

Chapter 23. Transition Metals and Coordination Chemistry

Common Student Misconceptions

- Students have difficulty naming coordination complexes.
- Students often think that chirality is only possible for organic compounds.
- Students often think that metals ions, M^{n+} (aq) and their aqueous complex ions should have similar physical and chemical properties.

Teaching Tips

- Students should be encouraged to review Chapters 2, 6, 7, 9, 11, 17 and 19 prior to covering this chapter.

Lecture Outline

23.1 The Transition Metals¹

- Transition metals occupy the *d* block of the periodic table.
- Most metals are found in nature in the form of solid inorganic compounds called **minerals**.
 - Names of minerals are based on the location of their discovery, the person who discovered them, or some characteristic of the mineral.
 - For example, some minerals are named after their colors
 - The oxidation state of transition metals in minerals are commonly +1, +2 or +3.
 - Various chemical processes are required to reduce the metal to the 0 oxidation state.
- **Metallurgy** is the science and technology of extracting metals from natural sources and preparing them for practical use.
- There are five important steps:
 - mining (getting the ore out of the ground)
 - concentrating (preparing it for further treatment)
 - Differences in the chemical and physical properties of the mineral of interest and the undesired material, called *gangue*, are used to separate these components.
 - Example: Iron can be separated from gangue in finely ground magnetite by using a magnet to attract the iron.
 - reduction (to obtain the free metal in the 0 oxidation state)
 - purifying or refining (to obtain the pure metal)
 - mixing with other metals (to form an *alloy*)
 - Alloys are metallic materials composed of two or more elements.

Physical Properties²

- The physical properties of transition metals can be classified into two groups: atomic properties (e.g., atomic radius, ionization energy) and bulk properties (e.g., density, melting point).
- Most of the trends in bulk properties are less smooth than the atomic properties.
- The atomic trends tend to be smooth for the transition metals.
- The trends in atomic properties of the transition metals can be exemplified with atomic radii.
 - Atomic radius decreases and reaches a minimum around group 8B (Fe, Co, Ni) and then increases for groups 1 and 2.
 - This trend is again understood in terms of effective nuclear charge.

¹ Figure 23.1 from Transparency Pack

² “Trends in Ionization Energy of Transition-Metal Elements” from Further Readings

- The increase in size of the Cu and Zn triads is rationalized in terms of the completely filled d orbital.
- In general, atomic size increases down a group.
- An important exception: Hf has almost the same radius as Zr (group 4B); we would expect Hf to be larger than Zr.
 - Between La and Hf the $4f$ shell fills (lanthanides).
 - As $4f$ orbitals fill, the effective nuclear charge increases and the lanthanides contract smoothly.
 - The **lanthanide contraction** balances the increase in size we anticipate between Hf and Zr.
 - The second and third series are usually about the same size, with the first series being smaller.
 - Second and third series metals are very similar in their properties (e.g., Hf and Zr are always found together in ores and are very difficult to separate).

Electron Configurations and Oxidation States³

- Even though the $(n-1)d$ orbital is filled after the ns orbital, electrons are lost from the orbital with the highest n first.
- That is, transition metals lose s electrons before the d electrons.
 - Example: Fe: $[\text{Ar}]3d^64s^2$ Fe^{2+} : $[\text{Ar}]3d^6$.
- d electrons are responsible for some important properties:
 - Transition metals have more than one oxidation state.
 - Transition-metal compounds are colored.
 - Transition-metal compounds have magnetic properties.
- Note that all oxidation states for metals are positive.
 - The +2 oxidation state is common because it corresponds to the loss of both s electrons.
 - An exception is in Sc where the +3 oxidation state is isoelectronic with Ar.
 - The maximum oxidation state for the first transition series is +7 for Mn.
 - For the second and third series, the maximum oxidation state is +8 for Ru and Os (RuO_4 and OsO_4).

