Coordination and Special Materials Chemistry

Elective I or II or IV: WS 2007/8 (Lecture)

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Coordination and special materials Chemistry
Recommended Textbooks
How did the study of coordination compounds start?

The coordination chemistry was pioneered by Nobel Prize winner Alfred Werner (1866-1919). He received the Nobel Prize in 1913 for his coordination theory of transition metal-amine complexes.

Werner studied the metal-amine complexes such as [Co(NH$_3$)$_6$Cl$_3$] and recognized the existence of several forms of "cobalt-ammonia chloride". These compounds have different colour and other characteristics. The chemical formula has three chloride ions per mole, but the number of chloride ions that precipitate with Ag$^+$ ions per formula is not always three. He thought only ionised chloride ions will form a precipitate with silver ions. In the following table, the number below the ionised Cl$^-$ is the number of ionised chloride ions per formula. To distinguish ionised chloride from the coordinated chloride, Werner formulated the Complex formula and explained the structure of the cobalt complexes.
How did the study of coordination compounds start? Proposed Structures of Cobalt Ammine Complexes from the Number of Ionized Chloride ions

CoCl$_3$ 6NH$_3$:Yellow [Co(NH$_3$)$_6$]Cl$_3$
CoCl$_3$ 5NH$_3$ Purple [Co(NH$_3$)$_5$Cl]Cl$_2$
CoCl$_3$ 4NH$_3$ Green $trans$-[Co(NH$_3$)$_4$Cl$_2$]Cl
CoCl$_3$ 4NH$_3$ Violet $cis$-[Co(NH$_3$)$_4$Cl$_2$]Cl

The structures of the complexes were proposed based on a coordination sphere of 6. The 6 ligands can be ammonia molecules or chloride ions. Two different structures were proposed for the last two compounds, the $trans$ compound has two chloride ions on opposite vertices of an octahedron, whereas the two chloride ions are adjacent to each other in the $cis$ compound. The $cis$ and $trans$ compounds are known as geometric isomers. Isomerism is a very common feature of coordination compounds and will be discussed in more detail later.
**Coordination chemistry** is the chemistry of compounds formed between metal atoms/ions and other neutral or negatively charged molecules.

Complex compounds ↔ Coordination compounds.

![Coordination compound diagram](image)

Hexa-methyl-zirconate (IV) 
(CH₃)₂ZrCl₄

Isomers: Compounds with the same chemical formula but different structures.

Different types of isomerism: linkage isomerism, hydrate isomerism, cis-trans isomerism, coordination isomerism etc. (see seminar talk)
Naming of coordination compounds

- The names of complexes **start** with the **ligands (in alphabetical order)**, the **anionic ones first**, followed by **neutral ligands**, the **central atom** and the **oxidation state** (Roman numerals).
- If the complex is negative, the name ends with "**ate**".
- names of anionic ligands end with „o“: chloro-, oxo-, fluoro-, cyano.
- neutral ones **without** specific ending: (exception: H₂O: **aqua**, NH₃: **amine**)
  - C₅H₅N, **pyridine**, NH₂CH₂CH₂NH₂, **ethylenediamine**, C₅H₄N-C₅H₄N, dipyridyl,
  - P(C₆H₅)₃: **triphenylphosphine**, CO: **carbonyl**, CS: **thiocarbonyl**

[Co(NH₃)₅Cl]Cl₂: Chloro-penta-ammine-cobalt(III)chloride
[Cr(H₂O)₄Cl₂]Cl: Dichloro-tetra-aqua-chromium(III)chloride
K[PtCl₃NH₃]: Potassium-tri-chloro-ammine-platinate(II)
PtCl₂(NH₃)₂: Di-chloro-diammine-platinum(II)
[Co(en)₃]Cl₃: Tris(ethylenediamine)-cobalt(III)chloride
Ni(PF₃)₄: Tetrakis(phosphorus(III)fluoride)-nickel(0)
  or Tetrakis(phosphorus-tri-fluoride)-nickel(0)

**simple ligands:** di-, tri-, tetra-, penta-, hexa- ...
**complex ligands:** bis-, tris-, tetrakis- ...
### Table 7.1 Symmetry operations and symmetry elements

<table>
<thead>
<tr>
<th>Symmetry operation</th>
<th>Symmetry element</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identity</td>
<td>‘whole of space’</td>
<td>$E$</td>
</tr>
<tr>
<td>Rotation by $360^\circ / n$</td>
<td>$n$-fold symmetry axis</td>
<td>$C_n$</td>
</tr>
<tr>
<td>Reflection</td>
<td>mirror plane</td>
<td>$\sigma$</td>
</tr>
<tr>
<td>Inversion</td>
<td>centre of inversion</td>
<td>$i$</td>
</tr>
<tr>
<td>Rotation by $360^\circ / n$ followed by reflection in a plane perpendicular to the rotation axis</td>
<td>$n$-fold axis of improper rotation*</td>
<td>$S_n$</td>
</tr>
</tbody>
</table>

* Note the equivalences $S_1 = \sigma$ and $S_2 = i$. 
Coordination compounds with CN = 2 (linear)

CN = 2 is very common for complex ions and molecules of Cu(I), Au(I), Ag(I) and Hg(II).

\[
\begin{align*}
\text{Cu(I)} & : \quad X \rightleftharpoons \text{Cu} \rightleftharpoons X^- \\
& \quad X = \text{Cl, Br} \\
\text{Ag(I)} & : \quad \text{H}_3\text{N} \rightleftharpoons \text{Ag} \rightleftharpoons \text{NH}_3^+ \\
\text{Au(I)} & : \quad \text{R}_3\text{P} \rightleftharpoons \text{Au} \rightleftharpoons \text{PR}_3^+ \\
& \quad \text{H}_3\text{C} \rightleftharpoons \text{Hg} \rightleftharpoons \text{CH}_3
\end{align*}
\]

