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Coordination Chemistry Complexes

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Overview

Transition metals are found everywhere from vitamin supplements to electroplating baths. Transition metals also makeup the pigments in many paints and compose all minerals. Typically, transition metals are found in the cationic form since they readily oxidize and are surrounded by electron donors called ligands. These ligands do not form ionic or covalent bonds with the metal center, rather they take on a third type of bond known as coordinate-covalent. The coordinate-covalent bond between a ligand and a metal is dynamic, meaning that ligands are continuously exchanging and re-coordinating around the metal center. The identities of both the metal and the ligand dictates which ligands can bond preferentially over another. In addition, color and magnetic properties are also due to the types of complexes that are formed. The coordination compounds that form are analyzed using a variety of instruments and tools. This experiment explores why so many complexes are possible and uses a spectrochemical (color and chemical) method to help identify the type of coordination complex that forms.

Principles

Coordination complexes

Coordination complexes have at least one metal complex, which contains a metal center and is surrounded by electron-donating ligands. This is known as a complex ion. Counterions balance the charge of the complex ion to form the molecular coordination complex. Coordination complexes are soluble in water, where the counter-ion and metal ion complex dissociate. The metal ion and ligands behave like a polyatomic ion and do not dissociate.

The geometry of a complex ion takes on standard Valence-Shell Electron-Pair Repulsion Theory (VSEPR) geometries including linear, square planar, tetrahedral, and octahedral. Octahedral complex ions are the most common geometry. Crystal field theory explains energy splitting among *d*-orbitals in transition metal ions and the VSEPR geometries. Energy splitting is influenced by the shape and orientation of the *d*-orbital lobes.

Ligands and the spectrochemical series

Ligands are classified by the number of bonds, or attachments, they can make with a metal center. A single attachment is known as monodentate (one-toothed). A ligand that makes two attachments is called bidentate (two-toothed), and three attachments is known as tridentate.

Ligands donate electron density to the metal center to form the coordinate-covalent bond. Ligands may be charged or neutral. Ligands are classified as being strong or weak according to the spectrochemical series:

(weak) $I^- < Br^- < Cl^- < \underline{S}CN^- < F^- < OH^- < ox^{2-} < \underline{O}NO^- < H_2O < NCS^- < EDTA^{4-} < NH_3 < en < \underline{N}O_2^- < CN^-$ *(strong)*

Orbital splitting

When six ligands approach a metal center to form an octahedral complex, the five degenerate d-orbitals split into three lower-energy degenerate t_{2g} orbitals and two higher-energy degenerate e_g orbitals (**Figure 1**). The distance of the splitting between the t_{2g} and e_g orbitals is dictated by the strength of the ligand according to the spectrochemical series.

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Hund's rule still applies and electrons fill orbitals one at a time, but they fill in accordance to size of the splitting of the t_{2g} and e_g orbitals. If the split is small, electrons will fill all the orbitals singly before pairing. This maximizes the number of unpaired electrons and is called high-spin. Likewise, a strong-field causes a large t_{2g}-e_g split- electrons pair in the t_{2g} set before filling the higher-energy e_g orbitals. This minimizes the number of unpaired electrons and is called low-spin. The drive for electrons to pair is governed by the energy (or size) of the orbital splitting compared to the energy of electron pairing. If the energy of pairing is high compared to the energy of moving into the e_g orbitals, then electrons are high-spin. If the energy of pairing is low compared to the energy of moving into the higher e_g orbitals, then electrons are low-spin.

The distance that electrons have to move from the lower t_{2g} state to the higher e_g state in the metal center dictates the energy of electromagnetic radiation that the complex absorbs. If that energy is in the visible region (400-700 nm, 1.77 eV – 3.1 eV), the complex generally has a color. Weak-field ligands (I^- → OH^-) cause small splittings and complexes absorb low-energy light (i.e. red) which appear green in color. Strong-field ligands (EDTA → CN^-) absorb high-energy light (i.e. blue-violet) and appear red-yellow in color. Complexes with ligands that are between strong and weak on the spectrochemical series, like ammonia, can adopt either a weak- or strong-field geometry.

The color-ligand relationship is the rationale for the name "spectrochemical series". The number of paired and unpaired electrons also gives rise to paramagnetic diamagnetic properties in metal complexes.