Magnetism⁴

- Magnetism provides important bonding information.
- Electron spin generates a magnetic field with a *magnetic moment*.
- There are several types of magnetic behavior:
 - *diamagnetic* (no atoms or ions with magnetic moments)
 - When two spins are opposite, the magnetic fields cancel (diamagnetic).
 - Diamagnetic substances are weakly repelled by external magnetic fields.
 - *paramagnetic* (magnetic moments not aligned outside a magnetic field)
 - When spins are unpaired, the magnetic fields do not cancel (paramagnetic).
 - Generally, the unpaired electrons in a solid are not influenced by adjacent unpaired electrons.
 - That is, the magnetic moments are randomly oriented.
 - When paramagnetic materials are placed in a magnetic field, the electrons become aligned.
 - **ferromagnetic** (coupled magnetic centers aligned in a common direction)
 - Ferromagnetism is a special case of paramagnetism where the magnetic moments are permanently aligned (e.g., Fe, Co, and Ni).
 - Ferromagnetic oxides are used in magnetic recording tape (e.g., CrO_2 and Fe_3O_4).
 - Two additional types of magnetism involve ordered arrangements of unpaired electrons.
 - **Antiferromagnetism** (the unpaired electrons on a given atom align so that their spins are oriented in the opposite direction as the spins on neighboring atoms).
 - **Ferrimagnetism** (has characteristics of both a ferromagnet and an antiferromagnet).

³ Figure 23.4 from Transparency Pack

⁴ Figure 23.5 from Transparency Pack

- All magnetically ordered materials become paramagnetic when heated above a critical temperature.
 - *Curie temperature* (T_c): critical temperature for ferromagnets and ferrimagnets.
 - *Néel temperature* (T_n): critical temperature for antiferromagnets.

FORWARD REFERENCES

- Nickel used as a heterogeneous catalyst in hydrogenation of alkenes will be mentioned in Chapter 24 (section 24.3).
- Transition metals as catalysts in carbonylation reactions will be mentioned in Chapter 24 (section 24.4).
- Metal oxides used as catalysts in formation of methanol will be mentioned in Chapter 24 (section 24.4).

23.2 Transition-Metal Complexes^{5,6,7}

- **Metal complexes** (or *complexes*) have a metal ion (which can have a 0 oxidation state) bonded to a number of molecules or ions.
 - If the complex has a net electrical charge, it is called a *complex ion*.
- Compounds that contain complexes are known as **coordination compounds**.
- Most coordination compounds are metal compounds formed by Lewis acid-base interactions involving transition metal ions.
 - The molecules or ions surrounding the metal ion in a complex are called **ligands**.
 - The ligands act as Lewis bases.
 - Ligands are usually either anions or polar molecules.
 - They have at least one unshared pair of valence electrons.
 - The metal ion functions as a Lewis acid (electron-pair acceptor).
 - The ligands are said to *coordinate* to the metal.

The Development of Coordination Chemistry: Werner's Theory^{8,9,10,11}

- Alfred Werner proposed:
 - Metal ions exhibit a primary and secondary valence.
 - Primary valence: The oxidation state of the metal.
 - Secondary valence: The number of atoms directly bonded to the metal ion.
 - This is the **coordination number**.
 - The central metal and ligands bound to it are the **coordination sphere** of the complex.
 - Example: $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$
 - Co^{3+} is the metal ion.
 - NH_3 groups are ligands.
 - When Cl^- is part of the coordination sphere, it is tightly bound and not released when the complex is dissolved in water.
 - Example: $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$
- Different arrangements of ligands are possible.
 - Example: There are two ways to arrange the ligands in $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$.
 - In *cis*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$:
 - the chloride ligands occupy adjacent vertices of the octahedral arrangement.
 - In *trans*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$.

