

Chapter 19 – Transition Metals and Coordination Compounds

We see color all around us, but what is color? When we see white, we see all of the wavelengths of light in the visible region of the electromagnetic spectrum (*ca.* 400 – 700 nm) transmitted or reflected in roughly equal amounts. Black is the opposite, it is the transmission or reflection of no light. We see color when one or more wavelengths of light are transmitted or reflected to a greater extent than the others (or exclusively).

Broadly stated, there are inorganic and organic sources of color. In CHM 355/356 you will learn how organic compounds can produce color. Examples of colored organic compounds include the dyes that color your clothing, the ink on a newspaper, and the indicators used in the titrations you did in CHM 217. We will discuss the origin of inorganic color in one type of compound, coordination compounds, in this chapter, but in reality the discussion applies to the large majority of inorganic compounds. Inorganic sources of color include many paints, gemstones, and hemoglobin and chlorophyll (although, strictly speaking, these last two also have an organic component as well).

19.1 Occurrence, Preparation, and Properties of Transition Metals and Their Compounds

Technically, the transition metals are defined as those elements whose atoms have or form partially filled *d*-orbitals. This would include the “*d*-block” elements, but also the lanthanides and actinides. Traditionally, only the *d*-block elements are thought of as transition elements and I will use that definition moving forward. We will mostly ignore the lanthanides and actinides for the rest of the chapter, although they may show up in examples and problems in ways just like the transition metals. The rows are frequently referred to as the first transition series (beginning with scandium, Sc), followed by the second (Y), third (La), and fourth (Ac) transition series.

Properties of the Transition Metals

The generic properties of transition metals (TMs) are the same as the main group metals. That is, they conduct electricity well, are ductile, etc. The thing that makes TMs special is the properties of their ions. For example, none of the main group metal cations is innately colored, while many transition metal ions are. Notably, unlike main group metal ions, nearly all TMs form ions of varying oxidation numbers. For example, manganese forms salts with every oxidation state between +1 and +7 (the table on p. 1044, Figure 19.4, lists only the common oxidation states for most of these metals). In contrast, only a few main group metals form ions with even two oxidation numbers. Likewise, nearly all TM ions form complex ions by associating with Lewis bases, while this is very uncommon for main group metal ions.

On p. 1044, the book notes a trend for TM ions, that is worth expanding upon. It notes that higher oxidation numbers become more stable going down a group, which is true. Interestingly, the reverse is true for main group metal ions. For example, +4 is the most stable oxidation number for carbon, silicon (which are nonmetals, of course), and germanium. For tin, +2 and +4 have similar stabilities, while +2 is decidedly more stable for lead. The same basic trend is observed for Groups 15 and 16.

Skip all of the discussion on the isolation of TMs.

Transition Metal Compounds

The book provides a lot of preparative reactions here. You shouldn't memorize the specific examples, but rather be familiar with them in a general way. For example, metal + halide reacts to form metal halide, rather than the specific iron example. In contrast, metal carbonates are formed from the reaction of metal ions with carbonate ion via precipitation reactions, rather than through some kind of reaction with the metals in their elemental forms (i.e. zero oxidation numbers).

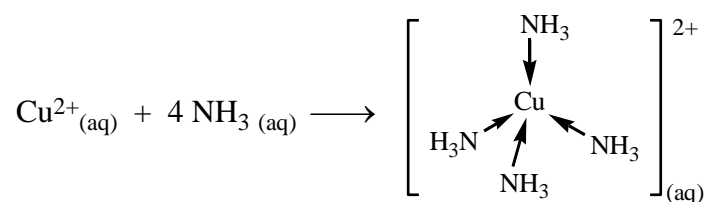
One topic briefly mentioned in this section that is quite important is that these metals form covalent bonds. This might not be very surprising. For a metal salt where the metal and non-metal have +1 and -1 charges, respectively, one would expect an ionic bond. However, as the metal and non-metal charges increase, the relatively simple description of an ionic bond begins to break down. To understand this, remember that we envisioned an ionic bond as a spherical cation adjacent to a spherical anion. In reality, the spheres would be distorted a little because the cation would pull some electron density towards the anion. For low charge ions, this distortion is small and can be ignored. As the charge on the cation increases, the distortion of the anion increases, ultimately reaching the point that the bond is no longer ionic. An example that you have already encountered is permanganate ion, MnO_4^- . The 7+ manganese ion is so highly charged, that when the MnO_4^- ion is dissolved in water, it remains intact, with a structure analogous to ClO_4^- , perchlorate. Even the ion name suggests the bonding is the same in these two entities. Chromate and dichromate are also complex ions with covalent M-O bonds.

