CHAPTER TWENTY-ONE

TRANSITION METALS AND COORDINATION CHEMISTRY

For Review

1. Chromium ([Ar]:4s$^0$3d$^5$) and copper [Ar]:4s$^1$3d$^{10}$) have electron configurations which are different from that predicted from the periodic table. Other exceptions to the predicted filling order are transition metal ions. These all lose the s electrons before they lose the d electrons. In neutral atoms, the ns and (n!1)d orbitals are very close in energy, with the ns orbitals slightly lower in energy. However, for transition metal ions, there is an apparent shifting of energies between the ns and (n!1)d orbitals. For transition metal ions, the energy of the (n!1)d orbitals are significantly less than that of the ns electrons. So when transition metal ions form, the highest energy electrons are removed, which are the ns electrons. For example, Mn$^{2+}$ has the electron configuration [Ar]:4s$^0$3d$^5$ and not [Ar]:4s$^2$3d$^3$.

Most transition metals have unfilled d orbitals, which creates a large number of other electrons that can be removed. Stable ions of the representative metals are determined by how many s and p valence electrons can be removed. In general, representative metals lose all of the s and p valence electrons to form their stable ions. Transition metals generally lose the s electron(s) to form +1 and +2 ions, but they can also lose some (or all) of the d electrons to form other oxidation states as well.

2. a. Coordination compound: a compound composed of a complex ion (see b) and counterions (see c) sufficient to give no net charge.

b. Complex ion: a charged species consisting of a metal ion surrounded by ligands (see e).

c. Counterions: anions or cations that balance the charge on a complex ion in a coordination compound.

d. Coordination number: the number of bonds formed between the metal ion and the ligands (see e) in a complex ion.

e. Ligand: Species that donates a pair of electrons to form a covalent bond to a metal ion. Ligands act as Lewis bases (electron pair donors).

f. Chelate: Ligand that can form more than one bond to a metal ion.

g. Bidentate: Ligand that forms two bonds to a metal ion.

Because transition metals form bonds to species that donate lone pairs of electrons, transition metals are Lewis acids (electron pair acceptors). The Lewis bases in coordination compounds are the ligands, all of which have an unshared pair of electrons to donate. The coordinate covalent bond between the ligand and the transition metal just indicates that both electrons in the bond originally came from one of the atoms in the bond. Here, the electrons in the bond come from the ligand.
3. Linear geometry (180° bond angles) is observed when the coordination number is 2. Tetrahedral geometry (109.5° bond angles) or square planar geometry (90° bond angles) is observed when the coordination number is 4. Octahedral geometry (90° bond angles) is observed when the coordination number is 6.

For the following complex ions, see Table 21.13 if you don’t know the formula, the charge, or the number of bonds the ligands form.

a. \( \text{Ag(CN)}_2^- \); \( \text{Ag}^+ \): \([\text{Kr}]4d^{10}\)

b. \( \text{Cu(H}_2\text{O)}_4^{2+} \); \( \text{Cu}^{2+} \): \([\text{Ar}]3d^{10}\)

c. \( \text{Mn(C}_2\text{O}_4)^2- \); \( \text{Mn}^{2+} \): \([\text{Ar}]3d^5\)

d. \( \text{Pt(NH}_3)_4^{2+} \); \( \text{Pt}^{2+} \): \([\text{Xe}]4f^{14}5d^8\)

e. \( \text{Fe(EDTA)}^3+ \); \( \text{Fe}^{3+} \): \([\text{Ar}]3d^5\); Note: EDTA has an overall 4! charge and is a six coordinate ligand.

f. \( \text{Co(Cl)}_6^{4-} \); \( \text{Co}^{2+} \): \([\text{Ar}]3d^7\)

g. \( \text{Cr(en)}_3^{3+} \) where en = ethylenediamine (\( \text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \)); \( \text{Cr}^{3+} \): \([\text{Ar}]3d^3\)