CN = 3 is very rare among normal coordination compounds of d-metals.
Coordination compounds with CN = 4 (tetrahedral)

5 Tetrahedral complex, $T_d$

<table>
<thead>
<tr>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{O} \quad ^{-3}_3$</td>
<td>$\text{O} \quad ^{-2}_2$</td>
<td>$\text{O} \quad ^{-1}_1$</td>
</tr>
<tr>
<td>$\text{O} \quad \text{V} \quad \text{O}$</td>
<td>$\text{O} \quad \text{Cr} \quad \text{O}$</td>
<td>$\text{O} \quad \text{Mn} \quad \text{O}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
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<tbody>
<tr>
<td>$\text{Cl} \quad ^{-2}_2$</td>
<td>$\text{Cl} \quad ^{-2}_2$</td>
<td>$\text{Br} \quad ^{-2}_2$</td>
<td>$\text{Br} \quad ^{-2}_2$</td>
</tr>
<tr>
<td>$\text{Cl} \quad \text{Fe} \quad \text{Cl}$</td>
<td>$\text{Cl} \quad \text{Co} \quad \text{Cl}$</td>
<td>$\text{Br} \quad \text{Ni} \quad \text{Br}$</td>
<td>$\text{Br} \quad \text{Cu} \quad \text{Br}$</td>
</tr>
</tbody>
</table>
Coordination compounds with \( CN = 4 \) (square planar)

**8 Square-planar complex, \( D_{4h} \)**

**6 cis-[Pt(Cl)\(_2\)(NH\(_3\))\(_2\)]**

**Preferred coordination of d\(^8\) central atoms !!**
Coordination compounds with CN = 5 (Square pyramidal) (e.g. active center of myoglobin and haemoglobin)
Coordination compounds with CN = 5 (trigonal bipyramidal)

8

9b $[\text{Ni}(_3\text{CN})_6]^{3-}$ (trigonal-bipyramidal conformation)
Pseudorotation (CN = 5): square pyramidal $\leftrightarrow$ trigonal pyramidal
Coordination compounds with CN = 6 (octahedral)

13 Octahedral complex, $O_h$

Types of distortions of octahedra

(a)  
(b)  
(c)  
(d)
Coordination compounds with CN = 6 (trigonal prismatic)

14 Trigonal prism, $D^{3h}_{3h}$
Constitution and Coordination Number, higher CN's

The most important factors that determine the constitution and coordination number of a complex are:

- size of the central atom
- steric interactions between ligands
- electronic interactions

Higher coordination numbers (CN's) are favoured:

- in complexes with atoms (and ions) of the periods 5 and 6
- on the left of a row of the d-block where atoms are relatively large and have a small number of d-electrons
- for central atoms with a high oxidation number and thus a small number of remaining d-electrons (e.g. [Mo(CN)_8]^{4-}
Coordination compounds with CN = 7 („capped“)

- rare with 3d elements but more common with 4d and 5d metals

**CN = 7:** pentagonal bipyramid, (mono-) capped **trigonal prism**, capped octahedron
e.g. \([\text{ZrF}_7]^{3-}\), \([\text{ReOCl}_6]^{2-}\), \([\text{UO}_2(\text{OH}_2)_5]^{2+}\) ...

**16** Pentagonal bipyramid, \(D_{5h}\)

**18** Capped trigonal prism

**17** Capped octahedron
Coordination compounds with $\text{CN} = 8$

$\text{CN} = 8$: square antiprism ("archimedian" antiprism), trigonal dodecahedron, cube
Coordination compounds with $CN = 9$ ("capped trigonal prism")

$CN = 9$: common with Re (e.g. $[\text{ReH}_9]^{2-}$) and f-block elements (e.g. $[\text{Nd(OH}_2)_9]^{3+}$)

$CN > 9$: important only for complexes with heavy metal central atoms (e.g. f-elements)
1 Preferably without using reference material, write out the 3d elements in their arrangement in the periodic table. Indicate the metal ions that commonly form tetrahedral complexes of formula $[MX_4]^{2-}$ where $X$ is a halide ion.

2 (a) On a chart of the d-block elements in their periodic table arrangement, identify the elements and associated oxidation numbers that form square-planar complexes. (b) Give formulas for three examples of square-planar complexes.

3 (a) Sketch the two structures that describe most six-coordinate complexes. (b) Which one of these is rare? (c) Give formulas for three different d-metal complexes that have the more common six-coordinate structure.

4 Name and draw structures of the following complexes: (a) $[\text{Ni(CO)}_4]$; (b) $[\text{Ni(CN)}_4]^{2-}$ (c) $[\text{CoCl}_4]^{2-}$ (d) $[\text{Ni(NH}_3)_6]^{2+}$.

5 Draw the structures of representative complexes that contain the ligands (a) en, (b) ox$^{2-}$, (c) phen, and (d) edta$^4$.

6 Draw the structure of (a) a typical square-planar four-coordinate complex; (b) a typical trigonal prismatic six-coordinate complex; (c) a typical complex of coordination number 2. Name each complex.

