

Investigating Complex Ions of Copper(II)

Background

Transition metal ions in aqueous solutions generally exist as complex ions in which water molecules, acting as Lewis bases, "coordinate" or bond with the small cation (which acts as a Lewis acid). The water molecules in these structures are known as *ligands*. Historically this kind of attachment has been called either a *coordinate covalent bond* or a *dative bond*. The distinguishing characteristic of such bonds is that the shared electron pairs which constitute the bonds come from only one of the bonded species. In normal covalent bonding the assumption is that each atom donates one electron to the shared pair that is the bond.

The number of ligand attachments to the metal ion is called the *coordination number*. Ligands which can make only one bond with an ion are called *monodentate* ligands ("one tooth"). *Bidentate* ligands are generally larger structures which can attach twice to an ion (e.g. ethylene diamine). A few ligands are *polydentate* (such as EDTA).

The existence of metal ion-water complexes is mainly due to the attraction of the lone pairs of the water molecules for the high, concentrated, positive charge on the metal cations. Silver ion, for example, is typically coordinated with two water molecules. Although it is usual to write aqueous silver ions as Ag^+ , a more accurate representation would be $[\text{Ag}(\text{H}_2\text{O})_2]^+$ (diaquasilver ion). Similarly, aqueous copper(II) ions are generally coordinated with four water molecules resulting in the species $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ (tetraaquacopper(II) ion). Although these examples include only water molecules as ligands, other neutral molecules, anions, and even some cations are also possible.

The structure of such ions and their compounds (in copper(II) sulfate pentahydrate, only one of the waters is actually a water of hydration; the others are coordinated with the copper ion) was a subject of much interest to Alfred Werner who began a systematic study of them in the 1890's. Although many of the substances had been known for nearly 200 years before Werner began his work, very little was known about the structure or bonding of the compounds. Werner's work led to a better understanding of synthetic methods for producing different compounds and eventually various models for describing how the bonding might take place and how some of the more interesting properties of the compounds might come about.

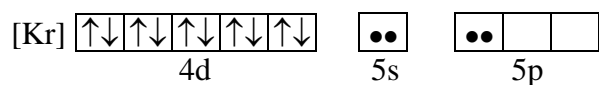
One of the early approaches to understanding the bonding in complex ions was to adapt Valence Bond Theory. Werner's work showed that complexes had definite geometries (some of which gave rise to isomers similar to the geometric and optical isomers of hydrocarbon compounds) which were the same as geometries of ordinary molecular compounds. Accordingly, bonding in complexes can be treated as occurring within hybrid orbitals. In the example of $[\text{Ag}(\text{H}_2\text{O})_2]^+$ cited earlier, the orbital diagram for Ag^+ would be represented as:



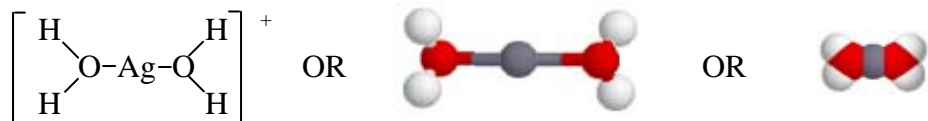
(recall that silver has an irregular electron configuration of $[\text{Kr}]5s^14d^{10}$).

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Complex Ions and the Spectrochemical Series, Woodrow Wilson Leadership Program in Chemistry,
Eva Lou Apel, Larry Ferguson, Glenda Marshman, Regina Monks, Sam Sakurada, Joe Trebella

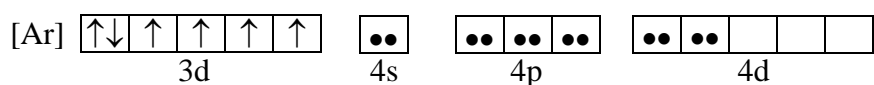
Any kind of covalent bonding will have to occur in unoccupied orbitals. In this case, those orbitals are in the next valence level, $n = 5$:



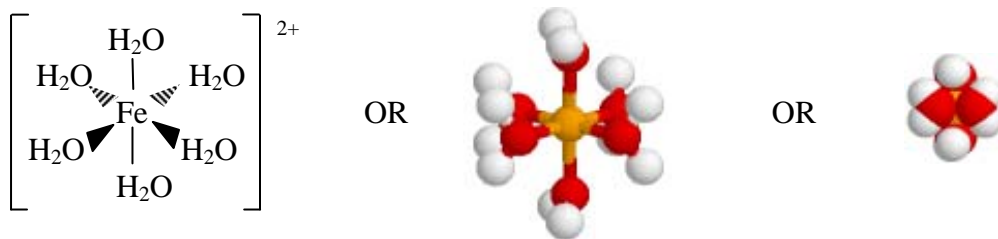
The sharing of the water lone pair electrons in the 5s and 5p orbitals means the bonding can be described as "sp" and that tells us the complex will be linear:



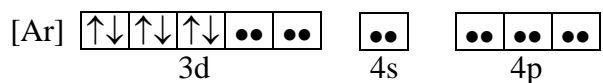
Valence Bond theory can also be used to "explain" why some complexes are paramagnetic while others are diamagnetic. The complex ion $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ (hexaaquairon(II) ion) would have an orbital diagram as shown below:



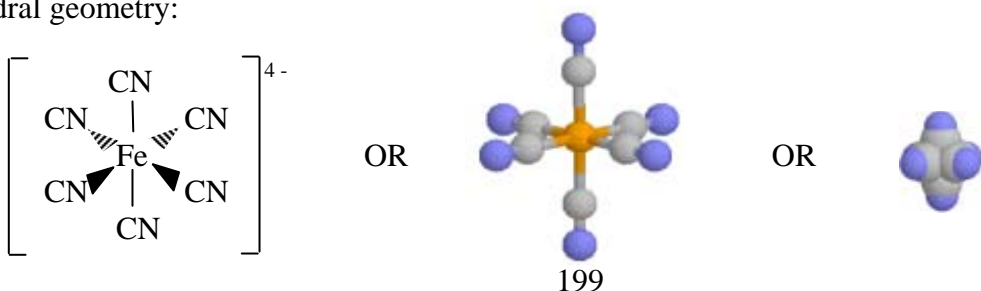
This complex is paramagnetic due to the four unpaired electrons in the 3d orbitals. The water molecules are also easily displaced by other species since they are bonded using the "outer" 4d orbitals. Complexes which exchange ligands rapidly are known as *labile* [note that this is a kinetic designation]. This particular complex is also less *stable* [a thermodynamic term] than iron complexes with other ligands. Because the hybrid orbital configuration used in bonding is "sp³d²", the geometry of the ion is octahedral:



In contrast, $[\text{Fe}(\text{CN})_6]^{4-}$ (hexacyanoferrate(II) ion) would have this configuration:



This complex is diamagnetic since all of the electrons are paired. Also, since the "inner" 3d orbitals are being used for bonding, cyanide is difficult to dislodge [more *stable*] and this complex exchanges ligands more slowly than the previous example. Such complexes are known as *inert*. The hybrid orbital configuration, although written somewhat differently, is the same: "d²sp³". This complex also has octahedral geometry:

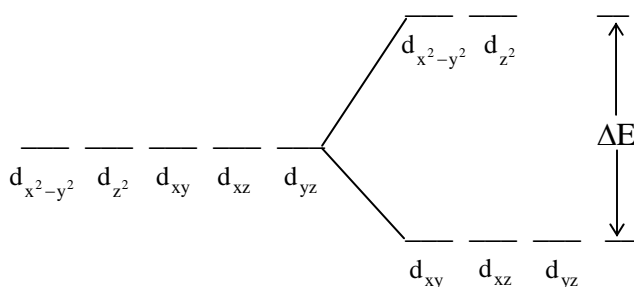


Despite its apparent success at "explaining" magnetic properties and geometries, Valence Bond Theory gives an incomplete description of other aspects of coordination compounds. For example, there is no clear reason why the six 3d electrons in the H_2O complex follow Hund's rule while those in the CN^- complex do not. This is critical to predicting the magnetic properties. Also, since the population of shared lone pairs in "inner" and "outer" d-orbitals affects the stability of the complex, it would be helpful to be able to predict which coordinating species will behave in which way with a given ion---and why.