When four ligands coordinate around a metal center, either a square planar or tetrahedral complex can result (**Figure 2**). The orbital energies in tetrahedral complexes are flipped compared to octahedral complexes, with e_g being lower in energy than t_{2g}. This is due to the orientations of d-orbitals with respect to the coordinating ligands. In square planar complexes, there are several differences in orbital energies, with d_{yz} and d_{xz} being degenerate and lowest in energy (lower than $d_{z2,}$), then d_{xy}, and finally the highest energy d_{x2-y2} orbital.

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Structure and Color

Because the distance in orbital splitting varies with ligand strength, a coordination complex with the same metal center can have a variety of colors based upon the coordinating ligand. For example, an aqueous solution of $Ni(H_2O)_6^{2+}$ has a light green color, but $Ni(NH_3)_6^{2+}$ is deep blue. The color arises from the change in energy between the t_{2g}-e_g orbitals. NH_3 is a stronger field ligand, which pushes the orbitals further apart from one another as well as displaces the H_2O ligands from the metal center. We will further explore the effect of ligands on color and coordination complexes in this experiment.

Procedure

1. Nickel complexes and colors

    1.1. $Ni(H_2O)_6^{2+}$ complex (**Figure 3a**)

        1.1.1. Prepare a 1M solution of $Ni(H_2O)_6^{2+}$ by dissolving $NiSO_4$ in the appropriate volume of water.

        1.1.2. Further dilute the $Ni(H_2O)_6^{2+}$solution by adding 70-mL of the 1M solution to 1000-mL of deionized water.

        1.1.3. Divide the $Ni(H_2O)_6^{2+}$ among seven 400-mL beakers.

        1.1.4. The aqueous nickel solution takes on a light green color since water is a weak-field ligand.

        1.1.5. The absorbance spectrum indicates red wavelengths are absorbed, justifying the opposite, green, which is observed.

    1.2. $Ni(NH_3)_6^{2+}$ complex (**Figure 3b**)

        1.2.1. Add a 5M aqueous ammonia solution to one beaker and stir.

        1.2.2. The solution takes on a deep blue color, indicating the solution is absorbing orange light which is higher in energy than red light.

        1.2.3. The absorbance spectrum indicates yellow wavelengths are absorbed, justifying the opposite, blue, which is observed.

            1.2.3.1. Ammonia is a stronger field ligand than water, which increases the splitting between the t_{2g} and e_g orbitals.

        1.2.4. $Ni(en)_3^{2+}$ complex (**Figure 3c**)

            1.2.4.1. Add a 30% ethylenediamine (en) solution to the aqueous $Ni(H_2O)_6^{2+}$ complex and stir.

            1.2.4.2. The solution progressively turns from light blue to blue to purple as ethylenediamine molecules progressively coordinate around the metal center to eventually form $Ni(en)^{3+}$.

            1.2.4.3. Ethylenediamine is a stronger ligand than water or ammonia and it is bidentate. The purple color indicates the solution is absorbing yellow light which is higher in energy than orange or red light.

1.2.4.4. The absorbance spectrum indicates yellow wavelengths are absorbed, justifying the opposite, purple, which is observed.

1.2.5. $Ni(dmg)_2^{2+}$ complex (**Figure 3d**)

1.2.5.1. Dimethylgloxine (dmg) is a bidentate ligand that chelates a large number of metals. Only two dmg molecules are required per metal center because $Ni(dmg)_2^{2+}$ has a square-planar geometry.

1.2.5.2. Add 1% dmg to the aqueous complex.

1.2.5.3. A solid pink/red precipitate forms, the insoluble $Ni(dmg)_2^{2+}$ complex.

1.2.5.4. A visible transmission spectrum of the complex is not possible, but the red color indicates green light is being absorbed. Green is higher energy than yellow, orange, and red.

1.2.6. $Ni(CN)_4^{2-}$ complex (**Figure 3e**)

1.2.6.1. The cyanide ion (CN^-) is monodentate, but a very strong field ligand, which also forms square-planar complexes with nickel (II).

1.2.6.2. Add a 1M KCN solution.

1.2.6.3. A yellow $Ni(CN)_4^{2-}$ complex forms almost immediately.

1.2.6.3.1. Note: Working with cyanide salts must be done with great care. Addition of acid may result in the formation of cyanide gas.

1.2.6.4. Cyanide is a stronger ligand than any of the other ligands because there is σ-bonding from the ligand to the metal and π-back bonding from the metal to the ligand. The yellow color indicates the solution is absorbing blue light, which is higher in energy than green, yellow, orange, and red.