7 Give formulas for (a) pentaamminechlorocobalt(III) chloride, (b) hexaaquairon(3+) nitrate; (c) cis-dichlorobis(ethylenediamine)ruthenium(II); (d) μ-hydroxobis[pentaamminechromium(III)] chloride.
Isomerism: cis-trans isomerism

a

\[ \text{cis-Form} \quad \text{trans-Form} \]

b

\[ \text{cis-Form} \quad \text{trans-Form} \]

c

\[ \text{fac-Form} \quad \text{mer-Form} \]

**mer**: meridional

**fac**: facial
Isomerism and Chirality (important terms)

- A **chiral** molecule is not superimposable on its own mirror image
- **Optical isomerism**: Rotation of the plane of polarized light shown by optical isomers
- **Enantiomeric pair (“racemate”)**: Two mirror-image isomers in one sample
- **Diastereomers**: Molecules with **more than one** center of chirality (e.g. organic sugar molecules)

**Criteria for absence of chirality**: 1. mirror plane through central atom \( (S_1) \), 2. inversion centre \( (S_2) \), 3. no improper rotation

49 [MABCD] enantiomers

\[ S_4 \]
Isomerism and Chirality

7.6 (a) and (b) Enantiomers of cis-
[CoCl₂(en)₂] and (c) the achiral trans
isomer. The curves represent the CH₃CH₂
bridges in the en ligands. The mirror plane
for testing whether there is an S₄ axis is
also shown.

7.7 Absolute configurations of
[M(L−L)₃] complexes; Δ is a right-hand
screw and Λ is a left-hand screw, as is
indicated in the diagrams at the top of
the figure by the direction that a screw
would turn when being driven in the
direction shown.
8 Name the octahedral complex ions (a) cis-[CrCl₂(NH₃)₄]⁺, (b) trans-[Cr(NCS)₄(NH₃)₂]⁻, and (c) [Co(C₂O₄)(en)₂]⁺. Is the oxalato complex cis or trans?

9 Draw all possible isomers of (a) octahedral [RuCl₂(NH₃)₄], (b) square-planar [IrH(CO)(PR₃)₂], (c) tetrahedral [CoCl₃(OH₂)]⁻, (d) octahedral [IrCl₃(PEt₃)₃], and (c) octahedral [CoCl₂(en)(NH₃)₂]⁺.

10 The compound Na₂IrCl₅ reacts with triphenylphosphine in diethylene glycol under an atmosphere of CO to give trans-[IrCl(CO)(PPh₃)₂], known as Vaska’s compound. Excess CO produces a five-coordinate species and treatment with NaBH₄ in ethanol gives [IrH(CO)₂(PPh₃)₂]. Draw and name the three complexes.

11 Which of the following complexes are chiral? (a) [Cr(ox)₃]³⁻, (b) cis-[PtCl₂(en)], (c) cis-(RhCl₂(NH₃)₄)⁺, (d) [Ru(bipy)₃]²⁺, (e) [Co(edta)], (f) fac-[Co(NO₂)₃(dien)], (g) mer-[Co(NO₂)₃(dien)]. Draw the enantiomers of the complexes identified as chiral and identify the plane of symmetry in the structures of the achiral complexes.

12 One pink solid has the formula CoCl₃ 5NH₃ H₂O. A solution of this salt is also pink and rapidly gives 3 mol AgCl on titration with silver nitrate solution. When the pink solid is heated, it loses 1 mol H₂O to give a purple solid with the same ratio at NH₃:Cl:Co. The purple solid releases two of its chlorides rapidly; then, on dissolution and after titration with AgNO₃, releases one of its chlorides slowly. Deduce the structures of the two octahedral complexes and draw and name them.

13 The hydrated chromium chloride that is available commercially has the overall composition CrCl₃ 6H₂O. On boiling a solution, it becomes violet and has a molar electrical conductivity similar to that of [Co(NH₃)₆]Cl₃. In contrast, CrCl₃·5H₂O is green and has a lower molar conductivity in solution. If a dilute acidified solution of the green complex is allowed to stand for several hours, it turns violet. Interpret these observations with structural diagrams.
All atoms/molecules are treated as electrical point charges.

Tetrahedral

Octahedral

Free-ion

\[ \Delta_{\text{tet}} \]

\[ \Delta_{\text{act}} \]

7.13 The effect of a tetrahedral crystal field on a set of \( d \) orbitals is to split them into two sets; the \( t_2 \) pair (which point less directly at the ligands) lies lower in energy than the \( e \) triplet.

7.8 The orientation of the five \( d \) orbitals with respect to the ligands of an octahedral complex.
Basic Crystal Field Theory: splitting of energy levels (spectrochemical series)

The influence of different ligands on the size of $\Delta = 10Dq$

$I^- < S^{2-} < Cl^- < NO_3^- < F^- < H_2O < NH_3 < en < NO_2^- < CN^- < CO$

The strength of the ligand field varies with:

a) the size and chemical properties of the ligand (no simple relation!)

b) the oxidation number of the central atom (the higher the oxidation number the stronger the ligand field)
Basic Crystal Field Theory: optical spectrum and ligand field

\[ \approx 500 \text{ nm (red)} - \text{absorption in the blue green region, complex has complementary color} \]

\[ [\text{Ti(H}_2\text{O})_6]^{3+} \]

\[ \text{Ti}^{3+}: (\text{Ar})d^1, \text{octahedral complex} \]
Basic Crystal Field Theory: Weak Field – Strong Field

Spin pairing energy versus ligand field splitting

 octahedral complex
weak field strong field

d⁶ high spin (paramagnetism)
d⁶ low spin (diamagnetism)

high spin: maximum number of unpaired electrons
low spin: minimum number of unpaired electrons

→ tetrahedral: high spin (preferably)  octahedral: low spin (preferably)
**Basic Crystal Field Theory: Ligand field stabilization energies (LFSE)**

**LFSE:** Energetic stabilization relative to a field with **spherical** symmetry

**Tetrahedral case:**
\[
\text{LFSE} = (-0.6 \times x(e) + 0.4 \times y(t_2)) \times \Delta_T
\]

**Octahedral case:**
\[
\text{LFSE} = (-0.4 \times x(t_{2g}) + 0.6 \times y(e_g)) \times \Delta_O
\]

\(x, y\): number of electrons in the respective electronic states (e\(_g\) or t\(_{2g}\) )

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**Table 7.4 Ligand-field stabilization energies (absolute values)**