[Sorting out lability and stability is not a simple task. When a ligand is quickly replaced is it because the complex was very labile or just very unstable? Making comparisons among a series of central ions is even more difficult. *Most* complexes of the first-row transition metals are labile. Differences in the ease of replacement of ligands may therefore be interpreted as differences in stability. Equilibrium formation constants (K_f) for complex ions can be used to help support conclusions based on visual observations. In this experiment a single central ion is used with different ligands. It is therefore reasonable to assume that differences in ligand replacement reflect differences in stability rather than lability, absent any other contributing factors. One major contributing factor is the "chelation" effect in which ligands that bind at several positions on the central ion and form ring structures enhance the stability of the complex markedly.]

One of the more conspicuous inadequacies of Valence Bond Theory when applied to coordination complexes is the inability to explain the vivid colors many of the species exhibit. Because of this and other limitations of VB, additional models were developed which better address some of the properties of these ions and compounds.

Crystal Field Theory is particularly successful in explaining not only color, but also magnetic properties and lability. In this newer approach the focus is shifted away from the orbitals occupied by the donated electron pairs and toward the d-orbitals of the central ion and the electrons already there. The theory assumes that while the d-orbitals are initially more or less *degenerate* (all of the same energy), the electrostatic repulsions of incoming ligands are higher for some orbitals than for others (based on their orientation in a Cartesian coordinate system). So while the average energy of the d-orbitals rises when bonding takes place (even if that bonding occurs in hybrid orbitals that do not utilize d-orbitals) there is actually a split in the new energy level. The diagram below illustrates the splitting in an octahedral complex:



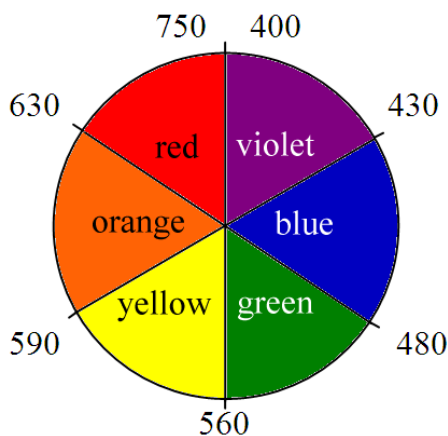
The magnitude of ΔE depends on the strength of the electrostatic field produced by the ligands and the identity of the ion. Stronger field ligands produce larger splitting and generally result in more stable (and possibly more inert) complexes while weaker field ligands produce smaller splitting and generally less stable (and possibly more labile) complexes. The connections between field strength and magnetic properties will be explored in later experiments.

While different geometric arrangements of ligands (and hence different hybrid orbital bonding) results in different splitting patterns, there is always some energy difference among the d-orbitals of the central metal ion. According to Crystal Field Theory this energy difference is in the range of visible light photons. Thus visible light absorbed by the complexes may initiate an electron transition from a lower level orbital to a higher level orbital. The absorption of visible light is responsible for the colors of the complexes.

This simple model can easily be tested against the two common exceptions to the generally vivid colors of transition metal complexes and compounds: silver and zinc. Both ions have d^{10} configurations. Thus all of the d-orbitals are filled and no transitions are possible.

The actual colors of various complexes are *complementary* to the colors of light absorbed. For example, a weak field ligand will produce a small energy split. Longer wavelengths (red) may excite electrons to the higher level. Subtracting red from the visible spectrum results in a mix of colors that appears green or blue. Strong field ligands may produce a large energy split comparable to violet. Subtracting violet from the visible spectrum generally leaves light that appears yellowish.

Complementary colors can be ascertained from the simple diagram and rule below:



Any two primary colors on the wheel above (red, blue, yellow) form one of the other secondary colors when combined (e.g., blue + yellow = green). This new color is the complement of the remaining primary color (in this case, red). So by observing the color of a complex ion it is possible to get some idea of whether the ligands attached exert relatively strong or weak repulsions.

"Possible", but not always simple. The previous general description of Crystal Field Theory principles assumes that there is a single wavelength which can be absorbed. Multi-electron interactions introduce small differences within the split levels, often resulting in several possible transitions in a single complex. Nonetheless, absorption spectra of complex ion solutions typically show one primary wavelength (λ_{\max}) at which there is a strong absorbance which at least determines the color family of the complex. There may be additional minor absorbances. The sum of the absorbances and their intensities gives complexes their many hues.

Ligands may therefore be arranged in order of their field strengths based on observations of color. This arrangement is known as a *spectrochemical series*. The order, however, is not strictly observed in all complexes since the identity of the central ion does influence the magnitude of ΔE .

