NO}_3^-] = 0.1M$. The silver ion reacts with ammonia to form complexes. Since the $K_{\text{inst}}$ is a small number we can consider that “all” the silver is in the complex $\text{Ag}(\text{NH}_3)_2^{+3}$ and therefore $[\text{Ag}(\text{NH}_3)_2^{+3}] \approx 0.1M$. Looking at the stoichiometry we find that 2 moles of $\text{NH}_3$ are used for each mole of the $\text{Ag}(\text{NH}_3)_2^{+3}$ complex. Thus, $[\text{NH}_3] \approx 1.0 - 2 \times 0.1 = 0.8$. Now look at the dissociation of $\text{Ag}(\text{NH}_3)_2^{+3}$.

---

3Silver chloride, $\text{AgCl}$, is an insoluble substance with $K_{sp} = 1.8 \times 10^{-10}$. On the addition of ammonia the $\text{AgCl}$ ppt. dissolves forming the silver ammonia complex.
\[ Ag(NH_3)_2^+ \rightarrow Ag(NH_3)^+ + NH_3 \quad K_{d1} = 1.2 \times 10^{-4} \]

\[ 0.1 - x \quad x \quad x + 0.8 \]

So,
\[ K_{d1} = 1.2 \times 10^{-4} = \frac{x(x + 0.8)}{0.1 - x} \approx \frac{x(0.8)}{0.1} \]

and \( x = [Ag(NH_3)^+] = 1.5 \times 10^{-5} \). From the \( Ag(NH_3)^+ \) dissociation equilibrium expression
\[ [Ag^+] = \frac{K_{d2}[Ag(NH_3)^+]}{[NH_3]} \approx \frac{5 \times 10^{-4} \times 1.5 \times 10^{-5}}{0.8} = 9.4 \times 10^{-9} \]

<table>
<thead>
<tr>
<th>ion</th>
<th>concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>([Ag^+])</td>
<td>(9.4 \times 10^{-9})</td>
</tr>
<tr>
<td>([Ag(NH_3)^+])</td>
<td>(1.5 \times 10^{-5})</td>
</tr>
<tr>
<td>([Ag(NH_3)_2^-])</td>
<td>(0.1)</td>
</tr>
</tbody>
</table>