<table>
<thead>
<tr>
<th>(d^n)</th>
<th>Example</th>
<th>Octahedral</th>
<th>Tetrahedral</th>
<th>(N)</th>
<th>(\text{LFSE})</th>
<th>(N)</th>
<th>(\text{LFSE})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d^0)</td>
<td>Ca(^{2+}), Sc(^{3+})</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>(d^1)</td>
<td>Ti(^{3+})</td>
<td>1</td>
<td>0.4</td>
<td>1</td>
<td>0.6</td>
<td>1</td>
<td>0.6</td>
</tr>
<tr>
<td>(d^2)</td>
<td>V(^{2+}), V(^{3+})</td>
<td>2</td>
<td>0.8</td>
<td>2</td>
<td>1.2</td>
<td>2</td>
<td>1.2</td>
</tr>
<tr>
<td>(d^3)</td>
<td>Cr(^{3+}), V(^{4+})</td>
<td>3</td>
<td>1.2</td>
<td>3</td>
<td>0.8</td>
<td>3</td>
<td>0.8</td>
</tr>
<tr>
<td>(d^4)</td>
<td>Cr(^{4+}), Mn(^{3+})</td>
<td>2</td>
<td>1.6</td>
<td>4</td>
<td>0.6</td>
<td>4</td>
<td>0.4</td>
</tr>
<tr>
<td>(d^5)</td>
<td>Mn(^{4+}), Fe(^{3+})</td>
<td>1</td>
<td>2.0</td>
<td>5</td>
<td>0</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>(d^6)</td>
<td>Fe(^{4+}), Co(^{2+})</td>
<td>0</td>
<td>2.4</td>
<td>4</td>
<td>0.4</td>
<td>4</td>
<td>0.6</td>
</tr>
<tr>
<td>(d^7)</td>
<td>Co(^{3+})</td>
<td>1</td>
<td>1.8</td>
<td>3</td>
<td>0.8</td>
<td>3</td>
<td>1.2</td>
</tr>
<tr>
<td>(d^8)</td>
<td>Ni(^{2+})</td>
<td>2</td>
<td>1.2</td>
<td>2</td>
<td>0.8</td>
<td>2</td>
<td>0.8</td>
</tr>
<tr>
<td>(d^9)</td>
<td>Cu(^{2+})</td>
<td>1</td>
<td>0.6</td>
<td>1</td>
<td>0.4</td>
<td>1</td>
<td>0.4</td>
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<tr>
<td>(d^{10})</td>
<td>Cu(^{3+}), Zn(^{2+})</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</tr>
</tbody>
</table>

\(N\) is the number of unpaired electrons; \(\text{LFSE}\) is in units of \(\Delta_O\) for octahedra or \(\Delta_T\) for tetrahedra; the calculated relation is \(\Delta_T = \frac{2}{3}\Delta_O\).
Basic Crystal Field Theory: Ligand field stabilization energies (LFSE)

![Graph showing LFSE vs. number of electrons (n)](image)

Table 7.4 Ligand-field stabilization energies (absolute values)*

<table>
<thead>
<tr>
<th>$d^n$</th>
<th>Example</th>
<th>Octahedral</th>
<th>Tetrahedral</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$N$</td>
<td>$</td>
</tr>
<tr>
<td>$d^0$</td>
<td>Ca$^{2+}$, Sc$^{3+}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$d^1$</td>
<td>Ti$^{3+}$</td>
<td>1</td>
<td>0.4</td>
</tr>
<tr>
<td>$d^2$</td>
<td>V$^{2+}$, V$^{3+}$</td>
<td>2</td>
<td>0.8</td>
</tr>
<tr>
<td>$d^3$</td>
<td>Cr$^{3+}$, V$^{2+}$</td>
<td>3</td>
<td>1.2</td>
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<tr>
<td>$d^4$</td>
<td>Cr$^{2+}$, Mn$^{3+}$</td>
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<td>1.6</td>
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<tr>
<td>$d^5$</td>
<td>Mn$^{2+}$, Fe$^{3+}$</td>
<td>1</td>
<td>2.0</td>
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<tr>
<td>$d^6$</td>
<td>Fe$^{2+}$, Co$^{3+}$</td>
<td>0</td>
<td>2.4</td>
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<tr>
<td>$d^7$</td>
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<td>1.8</td>
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<tr>
<td>$d^8$</td>
<td>Ni$^{2+}$</td>
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<td>1.2</td>
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<tr>
<td>$d^9$</td>
<td>Cu$^{2+}$</td>
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<tr>
<td>$d^{10}$</td>
<td>Cu$^{+}$, Zn$^{2+}$</td>
<td>0</td>
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</table>

* $N$ is the number of unpaired electrons; LFSE is in units of $\Delta_0$ for octahedra or $\Delta_T$ for tetrahedra; the calculated relation is $\Delta_T \approx \frac{3}{2} \Delta_0$. 

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*Figure 19-11
Shriver & Atkins Inorganic Chemistry, Fourth Edition
Basic Crystal Field Theory: Ligand field stabilization energies (LFSE) – Ionic radii

Table 7.4 Ligand-field stabilization energies (absolute values)*

<table>
<thead>
<tr>
<th>d^0</th>
<th>Example</th>
<th>N</th>
<th>LFSE</th>
<th>N</th>
<th>LFSE</th>
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<td>V^2+</td>
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<td>0.8</td>
<td>2</td>
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<tr>
<td>d^3</td>
<td>Cr^3+, V^2+</td>
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<td>1.2</td>
<td>3</td>
<td>0.8</td>
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</table>