4. See section 21.3 for a nice summary of the nomenclature rules.

a. The correct name is tetraamminecopper(II) chloride. The complex ion is named incorrectly in several ways.

b. The correct name is bis(ethylenediamine)nickel(II) sulfate. The ethylenediamine ligands are neutral and sulfate has a 2! charge. Therefore, \( \text{Ni}^{2+} \) is present, not \( \text{Ni}^{4+} \).

c. The correct name is potassium diaquatetrachlorochromate(III). Because the complex ion is an anion, the –ate suffix ending is added to the name of the metal. Also, the ligands were not in alphabetical order (a in aqua comes before c in chloro).

d. The correct name is sodium tetracyanooxalatocobaltate(II). The only error is that tetra should be omitted in front of sodium. That four sodium ions are needed to balance charge is deduced from the name of the complex ion.

5. a. Isomers: species with the same formulas but different properties; they are different compounds. See the text for examples of the following types of isomers.

b. Structural isomers: isomers that have one or more bonds that are different.

c. Stereoisomers: isomers that contain the same bonds but differ in how the atoms are arranged in space.

d. Coordination isomers: structural isomers that differ in the atoms that make up the complex ion.

e. Linkage isomers: structural isomers that differ in how one or more ligands are attached to the transition metal.

f. Geometric isomers: (cis-trans isomerism); stereoisomers that differ in the positions of atoms with respect to a rigid ring, bond, or each other.
g. Optical isomers: stereoisomers that are nonsuperimposable mirror images of each other; that is, they are different in the same way that our left and right hands are different.

The trans form of Cr(en)Cl$_2$ is not optically active, but the the cis form is optically active. See Figure 21.17 for illustrations showing the cis and trans forms for a similar compound; shown also is the optical activity of the cis form. The only difference between the complex in this question, and the complex in Figure 21.17, is that Cr$^{2+}$ has replaced Co$^{2+}$. Note that not all cis isomers are optically active. For example, the cis isomer of Cr(NH$_3$)$_2$Cl$_2$ is not optically active because the mirror image is superimposable (prove it to yourself).

In Figure 21.17, a plane of symmetry exists through the square planar orientation of the two en ligands. Other planes of symmetry also exist in the trans isomer. In the cis isomer in Figure 21.17, no plane of symmetry exists, so this cis form is optically active (as we know).

6. The crystal field model focuses on the energies of the d orbitals and what happens to the energies of these d orbitals as negative point charges (the ligands) approach (and repel) the electrons in the d orbitals. For octahedral geometry, six ligands are bonded to the metal ion. Because of the different orientations of the d orbitals, not all d orbitals are affected the same when six negative point charges (ligands) approach the metal ion along the x, y, and z axis. It turns out that the d$_{xy}$, d$_{xz}$, and d$_{yz}$ orbitals are all destabilized by the same amount from the octahedrally arranged point charges, as are the d$_{x^2-y^2}$ and d$_{z^2}$ orbitals. These are the two sets that the d orbitals split into. The d$_{xy}$, d$_{xz}$, and d$_{yz}$ set is called the t$_{2g}$ set, while the d$_{x^2-y^2}$ and d$_{z^2}$ set is called the e$_g$ set.

Another major point for the octahedral crystal field diagram is that the e$_g$ set of orbitals is destabilized more than the t$_{2g}$ set. This is because the t$_{2g}$ orbital set (d$_{xy}$, d$_{xz}$, and d$_{yz}$) points between the point charges while the e$_g$ orbital set (d$_{x^2-y^2}$ and d$_{z^2}$) points directly at the point charges. Hence, there is more destabilization in the e$_g$ orbital set, and they are at a higher energy.

a. Weak field ligand: ligand that will give complex ions with the maximum number of unpaired electrons.

b. Strong-field ligand: ligand that will give complex ions with the minimum number of unpaired electrons.

c. Low-spin complex: complex ion with a minimum number of unpaired electrons (low-spin = strong-field).

d. High-spin complex: complex ion with a maximum number of unpaired electrons (high-spin = weak-field).