19.2 Coordination Chemistry of Transition Metals

A complex or complex ion is an assembly of a metal ion and bound Lewis bases. Compounds that contain complex ions are called coordination complexes. The Lewis bases that bind (coordinate) to the metal atom or ion are called ligands. Ligands are usually anions or polar, neutral molecules. Examples include halide ions, water, ammonia, cyanide ion, carbonate ion, hydroxide ion, and ethylene diamine ($\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$).

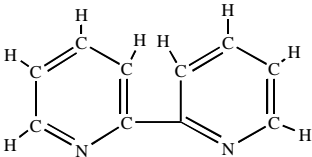
The metal is most usually a transition metal, although main group metals can form coordination complexes (e.g. $\text{Al}(\text{H}_2\text{O})_6^{3+}$ as seen in Chapter 15). The reason for this is transition metals generally have empty or partly filled valence *d*-orbitals. The result is that the ligands bind to the metal through a coordinate covalent bond (Chap. 15 notes, p. 7). The figure below shows

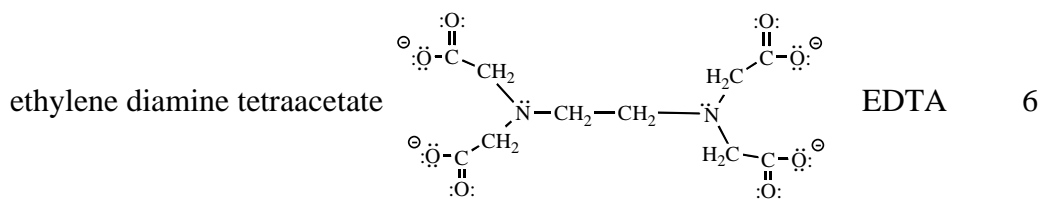
a typical coordination complex.



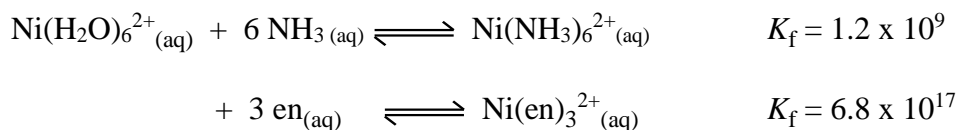
The ligands and metal combine to form the coordination sphere. The species that comprise the coordination sphere should be written in square brackets as follows: $[\text{Cu}(\text{NH}_3)_4]^{2+}$ or $[\text{Cu}(\text{NH}_3)_4]\text{Cl}_2$. The brackets indicate that the species generally behaves as a single unit. We will discuss this in greater detail shortly. Finally, the arrows represent bonds (but also show that the ligands are supplying all of the electrons). This way of writing the bonds is optional. The atoms in a ligand that actually bind to the metal are called donor atoms. In this example, the nitrogens in the ammonia are donor atoms.

Both of the ligands used in the examples thus far have had only one donor atom (i.e. one site of attachment). These ligands are called monodentate. Some ligands contain more than one donor atom. Ligands binding to a metal using two or more donor atoms are called polydentate. Bidentate ligands bind through 2 donor atoms. Tri-, tetra-, penta-, and hexadentate ligands bind through 3, 4, 5, and 6 donor atoms, respectively. Common polydentate ligands include:

<u>Name</u>	<u>Formula</u>	<u>abbr</u>	<u>CN</u>
ethylene diamine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	en	2
carbonate	CO_3^{2-}		2
oxalate	$^{-}\text{O}_2\text{CCO}_2^{-}$	ox	2
bipyridine		bpy	2



Polydentate ligands are commonly called chelates (or chelating ligands). The name derives for the Greek word for “claw” because these ligands grasp at the metal at multiple places. Chelates are an important class of ligands because they bind significantly more strongly to metals than to monodentate ligands. For example:



If one assumes the ligand concentration is significantly larger than the Ni^{2+} concentrations, then the ethylene diamine complex is about 100 million times more stable than the amine complex. Why is this so?