<table>
<thead>
<tr>
<th></th>
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<th>Strong-field</th>
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<th>Weak-field</th>
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<tbody>
<tr>
<td>d^4</td>
<td>Cr^3+, Mn^{3+}</td>
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<td>1.6</td>
<td>4</td>
<td>0.6</td>
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<tr>
<td>d^5</td>
<td>Mn^{2+}, Fe^{2+}</td>
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<tr>
<td>d^6</td>
<td>Fe^{3+}, Co^{3+}</td>
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<td>4</td>
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<tr>
<td>d^7</td>
<td>Co^{2+}</td>
<td>1</td>
<td>1.8</td>
<td>3</td>
<td>0.8</td>
</tr>
<tr>
<td>d^8</td>
<td>Ni^{2+}</td>
<td>2</td>
<td>1.2</td>
<td>2</td>
<td>0.8</td>
</tr>
<tr>
<td>d^9</td>
<td>Cu^{2+}</td>
<td>1</td>
<td>0.6</td>
<td>1</td>
<td>0.4</td>
</tr>
<tr>
<td>d^10</td>
<td>Cu^{3+}, Zn^{2+}</td>
<td>0</td>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

*N is the number of unpaired electrons; LFSE is in units of ΔΩ for octahedra or Δτ for tetrahedra; the calculated relation is Δτ = 2/3 ΔΩ.

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Basic Crystal Field Theory: Ligand field stabilization energies (LFSE) – Hydration enthalpy of $M^{2+}$ ions

Yellow points: after subtraction of LFSE from experimental value

Figure 19-11
Shriver & Atkins Inorganic Chemistry, Fourth Edition

Figure 19-6
Shriver & Atkins Inorganic Chemistry, Fourth Edition
Magnetism of coordination compounds: magnetic (dipole) moments

In general there are two components of the resulting magnetic moment of an atom (ion):

⇒ orbital angular momentum ($\mu_O$) ⇒ spin momentum ($\mu_S$)

- In most coordination compounds with 3d elements as central atoms the orbital angular momentum can be neglected (technical term: "quenched").
- Typical for 3d complexes with one central atom: spin only magnetism ($\mu_S$)

Definition of $\mu_S$:

$$\mu_S = \mu_B \times 2 \times (S(S+1))^{1/2}$$

$\mu_B = 9,27 \times 10^{-24} \text{ Am}^2$ (Bohr magneton, smallest quantity of a magnetic moment)

$S = \frac{1}{2} \times n$ (Total spin quantum number

$n$: number of unpaired electrons)

<table>
<thead>
<tr>
<th>$n$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_S$</td>
<td>1,73</td>
<td>2,83</td>
<td>3,87</td>
<td>4,90</td>
<td>5,91</td>
</tr>
</tbody>
</table>
Magnetism of coordination compounds: Gouy-balance

central atom with unpaired valence electrons ⇒ paramagnetism

central atom with paired valence electrons only ⇒ diamagnetism
SQUID: Superconducting Quantum Interference Device

Sophisticated physical background based on the quantization of magnetic flux (one or two weak links, "Josephson contacts") in a superconducting wire (loop) that allow the tunneling of "Cooper pairs".
Special aspects of the electronic structure of complexes with CN 4

1. Tetrahedral coordination

- inverse splitting (compared to octahedral case)
  - only the weak field case is of importance (⇒ high spin magnetism)

2. Tetragonal and square planar coordination ⇒ (Jahn-Teller-effect)
Special aspects of the electronic structure of complexes with CN 4

- **Dynamic Jahn-Teller effect**: temperature driven intramolecular change of the elongation direction

- **Oktaederfield**

- **d^4**
  - square planar

- **d^9**
  - tetragonally elongated

- **d^7**

- **d^8**

- **d^4**

- **d^9**

- **d^7**

- **d^8**

- **Ni^{2+}, Pd^{2+}, Pt^{2+}, Rh^{+} ...**

- **Cr^{2+}, Mn^{3+} (high-spin)**

- **Cu^{2+}**

- **Co^{2+}, Ni^{3+} (low-spin)**
1. Determine the configuration (in the form $t_{2g}^x e_g^y$ or $e^{x+y}$, as appropriate), the number of unpaired electrons and the ligand field stabilization energy (LFSE) as a multiple of $\Delta_{\text{oct}}$ or $\Delta_{\text{tet}}$ for each of the following complexes: $[\text{Co(NH}_3\text{)}_6]^{3+}$, $[\text{Fe(H}_2\text{O)}_6]^{2+}$, $[\text{Fe(CN)}_6]^{3-}$, $[\text{W(CO)}_6]$ and $[\text{FeCl}_4]^{2-}$. Estimate the spin only contribution to the magnetic moment in each complex.

2. Solutions of the complexes $[\text{Co(NH}_3\text{)}_6]^{2+}$, $[\text{Co(H}_2\text{O)}_6]^{2+}$ (both $O_h$) and $[\text{CoCl}_4]^{2-}$ (T₄) are colored. One is pink, another yellow and the third is blue. Considering the spectrochemical series and the relative magnitudes of $\Delta_{\text{tet}}$ and $\Delta_{\text{oct}}$ assign each color to one of the complexes.

3. For each of the following pairs of complexes identify the one that has the larger LFSE:

- $[\text{Cr(H}_2\text{O)}_6]^{2+}$ - $[\text{Mn(H}_2\text{O)}_6]^{2+}$
- $[\text{Mn(H}_2\text{O)}_6]^{2+}$ - $[\text{Fe(H}_2\text{O)}_6]^{3+}$
- $[\text{Fe(H}_2\text{O)}_6]^{3+}$ - $[\text{Fe(CN)}_6]^{3-}$

4. Estimate the spin only contribution to the magnet moments for each of the complexes in 1.
Ligand-field theory

Crystal field theory has problems to explain why the ligand field splitting for some uncharged molecules (e.g. CO) is unusually large and is moderate for others (e.g. NH₃).