1.2.6.5. The absorbance spectrum indicates yellow wavelengths are absorbed, justifying the opposite, purple, which is observed.

1.3. Ligand strength

1.3.1. According to the spectrochemical series, some ligands are stronger-field than others, which correspond to the size of the splitting of the d-orbitals of the central metal ion.

1.3.2. Stronger field ligands replace weaker field ligands in solution.

1.3.3. An aqueous solution of nickel sulfate appears light green because the $Ni(H_2O)_6^{2+}$ complex forms.

1.3.4. Sequentially add solutions of ammonia, ethylenediamine, dimethylglyoxime, and cyanide to the nickel-containing solution while stirring.

1.3.5. After each addition, the previous color disappears and the new color appears.

1.3.6. The color change indicates the formation of a new coordination complex driven by the strength of the ligand. These can be quantified by the equilibrium constant for each reaction:

$Ni(H_2O)_6^{2+}(aq) + 6NH_3\ (aq) \rightarrow Ni(NH_3)_6^{2+}\ (aq) + 6H_2O$ $K_{eq} = 1.2 \times 10^9$
$Ni(NH_3)_6^{2+}\ (aq) + 3en(aq) \rightarrow Ni(en)_3^{2+}\ (aq) + 6NH_3\ (aq)$ $K_{eq} = 1.1 \times 10^9$
$Ni(en)_3^{2+}\ (aq) + 2Hdmg(aq) \rightarrow Ni(dmg)_2\ (s) + 3en(aq) + 2H^+\ (aq)$ $K_{eq} = 1.35 \times 10^5$
$Ni(dmg)_2\ (s) + 4CN^-\ (aq) \text{-}\rightarrow Ni(CN)_4^{-2}\ (aq) + 2dmg^-\ (aq)$ $K_{eq} = 6.3 \times 10^7$

1.3.7. The equilibrium constant in each reaction is very large (>1), indicating that the reactions are all product driven.

Applications

From pigments to people, transitional metals are found throughout fields of chemistry, biology, geology and engineering. Understanding the behavior of transition metals under different chemical states can be as simple as monitoring color or magnetic behavior. Nearly every 3d (4th row) transition metal is vital to physiological function and, in all cases, these metals are bound by ligands to form coordination complexes. For example, iron is vital to oxygen transport in all vertebrates. Hemoglobin, a complex protein, contains four heme subunits with Fe^{2+} in the center of each. In hemoglobin, the Fe^{2+} is chelated by a tetradentate ring and a histidine residue, making it square pyramidal (five-sided). When oxygen is present, the subunits become octahedral. O_2 is considered a strong-field ligand, which causes large d-orbital t_{2g}-e_g splitting, making it low-spin. Relatively high-energy light is required to promote an electron to the e_g state, so blue light is absorbed making oxygenated (arterial) blood appear bright red. In contrast, deoxygenated (venous) blood has a smaller d-orbital splitting and lower energy light red light is absorbed, making deoxygenated blood appear dark, purplish-red. In the same respect, carbon monoxide, CO, is a strong-field ligand and will displace oxygen. It gives blood an even brighter red appearance due to strong-field splitting. The preferential binding for CO over O_2 in blood is often fatal.

Another application of coordination chemistry is in paints and pigments. While many pigments are simple metal oxides, others like Prussian Blue and Phthalocyanine Blue are coordination complexes whose color arises from the splitting in d-orbitals (Figure 4). In Prussian Blue, iron is surrounded by six cyanide ligands, creating the high-spin iron (III) hexacyanoferrate complex, $Fe(CN)_6^{3-}$. Another compound, Phthalocyanine Blue, is a square planar complex with a copper (II) ion in the center surrounded by a tetradentate phthalocyanine molecule.

Conclusions

Coordination compounds have a metal ion center with surrounding ligands and a counterion to balance charge. The ligands can be monodentate or chelating with two-four attachment sites. Ligands are also categorized by the spectrochemical series, which classifies the relative strength of the ligands to split a metal's d-orbitals. Both color and magnetic properties are influenced by the metal and the ligands. Large d-orbital splitting requires large energies to promote electrons into the higher energy orbitals and absorbs high-energy light (short wavelength). These are low spin-complexes and have the maximum number of paired electrons. In contrast, a small d-orbital splitting is known as weak-field and absorbs low energy light as well as has the maximum number of unpaired electrons. The charge and identity of the metal ion as well as the bound ligands define both the observed color and magnetic properties in coordination compounds.