If you think about the reverse reaction, you see that it is much more difficult to remove ethylene diamine ligands than ammonia molecules. Both reactions demonstrate that Ni^{2+} has a significant preference for amine type ligands over water, thus the likelihood of an N donor atom letting go at any given time is quite small, nonetheless there is a difference. Let's assume that we have one of each of the above complexes and that one of the N donor atoms has let go in each complex. In the case of $\text{Ni}(\text{NH}_3)_6^{2+}$, the resultant complex ion will be $\text{Ni}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$. Once the released, ammonia molecule may drift away. If this happens, the complex must wait until it encounters another ammonia molecule before it can reform the original complex. When $\text{Ni}(\text{en})_3^{2+}$ releases an N donor atom, the product complex has the formula $\text{Ni}(\text{en})_2(\text{en}')(\text{H}_2\text{O})^{2+}$ (where en' is a singly bound ethylene diamine). At first glance, this appears little different from the ammonia case, but there is an important difference. While one end of the en is loose, the

other is bound, so the unbound end cannot drift away like the ammonia. Thus, there is a very high likelihood that it will rebind rapidly to reform the original complex ion. The more points of attachment for a ligand, the less likely that all will release from the metal. Thus, formation constants tend to increase with increasing numbers of donor atoms on chelates. It is for this reason that EDTA is added to many foods (e.g. mayonnaise and salad dressings) to preserve freshness. If metal ions that would catalyze spoilage get into the food (from a spoon, for example), the EDTA binds to them so they are effectively deactivated.

The Naming of Complexes

The system of naming coordination complexes is in some ways similar to and in other ways different from naming simple inorganic salts. The rules for nomenclature are:

- 1) Name the cation first and anion second.
- 2) Within a complex ion, the ligands are named alphabetical order. **Numbering prefixes (e.g. di, tri, ...) are not used in alphabetizing.**
- 3) Anionic ligands end in the letter “-o,” while neutral molecules (with a few exceptions) retain their names.
- 4) The prefixes di-, tri-, tetra-, penta-, and hexa- are used to indicate the number of each ligand. If the ligand name includes such a prefix, the ligand name should be placed in parentheses and preceded by bis- (2), tris- (3), tetrakis- (4), pentakis- (5), and hexakis- (6).
- 5) If a complex is an anion, it should end in “-ate.”
- 6) Place the metal oxidation number in parentheses as a Roman numeral following the metal name.

Table 19.1 lists some common anionic ligands and their names as ligands. Notably, two neutral ligands, water and ammonia have significant name changes to “aqua” and “ammine,” respectively. A few examples that demonstrate these rules appear below.

- Ex. $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2$ hexaaquanickel(II) chloride
- $\text{Na}_3[\text{Fe}(\text{CN})_6]$ sodium hexacyanoferrate(III)
- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ diamminedichloroplatinum(II)
- $[\text{Co}(\text{en})_3]\text{Br}_2$ tris(ethylene diamine)cobalt(II) bromide

In these examples, it is important to note that the alkali metal and halide counterions don't have numbering prefixes. It is presumed that you can calculate their number from the other information in the name.

The Structures of Complexes

The structures of complexes largely follow the rules that were set up in Chapter 7, Section 6 for VSEPR (Valence Shell Electron-Pair Repulsion) Theory. As your book notes, there are a few other possible geometries for coordination complexes, some of which can have more than 9 groups bound to a central atom/ion. You can ignore the additional geometries, with the exception of square planar which is moderately common, but arises for different reasons than it does for normal covalent compounds.

Isomerism in Complexes

Compounds with the same composition, but different structures are called isomers. Isomers are very important in both coordination chemistry and in the organic chemistry that many of you will study next year. The text below is organized a little differently from the book and contains a few more terms involved in organizing the topics.

Two broad categories of isomers are structural isomers, which have different atoms bound to each other, and stereoisomers, which have the same atoms bound to each other, but differ in their spatial arrangement. It is easiest to learn this by seeing examples.

Structural Isomerism

One type of structural isomerism is linkage isomerism. This may arise when a ligand has



more than one chemically distinct donor atom. For example, $\text{Co(NH}_3\text{)}_5(\text{NO}_2)^{2+}$ and $\text{Co(NH}_3\text{)}_5(\text{ONO})^{2+}$ are linkage isomers. The blue letter indicates the donor atom.

pentaamminenitrocobalt(III) pentaamminenitritocobalt(III)

Note the difference in the names. Frequently linkage isomer ligands will have a different name for each coordination mode.