⇒ solution: the interaction between ligands and central atom has to be discussed in terms of atomic and molecular orbitals and not only in terms of point charges (as in crystal field theory)

⇒ σ- and π-bonding contributions have to be analyzed separately

1. Analyze the symmetry properties of groups of atomic orbitals (separate for ligands and central atoms) ⇒ symmetry adapted orbitals

2. Overlap atomic orbitals of similar symmetry to form molecular orbitals (necessary: basic knowledge in group theory and basic MO-theory)

<table>
<thead>
<tr>
<th>Central atom (3d-element) orbital</th>
<th>symmetry label</th>
<th>Degeneracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>s</td>
<td>a₁g</td>
<td>1</td>
</tr>
<tr>
<td>pₓ, pᵧ, pₗ</td>
<td>t₁u</td>
<td>3</td>
</tr>
<tr>
<td>dₓᵧ, dₓz, dᵧz</td>
<td>t₂g</td>
<td>3</td>
</tr>
<tr>
<td>dₓ², -y², dᵧ²</td>
<td>eₐ</td>
<td>2</td>
</tr>
</tbody>
</table>
Ligand-field theory: symmetry-adapted groups of orbitals: \( \sigma \)-bonding only

central atom: \( s-, p- \) and \( d-\) Orbitals are taken into account

ligands: only \( s-\) orbitals but no \( p-\) orbitals are not taken into account
Synergistic bonding in carbonyl complexes with transition metals: the CO-molecule is a $\sigma$-donor and a $\pi$-acceptor at the same time.
Ligand-field theory: phosphines, $\sigma$-donors and $\pi$-acceptors

The bonding of phosphines PR$_3$ to transition metal atoms is basically similar to that of CO; dependent on the respective substituents $\sigma$-donor and $\pi$-acceptor-strength, however, are different.

$\sigma$-donor-effect: lone pair at phosphorous atom

$\pi$-acceptor-effect: empty p- (and d-)orbitals at the P-atom

electron rich phosphines are good $\sigma$-donors and bad $\pi$-acceptors whereas for electron poor ones the inverse statement holds.

order of „Lewis basicity“:

e.g.: PMe$_3$ > P(OMe)$_3$ > PF$_3$

$\sigma$-/\pi$-$donor: Lewis base

$\sigma$-/\pi$-$acceptor: Lewis acid
Ligand-field theory: dihydrogen complexes

examples

\( \sigma \)-donor and \( \pi \)-acceptor effect
Ligand-field theory: $\sigma$-donor strength

**Bad $\sigma$-donor:**
- Large energy difference between $M$- and $L$-orbitals,
  small ligand field splitting, small inter-orbital exchange due to large size differences between $M$ and $L$

**Good $\sigma$-donor:**
- Small energy difference between $M$- and $L$-orbitals,
  large ligand field splitting, strong inter-orbital-exchange due to small size differences between $M$ and $L
Ligand-field theory: $\sigma$-donor strength, examples

$\sigma$-donor strength is not an absolute property but requires a detailed analysis of the respective molecule

O- versus N-donor strength:
- free electron pairs of N are energetically higher than the ones of O, i.e. closer to the metal d-orbitals $\rightarrow$ N better $\sigma$-donor than O

O- versus S-donor strength:
- diffuse orbitals of the large S-atoms provide bad overlap with the contracted d-orbitals of M$^+$ $\rightarrow$ O better $\sigma$-donor than S
Ligand-field theory: $\pi$-donor and $\pi$-acceptor effect

$\pi$-donor ligand: completely filled low-energy $\pi$-orbitals, $t_{2g}$-$\pi$-overlap preferred: $\Delta_o$ reduced

$\pi$-acceptor ligand: incompletely filled low-energy $\pi^*$-orbitals, $t_{2g}$-$\pi$-overlap preferred: $\Delta_o$ increased
**Electronic Spectra - Spectroscopy**

**Charge Transfer transition (CT)**
electronic transition from a metal $\pi$-Orbital to a ligand $\pi^*$-Orbital or vice versa. *(high intensity, strongly influenced by the type of solvent)*

**Typical example:** The spectrum of the $d^3$ complex $[\text{Cr(NH}_3\text{)}_6]^{3+}$

![Graph](image)

- **ligand-field transitions (d-d)**
- **electronically „forbidden“ transition**
- **Magnified absorption**

![Diagram](image)

(a) 

(b)
**Charge-Transfer transitions**

Charge-transfer-transitions (CT) show up in electronic spectra by strong transitions in the visible region and are characterized by intense colour (high extinction)

- **metal-to-ligand** transitions: from a metal d-Orbital to a ligand $\pi^*$-orbital: preferably observed for **ligands with low-lying $\pi^*$-orbitals** (e.g. aromatic ligands with donor N-atoms like 2,2' bipyridine or 1,10 phenanthroline) and metal atoms with **low oxidation number** thus relatively **high** valence states

- **ligand-to-metal** transitions: from a **ligand $\pi$-orbital** (relatively high in energy: e.g. lone pairs of $S^{2-}$, $O^{2-}$) to an **empty and low lying d orbital** of the central metal atom (high oxidation number): e.g. $\text{MnO}_4^{-}$, $\text{CrO}_4^{2-}$, $\text{VO}_4^{3-}$ etc.
Coordination Chemistry: Spectroscopy - microstates

- Two sets of energetically different excited microstates for the excitation of one electron in \([\text{Cr(H}_2\text{O)}_6]^{3+}\) (d³)

- each threefold degenerate

- electron-electron repulsion is responsible for different excitation energies

**Multiplicity (M)** of a microstate: \(M = 2S + 1\) (S: total spin moment)

e.g. for above excited states (and the ground state) holds:

\[ S = 3 \times \frac{1}{2} = 3/2 \]

\[ M = 2 \times (3/2) + 1 = 4 \text{ (Quartett-term)} \]