The Experiment

There are three parts to this experiment:

- determine a spectrochemical series for the supplied ligands with Cu^{2+}
- determine which complexes are more stable with respect to ligand replacement
- determine the formula of the Cu(II) complex ion assigned to you

The following non-locker materials will be provided:

- 0.050 M solutions of CuSO_4 , NH_3 , $\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}_2$, EDTA, NaNO_2
- 24/96 combo well-plate w/plastic stirrer
- beral pipet
- micropipettor w/tips
- Fisher Model 415 Spectrophotometer and cuvettes

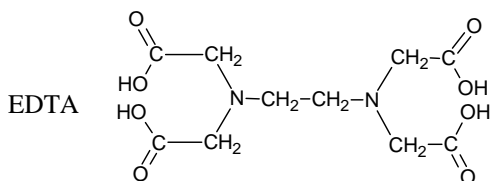
The Chemicals

Copper(II) sulfate is the source of the tetraaquacopper(II) complex ion in this experiment. Commonly available as the pentahydrate, the blue solid slowly effloresces (loses water) in air, two at 30°C and two more at 110°C . It is very soluble in water, less so in methanol.

The pentahydrate is used as a fungicide, algacide and herbicide. It is sometimes a precursor in the manufacture of other copper compounds and is useful as a mordant in textile dyeing and as a wood preservative. The compound is employed in a wide variety of ways, from tanning leather to toning photographs. It is available commercially in relatively high purity as a root killer for use in sewer pipes.

Ethylene diammine (1,2-diaminoethane), commonly abbreviated "en" in complex ion and coordination compound formulas, is a clear, colorless, thick liquid. It is strongly alkaline and has an odor reminiscent of ammonia with the stronger unpleasant overtones of many amines. It is freely soluble in both water and alcohol, the aqueous solution being the source of the ligand in this experiment. The compound is useful as a solvent for some smaller proteins such as casein and albumin. It is irritating to the skin and respiratory tract.

Na_2EDTA , $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8$, or ethylenediaminetetraacetic acid disodium salt, is very slightly soluble in water and exhibits the characteristics of a weak acid, including displacing CO_2 from carbonates and reacting with metals to form hydrogen. It is used as a sequestering agent, in particular as a chelating agent which combines with calcium, etc.



Sodium nitrite is a white or slightly yellow crystalline solid, soluble in 1.5 parts cold water, slightly soluble in ethanol. The source of the NO_2^- ligand in this experiment, it is decomposed by even weak acids with the evolution of brown fumes. It is used in the manufacture of dyes and in bleaching flax, silk and linen. It also has medical and veterinary applications, mainly as a relaxant for smooth muscle tissue.

Ammonia is a gas at room temperature. Laboratory solutions of aqueous ammonia have sometimes been erroneously called "ammonium hydroxide" although there is little evidence for the existence of that compound. Aqueous solutions of ammonia are basic.

Ammonia gas can be manufactured from industrial gases associated with the processing of "coke", a spongy form of carbon obtained from processing coal and essential in steel-making. In the Haber-Bosch process nitrogen and hydrogen from these industrial gas mixtures are combined at high temperature and pressure in the presence of a catalyst to form ammonia. The gas and its aqueous solutions are colorless with a very pungent odor (lower limit of human perception: 0.04 g/m^3). Mixtures of ammonia gas and air can explode when ignited under favorable conditions. At room temperature ammonia is soluble to the extent of 31% in water, only 16% in methanol. It is used in the manufacture of nitric acid, explosives, fertilizers and in refrigeration. In anhydrous liquid form it is a good solvent for many elements and compounds, notably the alkali metals which yield blue solutions when dissolved in liquid ammonia.

Inhalation of the concentrated vapor causes swelling in the respiratory tract, spasms and asphyxia.

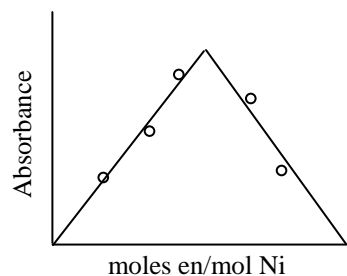
Technique Discussion

Complex ion formation is an equilibrium process, generally occurring in steps. Some of the species intermediate to complete coordination are relatively stable--including some precipitates. In order to insure that complexation is complete, significant excesses of ligand are advisable. Five drop quantities of the 0.050 M copper(II) solution and 15 drops of the 0.050 M ligand solutions should yield a sufficient quantity of material for the first two parts of the experiment. These mixtures are conveniently made in the large wells of a 24/96 combo well plate.