The other structural isomerism we will cover is coordination sphere (ionization) isomerism. This occurs when different ligands that are part of the overall formula bind to the metal. For example, three compounds exist with the general formula “ $\text{Cr(H}_2\text{O)}_6\text{Cl}_3$.” They are:

$[\text{Cr(H}_2\text{O)}_6]\text{Cl}_3$ violet

$[\text{Cr(H}_2\text{O)}_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ green

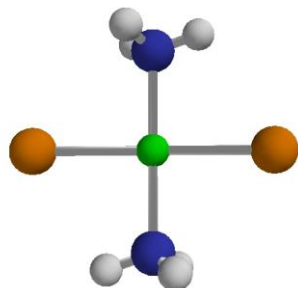
$[\text{Cr(H}_2\text{O)}_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ green

The last two complexes possess lattice solvent molecules. These are molecules of solvent that occupy spaces in the lattice, but are not chemically bound to the complex ions. What kind of experiment might distinguish these compounds from one another, if all you knew was the generic formula and possible alternative structures?

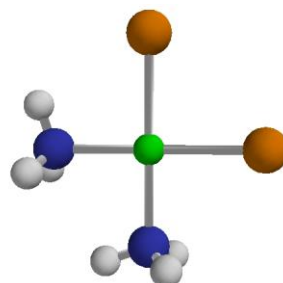
Stereoisomerism

This is the most common and most important class of isomerism. Geometrical isomerism occurs when the same ligands bind to different sites on the metal. There are several types of geometrical isomerism. In square planar complexes, systems with one or two pairs of different

ligands can usually exist in two different forms. All other formulations (e.g. 4 of the same ligand) are limited to only one isomer. In one isomer, the same ligands lie directly opposite one another (*trans*). In the other isomer, they lie in adjacent positions (*cis*).

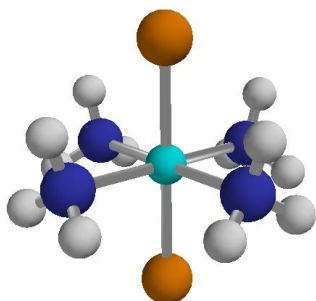


trans-diamminedichloroplatinum(II)

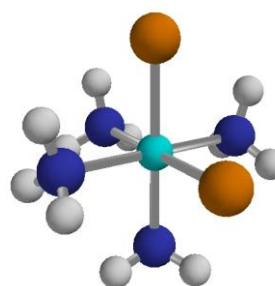


cis-diamminedichloroplatinum(II)

In octahedral complexes *cis/trans* isomerism is also possible, as is an isomerism associated with pairs of the same ligands.



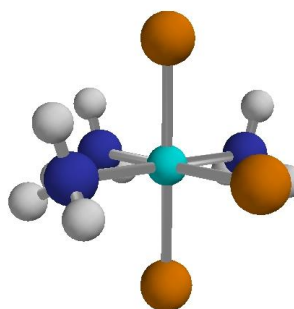
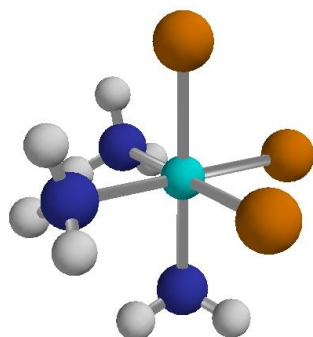
trans-tetraamminedichlorocobalt(III)



cis-tetraamminedichlorocobalt(III)

In this case, we assume the ligand appearing only twice is the ligand described by the prefix. Where multiple pairs of ligands appear, multiple prefixes are permitted.

Facial (*fac*) isomerism describes 3 of the same ligands lying on one face of an octahedron while meridional (*mer*) isomerism refers to 3 of the same ligands lying on a plane passing through the center of the complex (a meridian).



fac-triamminetrichlorocobalt(III)*mer*-triamminetrichlorocobalt(III)Optical Isomerism

This type of isomerism occurs when mirror images of a molecule cannot be superimposed on each other. The individual isomers are called enantiomers and molecules that exhibit optical isomerism are said to be chiral. Chirality is a very important property in biological systems because many biologically molecules are present as only one enantiomer. The other enantiomer is either biologically inactive or, in some cases, hazardous. Most biological optically active molecules are organic chemicals (composed solely of C and H, along with some or all of: Cl, N, O, and P). We can see chirality by using $\text{Co}(\text{en})_3^{2+}$ as an example. Figure 1 shows a $\text{Co}(\text{en})_3^{2+}$ ion (A) and its mirror image (B). The second shows ion "A" as it is rotated around the z-axis. As you can see, it is not the same as ion "B." No amount of rotating will get these molecules to appear identical to one another.