Legend:

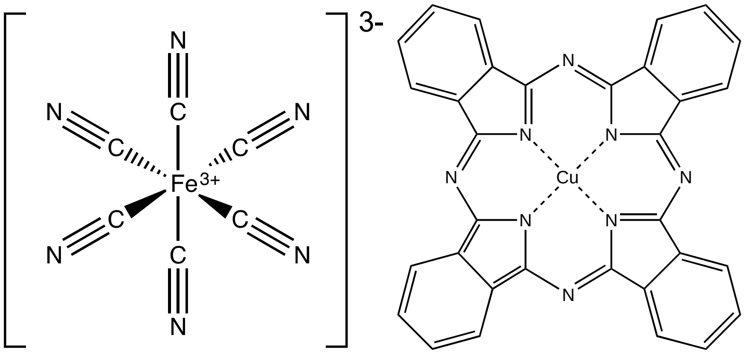
Figure 1. *d*-orbital splitting in an octahedral complex. *Redraw. Image is from chemwiki.ucdavis.edu.*

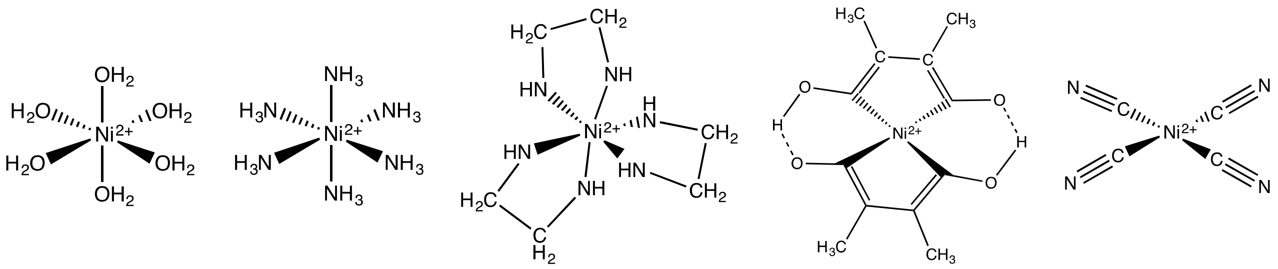
Figure 2. Tetrahedral and square planar *d*-orbital splitting. *Redraw. Image is from chemwiki.ucdavis.edu*

Figure 3. Structures of nickel (II) coordination complexes a-e.[1]

Figure 4. Prussian Blue, an iron-centered coordination complex and Phthalocyanine Blue, a copper-centered coordination complex.

References:
[1] Shakhashiri, Bassam Z.; Glen E. Dirreen, Glen. E; Juergens, Fred. Color, Solubility, and Complex Ion Equilibria of Nickel (II) Species in Aqueous Solution. J. Chem. Ed. 52 (12), 1980, 900-901.


Fe3+
3-
Cu



a) $Ni(H_2O)_6^{2+}(aq)$ b) $Ni(NH_3)_6^{2+}$ c) $Ni(en)_3^{2+}$ d) $Ni(dmg)_2$ e) $Ni(CN)_4^{-2}$

Figure 3. Structures of nickel (II) coordination complexes a-e.[1]