In both cobalt complex ions, Co$^{3+}$ exists which is a d$^6$ ion (6 d electrons are present). The difference in magnetic properties is that Co(NH$_3$)$_6$Co$^{3+}$ is a strong-field (low-spin) complex having a relatively large $\Delta$, while CoF$_6$Co$^{3-}$ is a weak-field (high-spin) complex having a relatively small $\Delta$. The electron configurations for Co$^{3+}$ in a strong field vs. a weak field is
shown in Figure 21.22. The strong-field $d^6$ ion is diamagnetic because all electrons are paired. This is the diagram for $\text{Co(NH}_3)_6^{3+}$. The weak field $d^6$ ion is paramagnetic because it has unpaired electrons (4 total). This is the diagram for $\text{CoF}_6^{3-}$.

Looking at Figure 21.22, $d^1$, $d^2$, and $d^3$ metal ions would all have the same number of unpaired electrons. This won’t happen again until we get all the way up to $d^8$, $d^9$, and $d^{10}$ metal ions (prove it to yourself that $d^4$, $d^5$, $d^6$, and $d^7$ metal ions have a different $d$ orbital electron configurations depending on a strong-field or a weak-field). $V^{3+}$ is a $d^2$ ion (2 unpaired electrons in the $t_{2g}$ set). It has the same diagram no matter how strong the field strength. The same is true for the $d^8$ Ni$^{2+}$ ion (filled $t_{2g}$ set and half-filled $e_g$ set). However, Ru$^{2+}$, a $d^6$ ion, will have different diagrams depending on a strong-field or a weak-field. If a weak-field is present, then there are four unpaired electrons. In the strong-field case, all six $d$ electrons are in the $t_{2g}$ set and all are paired (no unpaired electrons).

7. The valence $d$ electrons for the metal ion in the complex ion are placed into the octahedral crystal field diagram. If electrons are all paired, then the complex is predicted to be diamagnetic. If there are unpaired electrons, then the complex is predicted to be paramagnetic.

Color results by the absorption of specific wavelengths of light. The $d$-orbital splitting, $\Delta$, is on the order of the energies of visible light. The complex ion absorbs the wavelength of light that has energy equal to the $d$-orbital splitting, $\Delta$. The color we detect for the substance is not the color of light absorbed. We detect (see) the complementary color to that color of light absorbed. See Table 21.16 for observed colors of substances given the color of light absorbed.

From Table 21.16, if a complex appears yellow then it absorbs blue light on the order of $\lambda \sim 450$ nm. Therefore, $\text{Cr(NH}_3)_6^{3+}$ absorbs blue light.

The spectrochemical series places ligands in order of their ability to split the $d$-orbitals. The strongest field ligands (large $\Delta$) are on one side of the series with the weakest field ligands (small $\Delta$) on the other side. The series was developed from studies of the light absorbed by many octahedral complexes. From the color of light absorbed, one can determine the $d$-orbital splitting. Strong-field ligands absorb higher energy light (violet light, for example, with $\lambda \sim 400$ nm), while weak-field ligands absorb lower energy light (red light, for example, with $\lambda \sim 650$ nm).

The higher the charge on the metal ion, the larger the $d$-orbital splitting. Thus, the Co$^{3+}$ complex ion $[\text{Co(NH}_3)_6^{3+}]$, would absorb higher energy (shorter wavelength) light than a Co$^{2+}$ complex ion (assuming the ligands are the same).

$\text{Cu}^{2+}$: [Ar]$3d^9$; $\text{Cu}^{+}$: [Ar]$3d^{10}$; Cu(II) is $d^9$ and Cu(I) is $d^{10}$. Color is a result of the electron transfer between split $d$ orbitals. This cannot occur for the filled $d$ orbitals in Cu(I). Cd$^{2+}$, like Cu$^+$, is also $d^{10}$. We would not expect $\text{Cd(NH}_3)_4\text{Cl}_2$ to be colored because the $d$ orbitals are filled in this Cd$^{2+}$ complex.
Sc$^{3+}$ has no electrons in d orbitals. Ti$^{3+}$ and V$^{3+}$ have d electrons present. Color of transition metal complexes results from electron transfer between split d orbitals. If no d electrons are present, no electron transfer can occur, and the compounds are not colored.