**Importance of Multiplicity**: M of ground and excited state is similar \(\rightarrow\) allowed (strong) excitations!
Coordination Chemistry: Spectroscopy - microstates

- Three sets of energetically different excited microstates for the excitation of one electron in \([\text{Ni(H}_2\text{O)}_6]\text{]}^{2+}(\text{d}^8)

- each threefold degenerate

- Triplett terms, multiplicity unchanged with respect to ground state

- analysis of spectra in this way would be very time consuming

- Selection rules distinguish between allowed and forbidden electronic transitions. They are based on the magnitude of the transition dipole moment, which is a measure for the coupling strength of the electronic system of the complex molecule to the external field (special case: Laporte rules, transitions between even parity states are forbidden).
Coordination Chemistry: Tanabe-Sugano-diagram

A complete T.S. diagram contains all possible electronic excitations (including the forbidden ones)

**y-axis:** Excitation energy in units of B (B, typical energy for an electron-electron repulsion = Racah-parameter ~ 1000 cm⁻¹)

**x-axis:** crystal field splitting energy in units of B

A, E, T are symmetry symbols (group theory) that denote the degree of degeneration (A: non-degenerate, E: twofold degenerate, T: threefold degenerate)

(^3): multiplicity

(\(g\)): gerade symmetry information
Coordination Chemistry: Tanabe-Sugano-diagram

Tanabe-Sugano-diagram for a d^2 ground state

- One electron excitation
- Two electron excitation

m → 2 1 0 -1 -2

\( \left[ \begin{array}{c} x^2-y^2 \\ xz \\ z^2 \\ yz \\ xy \end{array} \right] \)

\( \left[ \begin{array}{c} x^2-y^2 \\ xz \\ z^2 \\ yz \\ xy \end{array} \right] \)

\( \left[ \begin{array}{c} x^2-y^2 \\ xz \\ z^2 \\ yz \\ xy \end{array} \right] \)

\( \left[ \begin{array}{c} x^2-y^2 \\ xz \\ z^2 \\ yz \\ xy \end{array} \right] \)

\( \left[ \begin{array}{c} x^2-y^2 \\ xz \\ z^2 \\ yz \\ xy \end{array} \right] \)
**Coordination Chemistry: Russel-Saunders and jj-coupling**

A more detailed treatment of the physical background is based on a sophisticated combined treatment of the total orbital momentum (L), total spin momentum (S), total momentum (J) and the spin multiplicity (M).

- definitions:

- \( L = \sum I_n \); \( S = \sum s_n \); \( J = L + S \), \( M = 2S + 1 \)

  (special: \( L = 0 \rightarrow S \), \( L = 1 \rightarrow P \), \( L = 2 \rightarrow D \), \( L = 3 \rightarrow F \))

- Symbol: \( ^M L_J \) (e.g. \( ^3P_2 \), \( ^3F_4 \))

- \( J = L + S \) refers to a Russel-Saunders-coupling (coupling of the total moments, preferably 3d elements)

- the spectra of heavier elements must be treated on the basis of jj-coupling (coupling of the individual moments: \( j_n = I_n + s_n \rightarrow J = \sum j_n \))
**Coordination Chemistry: Basic aspects of reactivity**

**Inert Complexes:** Thermodynamically unstable ($\Delta G > 0$ with respect to constituents) but kinetically stable (high activation energy); slow exchange of ligands.
- e.g. strong field d$^3$ and d$^6$ complexes of Cr$^{3+}$ and Co$^{3+}$

**Labile Complexes:** Thermodynamically stable (or unstable !) but rapid exchange of ligands (low activation energy).
- e.g. most aquo complexes with s-block elements ([Na(H$_2$O)$_6$]$^+$ ..) except those ones with Be$^{2+}$ or Mg$^{2+}$, complex molecules with low oxidation number d$^{10}$ ions (Zn$^{2+}$ ..)
Coordination Chemistry: Basic aspects of reactivity

- **Reaction mechanism**: model for a sequence of reaction steps with special emphasis on the activated state (transition state) and the rate determining step
- **Rate law**: differential equation for the rate of the change of molar concentrations of reactands (educts) and products
- **Rate determining step**: slowest step in the sequence of reactions; determines in a first approximation the total reaction rate.

Different types of reaction mechanisms are distinguished by the activated state:

**Dissociative**: activated state has lower coordination number due to dissociation of the leaving group

**Associative**: activated state has a higher coordination number due to bonding of the incoming group

\[
\text{W(CO)}_6 + \text{PPh}_3 \rightarrow \text{W(CO)}_5 \text{PPh}_3 + \text{CO}
\]

\[
[\text{Ni(CN)}_4]^{2-} + (^{14}\text{CN})^- \rightarrow [\text{Ni} (^{14}\text{CN})(\text{CN})_3]^{2-} + \text{CN}^-
\]
Coordination Chemistry: Basic aspects of reactivity

Rate determining step: dissociation of \( X \) (outgoing group) is slow

\[
X - M + Y \leftrightarrow X, M, Y \rightarrow X + MY
\]

Fast slow

long lifetime of the intermediate

Rate determining step: association of \( Y \) (incoming group) is slow

\[
X - M + Y \leftrightarrow X - M - Y \rightarrow X + MY
\]

slow fast

short lifetime of the intermediate

More detailed analyses require measurements of the “reaction order” (first, second etc.) and considerations about possible molecular mechanisms of the sequence of reactions.
Coordination Chemistry: square planar complexes - the "trans" effect

Mechanism for the substitution of a ligand X by a nucleophilic reactand Y in a square planar complex

A strong \(\sigma\)-donor or \(\pi\)-acceptor ligand \((T)\) greatly influences the substitution of a ligand that lies in the trans-position by favouring its dissociation.