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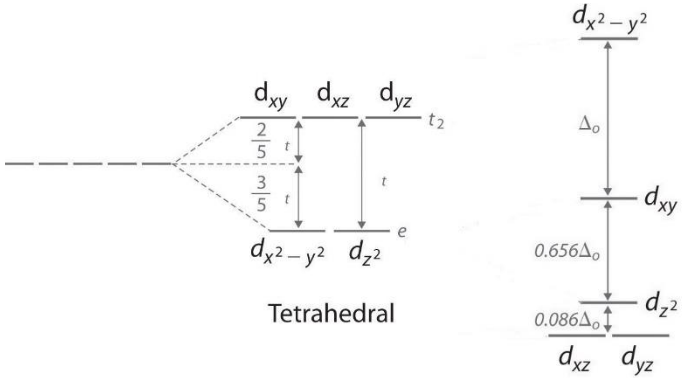
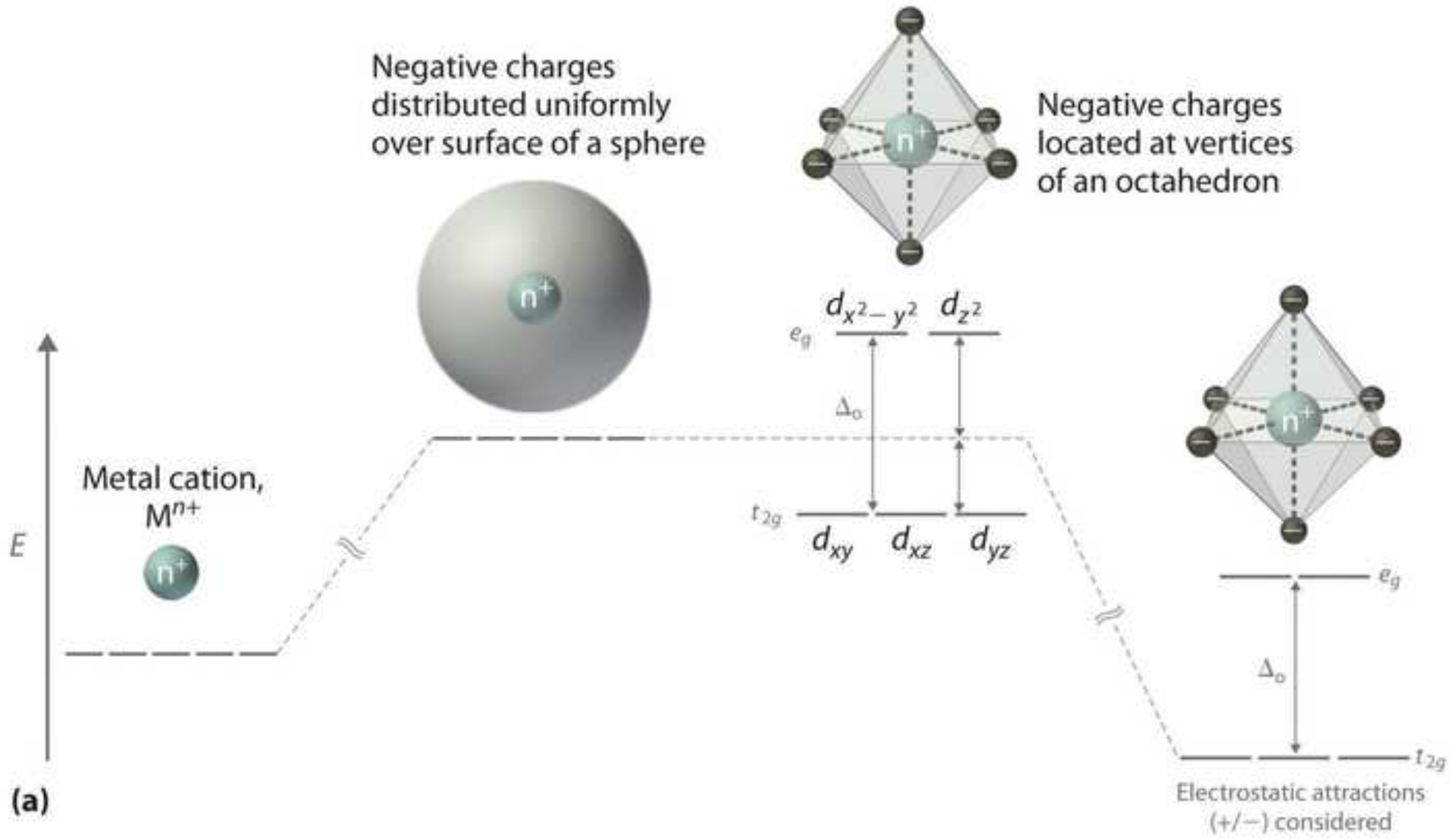


Figure 2. Tetrahedral and square planar *d*-orbital splitting. *Redraw. Image is from chemwiki.ucdavis.edu.*


Negative charges distributed uniformly over surface of a sphere
Negative charges located at vertices of an octahedron
Metal cation, M^{n+}
E
n+
e_g
$d_{x^2-y^2}$
d_{z^2}
Δ_o
t_{2g}
d_{xy}
d_{xz}
d_{yz}
e_g
Δ_o
t_{2g}
Electrostatic attractions (+/−) considered
(a)