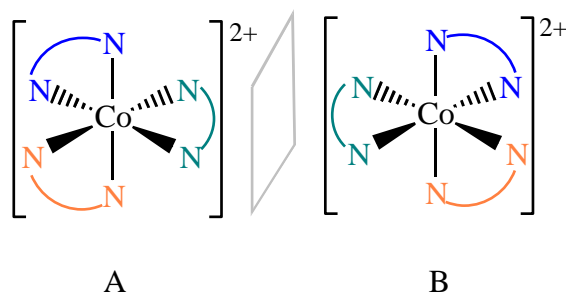


Figure 1

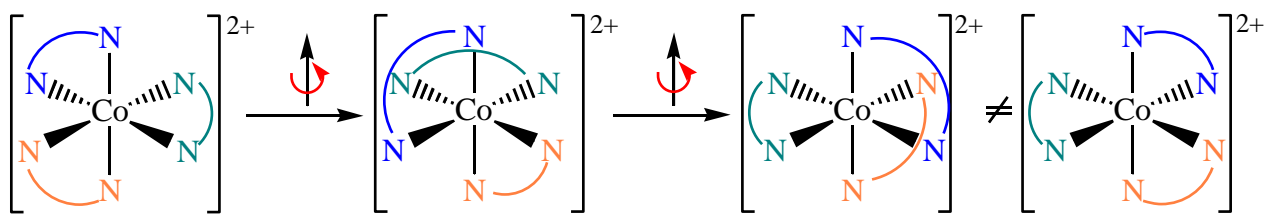


Figure 2

Almost all chemical physical properties of optical isomers are identical. For example,

enantiomers have identical boiling points, melting points, color, density, and reactivity with non-chiral molecules. However, they do differ from each other in two important ways:

1. Enantiomers rotate polarized light in opposite directions by an equal amount. (In polarized light, the waves are all aligned.)
2. They react differently with other chiral molecules. Since many biologically active molecules exhibit optical isomerism, this has important implications for living systems.

When chiral molecules form from achiral starting reagents, each enantiomer forms in equal proportion. The mixture of products is called a racemic mixture. When they form from chiral reagents, one enantiomer is usually preferred, sometimes exclusively.

Complex Ion Charge

The textbook doesn't cover assigning charges in complex ions, but doing so isn't always straightforward. The charges on coordination complexes are obtained by treating each constituent ion or group of the complex as if it were a free species. Thus, for $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$:

The Cl is a chloride ion so the complex ion is $[\text{Ag}(\text{NH}_3)_2]^+$. Ammonia is a neutral molecule, so the silver must be in the +1 oxidation state.

Ex. What is the oxidation number of cobalt in $[\text{Co}(\text{NH}_3)_5\text{Cl}](\text{NO}_3)_2$?

Let the oxidation number of Co be x . NH_3 is neutral. Cl is chloride (Cl^-) and NO_3 is nitrate (NO_3^-). Thus

$$0 = x + 5(0) + (-1) + 2(-1)$$

$$x = +3 \text{ (i.e. a } \text{Co}^{3+} \text{ ion)}$$

The atoms in a ligand that actually bind to the metal are called donor atoms. In the first example, the nitrogens in the ammonia are donor atoms. In the second example, there are five nitrogen donor atoms and one chlorine donor atom.

19.3 Spectroscopic and Magnetic Properties of Coordination Complexes

Almost all colored substances fall into one of two categories: (1) transition metals with partially filled *d*-orbitals and (2) organic molecules with extended, delocalized systems of π -bonding. These molecules include the dyes used to color your clothing and will be discussed next year in your organic chemistry class.

In this chapter we discuss case (1). Metals with no *d*-electrons (d^0) or 10 *d*-electrons (d^{10}) are usually colorless. Examples include Sc^{3+} , Ti^{4+} , and Zn^{2+} . (TiCl_4 is a colorless liquid and ZnCl_2 is a white solid that is colorless in solution.) Why do these ions yield colorless compounds? To answer this, we must first answer the question “what is color and why do we see it at all?”