Tentative sequence of the trans-effect for different ions (molecules): 
\[\text{CN}^- > \text{CO} > \text{PR}_3 > \text{H}^- > \text{SCN}^- > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{NH}_3 > \text{OH}^- > \text{H}_2\text{O}\]

Different synthetic routes to cis- or trans-\(\text{PtCl}_2(\text{NH}_3)_2\) utilizing the trans-effect.
Coordination Chemistry: Substitution in octahedral complexes

- several models for possible mechanisms: e.g. Eigen-Wilkins mechanism assuming the formation of an "encounter complex" (MX₆)Y in a pre-equilibrium step with products formed by subsequent rate determining steps

- reaction mechanism of type interchange

- incoming or leaving group determines whether interchange with an associative or dissociative rate determining step

- in general: analysis of thermodynamic data (e.g. activation-energy/entropy/volume) offers insight into possible reaction mechanisms
Substitution in octahedral complexes: retention and isomerization

- reaction via a square-pyramidal complex results in retention of the original geometry (top)
- reaction via a trigonal bipyramidal complex can lead to isomerization (bottom)
Isomerization via trigonal bipyramidal activated complex

(things can be more complicated !)

Isomerization in the activated complex (change of axial and equatorial ligands) can occur by a „twist“ through a square pyramidal conformation (pseudorotation)
Inner and Outer sphere mechanism: redox reactions $\rightarrow$ electron transfer

Figure 20-17
Shriver & Atkins Inorganic Chemistry, Fourth Edition
**Inner sphere mechanism**: Upon an electron transfer reaction occurring between two complex molecules an activated complex is formed in which the two participating molecules share a common ligand which serves as a bridge for the electron transfer.

- **Labile**: rapid exchange of ligands
- **Inert**: very slow exchange of ligands (although the molecule may be thermodynamically unstable)

\[
[\text{Cr(H}_2\text{O)}_6]^{2+} + [\text{Co(NH}_3)_5\text{Cl}]^{2+} + 5\text{H}^+ + 5\text{H}_2\text{O} \rightarrow [\text{Cr(H}_2\text{O)}_5\text{Cl}]^{2+} + [\text{Co(H}_2\text{O)}_6]^{2+} + 5\text{NH}_4^+
\]

- **Henry Taube**: Nobel prize 1983
Outer sphere mechanism: The electron transfer is achieved via a cascade of subsequent reactions without sharing a common ligand; a strong change of interatomic distances between ligands and central atom is characteristic.

\[ \text{[Fe}^*(\text{H}_2\text{O})_6]^{2+} + \text{[Fe(\text{H}_2\text{O})}_6]^{3+} \rightarrow \text{[Fe}^*(\text{H}_2\text{O})_6]^{3+} + \text{[Fe(\text{H}_2\text{O})}_6]^{2+} \]

Both Fe-O-bonds of equal length.
According to Marcus' ideas at least two factors determine the rate of electron transfer in an outer sphere mechanism:

a) the shape of the potential curves of the reactands

b) the magnitude of the standard reaction Gibbs free energy for the total reaction (the more negative it is the lower the activation energy of the reaction)

**Marcus Equation for the rate konstant k of the overall reaction:**

\[ k^2 \sim k_1 k_2 K \]

\( k_1 \) and \( k_2 \) are the two rate constants for the exchange reactions and \( K \) is the equilibrium constant for the overall reaction
Oxidative addition and reductive elimination

- An example of oxidative addition is the reaction of Vaska’s complex, trans-IrCl(CO)[P(C6H5)3]2, with hydrogen.

- In this transformation, the metal oxidation state changes from Ir(I) to Ir(III) because the product is described as Ir3+ bound to three anions: Cl-, and two hydride, H-, ligands.

- The metal complex initially has 16 valence electrons and a coordination number of four. After the addition of hydrogen, the complex has 18 electrons and a coordination number of six.
Oxidative addition and reductive elimination are two important classes of reactions in organometallic chemistry. Their relationship is shown below where \( y \) represents the number of ligands on the metal and \( n \) is the oxidation state of the metal.

\[
XY + L_yM^n \xrightarrow{\text{oxidative addition}} L_yM^{n+2}XY
\]

1 \hspace{2em} 2

- In oxidative addition, a metal complex with vacant coordination sites and a relatively low oxidation state is oxidized by the insertion of the metal into a covalent bond (X-Y).

- Both the formal oxidation state of the metal, \( n \), and the electron count of the complex increase by two.

- Oxidative additions are most commonly seen with H-H and carbon(sp\(^3\))-halogen bonds.
- The reverse of oxidative addition is **reductive elimination**. In this case hydrogen gas is lost and the metal complex is reduced.

- Reductive elimination is favored when the newly formed X-Y (H-H) bond is strong.

- For reductive elimination to occur the two groups (X and Y) should be adjacent to each other in the metal's coordination sphere.
Thermodynamics and catalytic cycle

Homogeneous catalysis: the oxidation of allylalcohol to propionaldehyde

Insertion, H-migration
Hydrogenation of alkenes

Wilkinson's catalyst

Reactive addition

Coord. unsaturated

Reductive elimination

H-migration

Dissociative
Hydrocarbonylation (-formylation)

alkene → aldehyde with one additional C
Just as a metal oxidatively inserts itself into a H-H bond, it can also oxidatively add to C-H bonds. This process is called C-H bond activation and is an active research area because of its potential value in converting petroleum-derived hydrocarbons into more complex products. Oxidative addition and reductive elimination are seen in many catalytic cycles such as the monsanto process and alkene hydrogenation using Wilkinson's catalyst.

„Monsanto“-process: formation of acetic acid from methanol using a Rh-iodide complex

\[
\text{CH}_3\text{OH} + \text{CO} \rightarrow \text{CH}_3\text{COOH}
\]
Alkene polymerisation (Ziegler-Natta)

empty site

attached to particle surface

migration-insertion