⁵ "A Stability Ruler for Metal Ion Complexes" from Further Readings

⁶ "The Copper Mirror" from Live Demonstrations

⁷ "Metals in Metal Salts: A Copper Mirror Demonstration" from Live Demonstrations

⁸ Figure 23.7 from Transparency Pack

⁹ "The Concept of Oxidation States in Metal Complexes" from Further Readings

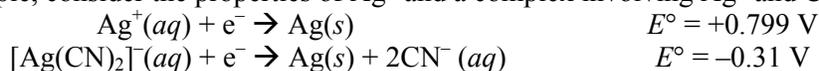
¹⁰ "*cis*-tetraamminedichlorocobalt(III)" 3-D Model from Instructor's Resource CD/DVD

¹¹ "*trans*-tetraamminedichlorocobalt(III)" 3-D Model from Instructor's Resource CD/DVD

- the chlorides are opposite each other.

The Metal-Ligand Bond

- The metal-ligand bond is an interaction between:
 - a Lewis acid (the metal ion with its empty valence orbitals) and
 - a Lewis base (the ligand with its unshared pairs of electrons).
- Ligands can alter the properties of the metal.
 - Complexes display physical and chemical properties different from those of the metal ion or the ligands.
 - For example, consider the properties of Ag^+ and a complex involving Ag^+ and CN^- :



Charges, Coordination Numbers, and Geometries^{12,13,14,15}

- The charge on a complex ion equals the sum of the charge on the metal plus the charges on the ligands.
- In a complex the **donor atom** is the atom bonded directly to the metal.
- The coordination number is the number of ligands attached to the metal.
 - The most common coordination numbers are 4 and 6.
 - Some metal ions have a constant coordination number (e.g., Cr^{3+} and Co^{3+} have coordination numbers of 6).
 - The size of the metal ion and the size of the ligand affect the coordination number (e.g., iron(III) can coordinate to six fluorides but only to four chlorides; thus $[\text{FeF}_6]^{3-}$ and $[\text{FeCl}_4]^-$ are stable).
 - The amount of charge transferred from ligand to metal affects the coordination number.
 - The greater the transfer of negative charge to the metal, the lower the coordination number tends to be.
 - For example, $[\text{Ni}(\text{NH}_3)_6]^{2+}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are both stable.
- Four-coordinate complexes have two common geometries: tetrahedral and square planar.
 - Square-planar complexes are commonly seen for d^8 metal ions such as Pt^{2+} and Au^{3+} .
- Six-coordinate complexes are usually octahedral.

23.3 Common Ligands in Coordination Chemistry^{16,17,18,19,20}

- A donor atom is the ligand atom that binds to the central metal ion in a coordination complex.
- **Monodentate ligands** bind through one donor atom only.
 - Therefore, they can occupy only one coordination site.
- **Some ligands bind through two or more donor atoms simultaneously.**
 - **Bidentate ligands bind through two donor atoms.**
 - **Polydentate ligands (or chelating agents)** have three or more donor atoms.
 - **Bidentate and polydentate species have multiple donor atoms** that can simultaneously coordinate to the metal ion.
 - They can thus occupy more than one coordination site.

¹² “Cobalt Complexes: Changing Coordination Numbers” from Live Demonstrations

¹³ Figure 23.9 from Transparency Pack

¹⁴ “Geometries of ML_n Complexes” Activity from Instructor’s Resource CD/DVD

¹⁵ “Changing Coordination Numbers; Nickel Complexes” from Live Demonstrations

¹⁶ Figure 23.11 from Transparency Pack

¹⁷ Figure 23.12 from Transparency Pack

¹⁸ “Some Linguistic Detail on Chelation” from Further Readings

¹⁹ “Selecting and Using Chelating Agents” from Further Readings

²⁰ “Ethylenediamminecobalt(III)” 3-D Model from Instructor’s Resource CD/DVD

- Because bidentate and polydentate ligands grasp the metal between two or more donor atoms and are called **chelating agents**.
 - Example: *ethylenediamine* ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$)
 - The abbreviation for ethylenediamine is “en.”
 - There are two nitrogen atoms that can act as ligands.
 - They are far enough apart on the molecule that it can wrap around a metal ion.
 - The molecule can simultaneously coordinate to two sites on the metal ion.
 - Ethylenediamine is thus an example of a bidentate ligand.
 - The octahedral $[\text{Co}(\text{en})_3]^{3+}$ is a typical “en” complex.
- Chelating agents form more stable complexes than do monodentate ligands.
 - Examples:

$$\begin{array}{l} [\text{Ni}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 6\text{NH}_3 \rightleftharpoons [\text{Ni}(\text{NH}_3)_6]^{2+}(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \quad K_f = 1.2 \times 10^9 \\ [\text{Ni}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 3\text{en} \rightleftharpoons [\text{Ni}(\text{en})_3]^{2+}(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \quad K_f = 6.8 \times 10^{17} \end{array}$$
 - The **chelate effect** refers to the larger formation constants for polydentate ligands as compared with corresponding monodentate ligands.
- Chelating agents are sometimes referred to as *sequestering agents*.
 - In medicine, sequestering agents are used to selectively remove toxic metal ions (e.g., Hg^{2+} and Pb^{2+}) while leaving biologically important metals.
- One very important chelating agent is ethylenediaminetetraacetate (EDTA^{4-}).
 - EDTA occupies six coordination sites; for example, $[\text{CoEDTA}]^-$ is an octahedral Co^{3+} complex.
 - Both N atoms and O atoms coordinate to the metal.
 - EDTA is used in consumer products to complex the metal ions that would otherwise catalyze unwanted decomposition reactions.

Metals and Chelates in Living Systems^{21,22,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37}

- Ten of the twenty-nine elements required for human life are transition metals (V, Cr, Mn, Fe, Co, Cu, Zn, Mo, Cd, and Ni).
- Many natural chelates coordinate to the *porphine* molecule.
 - Porphine forms a tetradentate ligand with the loss of the two protons bound to its nitrogen atoms.
 - A **porphyrin** is a metal complex derived from porphine.

²¹ “EDTA-Type Chelating Agents in Everyday Consumer Products: Some Medicinal and Personal Care Products” from Further Readings

²² “Toxicity of Heavy Metals and Biological Defense: Principles and Applications in Bioinorganic Chemistry, Part VII” from Further Readings

²³ “Heme (with bound O_2)” 3-D Model from Instructor’s Resource CD/DVD

²⁴ “Oxymyoglobin” 3-D Model from Instructor’s Resource CD/DVD

²⁵ “Deoxymyoglobin” 3-D Model from Instructor’s Resource CD/DVD

²⁶ Figure 23.14 from Transparency Pack

²⁷ “The Biochemistry of Some Iron Porphyrin Complexes” from Further Readings

²⁸ “Hemoglobin: Its Occurrence, Structure, and Adaptation” from Further Readings

²⁹ Figure 23.15 from Transparency Pack

³⁰ Figure 23.16 from Transparency Pack

³¹ “Iron as a Nutrient and Poison” from Further Readings

³² “Blood-Chemistry Tutorials: Teaching Biological Applications of General Chemistry Material” from Further Readings

³³ “The Chemical Pigments of Plants” from Further Readings

³⁴ “Iron Deficiency” from Further Readings

³⁵ “Separating Metallic Iron from Cereal” from Live Demonstrations

³⁶ “A Colorful Look at the Chelate Effect” from Live Demonstrations

³⁷ “Ethylenediaminetetraacetatecobalt(III)” 3-D Model from Instructor’s Resource CD/DVD