The human eye can only see wavelengths of light between about 400 and 700 nm. Your eyes cannot detect wavelengths significantly outside this range. “Seeing” occurs when light moves directly from a source to our eyes, passes through a substance on the way to our eyes, or reflects off an object on its way to our eyes. We’ll consider the final two methods as they are most relevant here.

If an object absorbs all the light passing through it or striking it, the object appears black because no reflected light makes it to our eyes. Assuming the incoming light is white, an object that absorbs little or none of the light appears white (opaque objects) or colorless (transparent objects). (Gray occurs when some, but not all of the light is absorbed and all wavelengths are absorbed equally.)

If an object absorbs all light except one wavelength, we see the color of that wavelength. If it absorbed only one wavelength of light, we would see the complementary color to that wavelength. Do you remember the color wheel from art class? The primary colors are red,

yellow, and blue. The secondary colors are their complements, green, purple, and orange, respectively. In actuality, there will be different shades of these colors and many compounds absorb at more than one wavelength, but the general idea still holds.

We determine the wavelength of maximum absorbance (λ_{max}) by passing a light beam containing each wavelength of light through a sample and measuring how much light is absorbed at each wavelength.

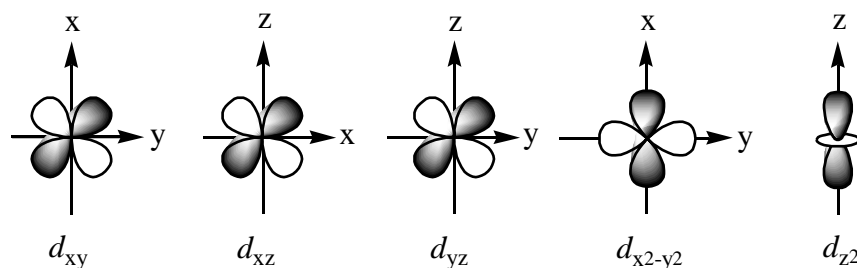
Magnetism

If one thinks of an electron as a spinning particle, then it will generate a magnetic field. Since each unpaired electron will generate a similar magnetic field (they won't be exactly equal because they interact with one another) knowing the size of a magnetic field for a complex tells us the number of unpaired electrons it possesses.

One might wonder why this is necessary since if you know the number of electrons in *d*-orbitals, the number of unpaired electrons should be easy to determine. It turns out it isn't so easy. For example, if an octahedral complex ion has five *d*-electrons it may have five unpaired electrons, or only one.

The previous observation (and others) led to the realization that the electronic structure of transition metal complexes must be more complicated than originally believed. A theory that does a very good job of predicting the electronic behavior of transition metal complexes is called crystal field theory. We will begin by considering an octahedral complex (6 donor atoms lying along the coordinate axes with the metal located where the axes intersect).

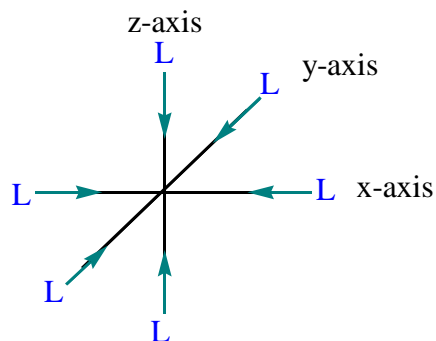
Remember there are five *d*-orbitals at each energy level (principal quantum number, *n*): d_{xy} , d_{xz} , d_{yz} , d_{z^2} , and $d_{x^2-y^2}$. Hereafter, I will refer to them as *xy*, *xz*, *yz*, z^2 , and x^2-y^2 , respectively.



It is easiest to approach this theory by considering a d^1 metal cation (a cation with only 1 electron in its d -orbitals) and extrapolating to the other cases. In this situation, there are two possible ways of placing the electron. In possibility #1, one in five complexes will have an electron in the xy orbital, where it remains forever. Likewise, 20% of the complexes will have the electron in the xz , yz , z^2 , and x^2-y^2 orbitals, respectively. Again, the electrons are locked into their respective orbitals. The other possibility is that the electron is free to roam from orbital to orbital, spending a statistical amount of time in each orbital. What this means is that the electron spends 20% of its time in the xy , 20% in xz , etc. Which is the correct view?

If you think of the electron as a wave, each orbital has a node at the nucleus. In other words, the wave equations that describe the five orbitals all equal the same value at this point. Thus, an electron at the nucleus is equally likely to exit the node in any of the five d -orbitals. This description is correct.