8. The crystal field diagrams are different because the geometries of where the ligands point is different. The tetrahedrally oriented ligands point differently in relationship to the d-orbitals than do the octahedrally oriented ligands. Plus, we have more ligands in an octahedral complex.

See Figure 21.27 for the tetrahedral crystal field diagram. Notice that the orbitals are reverse of that in the octahedral crystal field diagram. The degenerate $d_{x^2}$ and $d_{x^2−y^2}$ are at a lower energy than the degenerate $d_{xy}$, $d_{xz}$, and $d_{yz}$ orbitals. Again, the reason for this is that tetrahedral ligands are oriented differently than octahedral field ligands so the interactions with specifically oriented d-orbitals are different. Also notice that the difference in magnitude of the d-orbital splitting for the two geometries. The d-orbital splitting in tetrahedral complexes is less than one-half the d-orbital splitting in octahedral complexes. There are no known ligands powerful enough to produce the strong-field case, hence all tetrahedral complexes are weak-field or high spin.

See Figure 21.28 for the descriptions of the square planar and linear crystal field diagrams. Each is unique which is not surprising. The ligands for any specific geometry will point differently relative to the orientations of the five d-orbitals. Different interactions result giving different crystal field diagrams.

9. Each hemoglobin molecule can bind four O$_2$ molecules. It is an Fe$^{2+}$ ion in hemoglobin that binds an individual O$_2$ molecule, and each hemoglobin molecule has four of these Fe$^{2+}$ binding sites. The Fe$^{2+}$ ion at the binding site is six-coordinate. Five of the coordination sites come from nitrogens in the hemoglobin molecule. The sixth site is available to attach an O$_2$ molecule. When the O$_2$ molecule is released, H$_2$O takes up the sixth position around the Fe$^{2+}$ ion. O$_2$ is a strong field ligand, unlike H$_2$O, so in the lungs, O$_2$ readily replaces the H$_2$O ligand. With four sites, each hemoglobin molecule has a total of four O$_2$ molecules attached when saturated with O$_2$ from the lungs. In the cells, O$_2$ is released by the hemoglobin and the O$_2$ site is replaced by H$_2$O. The oxygen binding is pH dependent, so changes in pH in the cells as compared to blood, causes the release of O$_2$ (see Exercise 21.72). Once the O$_2$ is released and replaced by H$_2$O, the hemoglobin molecules return to the lungs to replenish with the O$_2$.

CN$^-$ and CO form much stronger complexes with Fe(II) than O$_2$. Thus, O$_2$ is not transported by hemoglobin in the presence of CN$^-$ or CO because the binding sites prefer the toxic CN$^-$ and CO ligands.
10. The definitions follow. See section 21.8 for examples.

   a. Roasting: converting sulfide minerals to oxides by heating in air below their melting points.

   b. Smelting: reducing metal ions to the free metal.

   c. Flotation: separation of mineral particles in an ore from the unwanted impurities. This process depends on the greater wetability of the mineral particles as compared to the unwanted impurities.

   d. Leaching: the extraction of metals from ores using aqueous chemical solutions.

   e. Gangue: the impurities (such as clay, sand, or rock) in an ore.

Advantages of hydrometallurgy: cheap energy cost; less air pollution; Disadvantages of hydrometallurgy: chemicals used in hydrometallurgy are expensive and sometimes toxic.

In zone refining, a bar of impure metal travels through a heater. The impurities present are more soluble in the molten metal than in the solid metal. As the molten zone moves down a metal, the impurities are swept along with the liquid, leaving behind relatively pure metal.