- Two important porphyrins are heme (which contains Fe^{2+}) and chlorophyll (which contains Mg^{2+}).
- Two important heme-containing molecules are myoglobin and hemoglobin.
 - These proteins are important oxygen-binding proteins.
 - Myoglobin is *globular protein* (it folds into a compact, roughly spherical shape) found in muscle tissue, while hemoglobin is made of four heme-containing subunits (each is similar to myoglobin); it is found in red blood cells.
 - In each case the heme iron is coordinated to six ligands.
 - Four of these are nitrogen atoms of the porphyrin ring.
 - One ligand is a nitrogen atom that is part of one of the amino acids of the protein.
 - The sixth coordination site around the iron is occupied by either O_2 or water.
 - Other ligands, such as CO, can also serve as the sixth ligand.
 - CO is poisonous due to its ability to bind very tightly to hemoglobin.
 - The binding constant for CO is 210 times greater than that for O_2 .
 - A different metal complex is important in the process of **photosynthesis**.
 - Photosynthesis is the conversion of CO_2 and water to glucose and oxygen in plants in the presence of light.
 - The synthesis of one mole of sugar requires the absorption and utilization of 48 moles of photons.
 - **Chlorophylls** are porphyrins that contain Mg(II). Photons of light are absorbed by chlorophyll-containing pigments in plant leaves.
 - Chlorophyll *a* is the most abundant chlorophyll.
 - The other chlorophylls differ in the structure of the side chains.
 - Mg^{2+} is in the center of the porphyrin-like ring.
 - The alternating or *conjugated* double bonds give chlorophyll its ability to absorb light strongly in the visible part of the spectrum.
 - Chlorophyll absorbs red light (655 nm) and blue light (430 nm), and transmits green light.
 - The absorbed energy is ultimately used to drive the endothermic reaction:

$$6\text{CO}_2 + 6\text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$$
 - Plant photosynthesis sustains life on Earth.

FORWARD REFERENCES

- Photosynthesis will be covered in Chapter 24 (section 24.6).
- Tertiary structure of myoglobin will be mentioned in Chapter 24 (section 24.7).

23.4 Nomenclature and Isomerism in Coordination Chemistry³⁸

- We can name complexes in a systematic manner using some simple nomenclature rules.
 - For salts, the name of the cation is given before the name of the anion.
 - Example: In $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ we name $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ before Cl^- .
 - Within a complex ion or molecule, the ligands are named (in alphabetical order) before the metal.
 - Example: $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ is pentaamminechlorocobalt(III).
 - Note that the *penta* portion indicates the number of NH_3 groups and is therefore not considered in alphabetizing the ligands.
 - The names of anionic ligands end in *o*, and for neutral ligands the name of the molecule is used.
 - Example: Cl^- is *chloro* and CN^- is *cyano*.
 - Exceptions are H_2O (aqua) and NH_3 (ammine).
 - Greek prefixes are used to indicate the number of ligands (di-, tri-, tetra-, penta-, and hexa-).
 - Exception: If the ligand name already has a Greek prefix.
 - Then enclose the name of the ligand in parentheses and use bis-, tris-, tetrakis-, pentakis-, and hexakis-.

³⁸ “Isomerism” Animation from Instructor’s Resource CD/DVD

- Example $[\text{Co}(\text{en})_3]\text{Cl}_3$ is tris(ethylenediamine)cobalt(III) chloride.
- If the complex is an anion, the name ends in -ate.
 - For example, $[\text{CoCl}_4]^{2-}$ is the tetrachlorocobaltate(II) ion.
- The oxidation state of the metal is given in Roman numerals in parenthesis after the name of the metal.
- Two compounds with the same formula but different arrangements of atoms are called **isomers**.
- There are two kinds of isomers:
 - **Structural isomers** have different bonds.
 - **Stereoisomers** have the same bonds but different spatial arrangements of the bonds.