Two drop quantities of both the 0.050 M ligand solutions and the prepared complexes are appropriate for investigating ligand replacement/displacement. Consistency is important since large excesses may give confusing results by forcing equilibrium or introducing unwanted dilution effects. These tests can be carried out in the smaller wells of the combo plate.

The determination of the complex formula could be accomplished in a variety of ways. One of the simpler techniques for determining the empirical composition of binary compounds or complexes is known as the *method of continuous variation* or **Job's Method**.

To apply Job's Method to the determination of a formula, the amount of one component is generally varied from a small value to a large value while the amount of the other component is varied from large to small. Some visual cue is typically used to judge the extent of reaction. For example, in the reaction of aqueous nickel ions with ethylene diamine, a deep violet color develops when the complex ion forms. Comparing the absorbance of different mixtures for the wavelength at which the complex absorbs most strongly indicates which combination gives the most product. A graph of the results is frequently helpful:



The formula for the Ni-en complex ion can be determined from the apex of the plot if sufficient data have been gathered to allow an accurate construction and if there is only one predominately stable combination of ligand and metal ion in solution. This is sometimes not the case and because the different species coexist in equilibrium with each other data from an experiment of this kind is often anything but tidy. Linearity is sometimes seen only in the immediate vicinity of the apex (or maximum absorbance) and the rest of the points generate some kind of gradual curve. Assuming that the correct λ_{\max} has been selected, such situations can sometimes be dealt with by using only the two or three points on either side of the apex to construct two intersecting lines.

A suitable starting point for the complexes in this experiment might be 300 μL of the 0.050 M CuSO_4 solution and the difference in 0.050 M ligand to make 3000 μL total. Continuing with 300 μL increments, a series of 6 solutions can be prepared spanning all reasonable combinations [although not absolutely necessary, absorbance readings for pure CuSO_4 solution, a mixture with less ligand than copper, and pure ligand solution may provide additional points from which to draw a more reliable construction].

Beer's Law gives the most reliable results when the wavelength used is strongly absorbed by the sample. The spectrophotometers in the lab are set appropriately for the ligand displayed on the attached label.

The Report

Based on the colors of the complexes prepared you should be able to arrange the five ligands (including water, which is the ligand in the original copper(II) sulfate solution) in a spectrochemical series from strongest field to weakest field. Explain your method briefly and compare your list to the one found in your text book or other resource. Attempt to account for any differences. The visible absorbance spectra for the complexes in this experiment will also be made available to you after the lab work is complete. Include these (and a brief discussion) as support for your series order.

The stability constants (K_f) of the complex ions included in your experiment are listed below:

$[\text{Cu}(\text{NH}_3)_4]^{2+}$	2.1×10^{13}	$[\text{Cu}(\text{en})]^{2+}$	4.7×10^{10}
$[\text{Cu}(\text{H}_2\text{O})_3\text{NO}_2]^+$	-----	$[\text{Cu}(\text{en})_2]^{2+}$	1.0×10^{20}
$[\text{CuEDTA}]^{2+}$	5.0×10^{18}	$[\text{Cu}(\text{en})_3]^{2+}$	1.0×10^{21}

Note that some ligands are polydentate. Attempt to account for any discrepancies between your results and the formation constants for the complexes.

Determine the formula of the complex from the data collected on the series of mixtures you prepared with copper(II) sulfate and the ligand assigned to you. Compare your result with the complexes listed above and discuss any deviation.

You may have been surprised in the lab to find that not all the spectrophotometers designated for "en" complexes were set to the same wavelength. It may not be so surprising that students assigned this ligand did not all arrive at the same complex ion formula. The three en complexes in the list above have λ_{\max} values of 625 nm, 550 nm, and 500 nm, respectively, from least to most en ligands. Explain this progression in light of Crystal Field Theory.

Finally, examine your results for the stability of the complexes and your spectrochemical series. Does there appear to be a correlation? Can you make (and support) an argument for/against one?