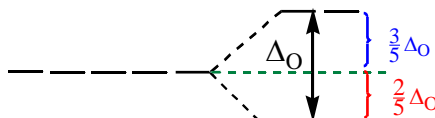
Now consider the 6 ligands that will attach to the metal when the complex forms. They begin at infinite distance from the metal and begin to approach it. To minimize their interaction



with each other (VSEPR theory), they will approach along opposite ends of the 3 coordinate

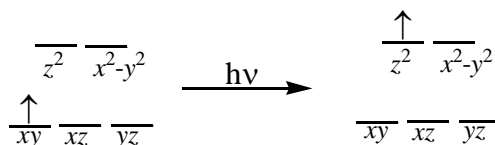
axes. (i.e. one each from the $+x$, $-x$, $+y$, $-y$, $+z$, and $-z$ directions). The lone pairs of electrons are attracted to the metal cation and are pulled towards it.

As the distance between the metal and ligands drops below infinity, the ligand electrons are not only attracted to the metal nucleus, they repel the metal d electron. The alignment of the d -orbitals now becomes important. Two orbitals line up along the coordinate axes (z^2 and x^2-y^2) and 3 in-between (xy , xz , and yz). Ligand electron- d -electron repulsion reaches a maximum along the coordinate axes, so as ligands approach the energy of the z^2 and x^2-y^2 orbitals increases relative to the xy , xz , and yz orbitals. This can be shown pictorially as:



When the d -orbitals split, the three that drop in energy lower by $\frac{2}{5}\Delta_0$, while those that increase in energy do so by $\frac{3}{5}\Delta_0$. Thus, there is no net change in energy for the orbitals (in total).

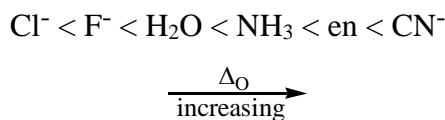
Since we only have one d -electron, it goes into the lower energy set. (Now it will spend one-third of the time in each of the three orbitals.) When light with an energy equal to the gap (Δ_0) is absorbed, the electron jumps from the lower set to the upper set. Light not equal to this gap (or any other gap in the compound) passes through or reflects off. Δ_0 is related to wavelength by $E = h\nu$ and $c = \lambda\nu$.



It just happens that the energy gap between the split d -orbitals corresponds to the visible region of the electromagnetic spectrum. We must now deal with the different colors observed for complexes. Why is it that different metals yield different colored complexes even though the

same ligands are bound to each (e.g. $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2 = \text{red}$ vs. $[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2 = \text{green}$)? Likewise, why do different ligands cause complexes to exhibit different colors ($[\text{Ni}(\text{H}_2\text{O})_6]\text{Cl}_2 = \text{green}$ vs. $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2 = \text{lavender}$)?

The oxygen in water is more electronegative than the nitrogen in ammonia. For this reason, its lone pair orbitals don't project out into space as far (i.e. it holds its electrons more tightly). Thus, as a water molecule approaches the metal its lone pairs interact less strongly with the metal than does nitrogen's lone pair. So one expects Δ_{O} to be smaller for water since the gap is proportional to the level of interaction. A general ordering of ligands has been determined:



In a similar manner, a higher charge on the metal draws ligands in closer and increases both interaction and Δ_{O} . In the complexes above, Ni^{2+} is smaller than Co^{2+} and this should lead to greater metal-ligand interaction and a larger Δ_{O} .

We now return to the topic that ended the last section, why does the number of unpaired electrons vary from complex to complex. In d^1 , d^2 , and d^3 complexes there is no ambiguity about filling the orbitals; they go in the lower orbital set (each into separate orbitals so that none is paired). In a d^4 metal things are a little different. The fourth electron may either go into the upper set of orbitals or it may pair with an electron in the lower set. In the latter case, energy must be supplied to overcome the repulsion of the electrons occupying the same orbital. If Δ_{O} is larger than the energy required to pair the electrons, the electron goes into the lower orbitals. If Δ_{O} is smaller than the pairing energy, it goes into the upper set of orbitals.



A complex with the larger number of unpaired electrons is called high spin, while the one with the smaller number is called low spin.

Complexes with other geometries yield analogous energy level diagrams, but with few exceptions, all such geometries (e.g. tetrahedral, square planar, etc.) are always low spin.

August 22, 2022