Structural Isomerism^{39,40}

- Two examples of structural isomerism in coordination chemistry are:
 - **linkage isomerism**
 - *Linkage isomers*: A ligand is capable of coordinating to a metal in two different ways.
 - Example: Nitrite can coordinate via a nitrogen or an oxygen atom.
 - If the nitrogen atom is the donor atom, the ligand is called *nitro*.
 - If the oxygen atom is the donor atom, the ligand is called *nitrito*.
 - The ligand thiocyanate (SCN^-) is also capable of being involved in linkage isomerism.
 - **coordination-sphere isomerism**
 - *Coordination-sphere isomers* differ in the ligands that are directly bound to the metal.
 - Example: $\text{CrCl}_3(\text{H}_2\text{O})_6$ exists in three different forms:
 - $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$
 - $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$
 - $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$

Stereoisomerism^{41,42,43,44,45,46,47,48,49,50,51,52,53}

- Stereoisomers have the same connectivity but different spatial arrangements of atoms.
- Two types of stereoisomerism are:
 - **geometric isomerism**
 - In *geometric isomerism* the arrangement of the atoms is different although the same bonds are present.
 - Examples are *cis* and *trans* isomers.
 - Consider square planar $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.
 - The two NH_3 ligands can either be 90° apart or 180° apart.

³⁹ Figure 23.19 from Transparency Pack

⁴⁰ “Pictorial Analogies VIII: Types of Formulas and Structural Isomers” from Further Readings

⁴¹ “Introducing Stereochemistry to Non-science Majors” from Further Readings

⁴² Figure 23.22 from Transparency Pack

⁴³ “Chirality” Animation from Instructor’s Resource CD/DVD

⁴⁴ “Chiral Drugs” from Further Readings

⁴⁵ “Optical Activity” Animation from Instructor’s Resource CD/DVD

⁴⁶ Figure 23.23 from Transparency Pack

⁴⁷ “Mirror–Image Molecules: New Techniques Promise More Potent Drugs and Pesticides” from Further Readings

⁴⁸ “A 1- and 2-Dimensional Introduction to Stereochemistry” from Further Readings

⁴⁹ “Demonstration of Enantiomer Specificity of Proteins and Drugs” from Live Demonstrations

⁵⁰ “*cis*-diamminedichloroplatinum(II) (cisplatin)” 3-D Model from Instructor’s Resource CD/DVD

⁵¹ “*trans*-diamminedichloroplatinum(II) (transplatin)” 3-D Model from Instructor’s Resource CD/DVD

⁵² “D-trisethylenediamminecobalt(III)” 3-D Model from Instructor’s Resource CD/DVD

⁵³ “L-trisethylenediamminecobalt(III)” 3-D Model from Instructor’s Resource CD/DVD

- Therefore, the spatial arrangement of the atoms is different.
- In the *cis* isomer, the two NH₃ groups are adjacent.
 - The *cis* isomer (cisplatin) is used in chemotherapy.
- In the *trans* isomer, the two NH₃ groups are across from each other.
- It is possible to find *cis* and *trans* isomers in octahedral complexes.
 - For example, *cis*-[Co(NH₃)₄Cl₂]⁺ is violet.
 - The *trans*-[Co(NH₃)₄Cl₂]⁺ isomer is green.
 - The two isomers also have different solubilities.
- **optical isomerism**
 - *Optical isomers* are nonsuperimposable mirror images.
 - These are referred to as **enantiomers**.
 - Complexes that exist as enantiomers are **chiral**.
 - Chiral species are molecules or ions that cannot be superimposed on their mirror image.
 - Most physical and chemical properties of enantiomers are identical.
 - Therefore, enantiomers are very difficult to separate.
 - Optical isomers are differentiated from each other by their interaction with plane-polarized light.
 - Enantiomers are capable of rotating the plane of polarized light.
 - Horizontally polarized light is passed through an optically active solution.
 - As the light emerges from the solution, the plane of polarity has changed.
 - The mirror image of an enantiomer will rotate the plane of polarized light by the same amount in the opposite direction.
 - **Dextrorotatory** solutions rotate the plane of polarized light to the right.
 - This isomer is called the *dextro* or *d* isomer.
 - **Levorotatory** solutions rotate the plane of polarized light to the left.
 - This isomer is called the *levo* or *l* isomer.
 - Chiral molecules are said to be **optically active** because of their effect on light.
 - **Racemic** mixtures contain equal amounts of *l* and *d* isomers.
 - They have no overall effect on the plane of polarized light.
 - The 2001 Nobel Prize in Chemistry was awarded to W. S. Knowles and K. B. Sharples of the United States and R. Noyori of Japan for work on the catalysis of chiral reactions.

FORWARD REFERENCES

- Arrangement of groups in geometric isomers will be covered in Chapter 24 (section 24.3)
- Chirality of organic compounds, enantiomers, and rotation of the light will be discussed in detail in Chapter 24 (section 24.5).

23.5 Color and Magnetism in Coordination Chemistry

Color^{54,55,56,57,58,59,60}

- The color of a complex depends on the metal, the ligands present, and the oxidation state of the metal.
 - For example, pale blue [Cu(H₂O)₆]²⁺ can be converted into dark blue [Cu(NH₃)₆]²⁺ by adding NH₃(aq).
- A partially filled *d* orbital is usually required for a complex to be colored.

⁵⁴ “Color Classification of Coordination Compounds” from Further Readings

⁵⁵ “Green and Blue Copper Complexes” from Live Demonstrations

⁵⁶ “Copper Sulfate: Blue to White” from Live Demonstrations

⁵⁷ “Color Wheel” Activity from Instructor’s Resource CD/DVD

⁵⁸ “Hope Springs Eternal” from Further Readings

⁵⁹ Figure 23.24 from Transparency Pack

⁶⁰ Figure 23.26 from Transparency Pack

- Thus, ions with completely empty (e.g., Al^{3+} or Ti^{4+}) or completely filled (e.g., Zn^{2+}) d subshells are usually colorless.
- Colored compounds absorb visible light.
 - The color perceived is the sum of the light reflected or transmitted by the complex.
 - An object will have a particular color if it reflects or transmits that color or if it absorbs light of the **complementary** color.
 - An object appears black if it absorbs all wavelengths of light.
 - An object appears white or colorless if it absorbs no visible light.
- A plot of the amount of absorbed light versus wavelength is called the **absorption spectrum**.

Magnetism of Coordination Compounds

- Many transition-metal complexes are paramagnetic (i.e., they have unpaired electrons).
- Consider a d^6 metal ion:
 - Compounds of $[\text{Co}(\text{NH}_3)_6]^{3+}$ have no unpaired electrons, but compounds of $[\text{CoF}_6]^{3-}$ have four unpaired electrons per metal ion.
- We need to develop a bonding theory to account for both color and magnetism in transition metal complexes.

23.6 Crystal-Field Theory^{61,62}

- **Crystal-field theory** describes bonding in transition-metal complexes.
- The formation of a complex is a Lewis acid-base reaction.
 - Both electrons in the bond come from the ligand and are donated into an empty hybridized orbital on the metal.
 - Charge is donated from the ligand to the metal.
- An assumption in crystal-field theory is that the interaction between ligand and metal is electrostatic.
 - Orbitals that point directly at the ligands have their energies raised more than those that point between the ligands.
 - The complex metal ion has a lower energy than the separated metal and ligands.
 - However, repulsion occurs between the ligands and the d electrons of the metal.
- In an octahedral field, the five d orbitals do not have the same energy: three degenerate orbitals have a lower energy than two degenerate orbitals.
 - We assume an octahedral array of negative charges placed around the metal ion (which is positive).
 - The d_{z^2} and $d_{x^2-y^2}$ orbitals lie on the same axes as negative charges.
 - Therefore, there is a large, unfavorable interaction between the ligand and these orbitals.
 - These orbitals form the degenerate high-energy pair of energy levels.
 - The d_{xy} , d_{yz} , and d_{xz} orbitals are oriented between the negative charges.
 - Therefore, there is a smaller repulsion between ligands and these orbitals.
 - These orbitals form the degenerate low-energy set of energy levels.
 - The energy gap between these two sets of d orbitals is labeled Δ .
 - Δ is referred to as the *crystal-field splitting energy*.
- For example, consider the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex.
 - Ti^{3+} is a d^1 metal ion.
 - Therefore, the one electron is in a low energy orbital.
 - For Ti^{3+} , the gap between energy levels, Δ , is of the order of the wavelength of visible light.
 - As the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex absorbs visible light the electron is promoted to a higher energy level.

⁶¹ Figure 23.28 from Transparency Pack

⁶² Figure 23.30 from Transparency Pack

- This transition is called a ***d-d transition*** because it involves exciting an electron from one set of *d* orbitals to the other.
- Because there is only one *d*, electron, there is only one possible absorption line for this molecule.
- The color of a complex depends on the magnitude of Δ , which, in turn, depends on the metal and the type of ligand.
 - $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is purple, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is light violet, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ is violet, and $[\text{Cr}(\text{NH}_3)_6]^{3+}$ is yellow.
- A **spectrochemical series** is a listing of ligands in order of their ability to increase Δ :

$$\text{Cl}^- < \text{F}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{en} < \text{NO}_2^- \text{ (N-bonded)} < \text{CN}^-$$
 - *Weak-field ligands* lie on the low- Δ end of the spectrochemical series.
 - *Strong-field ligands* lie on the high- Δ end of the spectrochemical series.
 - Example: When the ligand coordinated to Cr^{3+} is changed from the weak-field ligand F^- to the strong-field ligand CN^- , Δ increases and the color of the complex changes from green (in $[\text{CrF}_6]^{3+}$) to yellow (in $[\text{Cr}(\text{CN})_6]^{3-}$).

Electron Configurations in Octahedral Complexes⁶³

- Recall that when transition metals form cations, *s* electrons are lost first.
 - Thus, Ti^{3+} is a d^1 ion, V^{3+} is a d^2 ion, and Cr^{3+} is a d^3 ion.
- If one to three electrons add to the *d* orbitals in an octahedral complex ion, Hund's rule applies.
 - The first three electrons go into different *d* orbitals with their spins parallel.
- We have a choice for the placement of the fourth electron:
 - If it goes into a higher-energy orbital, then there is an energy cost (Δ).
 - If it goes into a lower-energy orbital, there is a different energy cost (called the **spin-pairing energy** due to pairing with the electron already present).
 - Weak-field ligands tend to favor adding electrons to the higher-energy orbitals (**high-spin complexes**) because Δ is less than the spin-pairing energy.
 - Strong-field ligands tend to favor adding electrons to lower-energy orbitals (**low-spin complexes**) because Δ is greater than the spin-pairing energy.

Tetrahedral and Square Planar Complexes^{64,65}

- By using the same arguments as for the octahedral case, we can derive the relative orbital energies for *d* orbitals in a tetrahedral field.
 - The splitting of the *d* orbitals is the opposite of that observed for an octahedral field.
 - Because there are only four ligands, Δ for a tetrahedral field is smaller than Δ for an octahedral field.
 - This causes all tetrahedral complexes to be high-spin.
- Square-planar complexes can be thought of as follows: Start with an octahedral complex and remove two ligands along the *z*-axis.
 - As a consequence the four planar ligands are drawn in towards the metal.
 - Most d^8 metal ions form square-planar complexes.
 - The majority of complexes are low-spin (i.e., diamagnetic).
 - Examples: Pd^{2+} , Pt^{2+} , Ir^+ , and Au^{3+} .

⁶³ "Crystal Field Theory: Chromium Complexes" Activity from Instructor's Resource CD/DVD

⁶⁴ "Octahedral vs. Square Planar" Activity from Instructor's Resource CD/DVD

⁶⁵ Figure 23.36 from Transparency Pack

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