

Chapter 11 – Coordination Chemistry: Bonding, Spectra, and Magnetism

Read through the top of p. 391 on your own. This is a description of the beginnings of modern inorganic chemistry. It is mostly history, but there is some interesting chemistry in there as well. You will be able to see the logic of how Alfred Werner was able to figure out the structures of coordination complexes with no modern spectroscopic or crystallographic instrumentation.

Bonding in Coordination Compounds & Valence Bond Theory

Read to the top of p. 393 on your own. With the exception of the hybridization scheme that leads to square planar geometry (sp^2d), this is review.

The Electroneutrality Principle and Back Bonding

Before we begin this section, here are three important definitions.

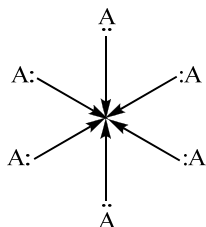
coordination complex - a molecule or ion in which a metal atom is covalently bound to one or more ligands.

ligand - a molecule, atom, or ion that is covalently bound in a coordination complex. Nearly all ligands donate 2 electrons.

coordinate covalent bond - a covalent bond that results from one of the atoms providing all of the electrons in a bond. It is sometimes called a dative bond.

Consider a generic coordination complex, ML_n^{2+} where the ligands are neutral 2 electron donors. Since all of the electrons in a coordinate covalent bond come from one of the atoms, formal charges suggest that each bond should place a -1 charge on the M^{2+} .

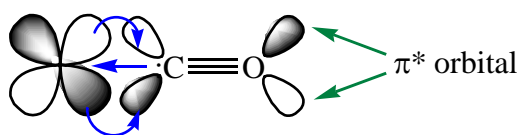
For an octahedral complex,



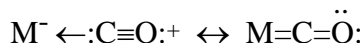
this would yield a formal charge of -4 on the metal of an octahedral complex. How can this be? As you would probably guess, since donor atoms on the ligand are more electronegative than the metal, they do not share their electron density equally. Calculations suggest that the ligands help

to lower the charge on the metal from its oxidation state, by spreading it out over several atoms, but not by so much as to place significant negative charge on the electropositive metal center. The closer the oxidation number of a metal is to zero, the closer will its actual charge be to zero. As you can see in the example for Be^{2+} and Al^{3+} (p. 394), the actual charges wind up very near zero. For OsO_4 , where the oxidation state is +8 the actual charge on osmium may be as high as only +1 to +2. As a result, metal-ligand bonds are typically about 50% covalent in character and 50% ionic.

A second way to remove electron density from a metal center is called back-bonding. If a metal atom has electron density in its d -orbitals, the electron density may be transferred to a ligand through the latter's π^* orbitals, e.g. CO.



This feeding of electron density into π^* orbitals on the ligand affects bond lengths in the complex. The M-C bond will shorten, while the C-O bond will lengthen. This can be easily seen using VB resonance structures.



The more electron rich a metal is, the more the right-hand form contributes to the actual structure. We can see this empirically through crystal structures and infrared spectroscopy (*vide infra*).

Crystal Field Theory

This is a relatively simplistic theory that does an amazingly good job of making predictions about complexes. Unfortunately, most of its underlying assumptions are wrong, even if their application works. It turns out the errors just about cancel each other out.

Crystal field theory treats the metal atom as a point charge with five d orbitals. The ligands are also treated as negative point charges. Thus, the bonds are thought of as purely ionic in character. The book shows representations of the d orbitals on pp. 396-97. You should commit these to memory. There is also discussion about the fact that mathematically one can come up

with 6 equations to describe d orbitals. This should be a bit of a review from earlier in the semester. Recall that the d_{xy} , d_{xz} , d_{yz} , and $d_{x^2-y^2}$ orbitals all look the same because mathematically the only difference between them is their orientation in space. The d_{z^2} orbital looks different because it is the average of the two remaining mathematical functions. The “doughnut” traditionally shown in general chemistry texts is inaccurate. The shape is more akin to a teardrop rotated around the nucleus with the tip pointing towards the metal. The averaging causes the lobes along the z -axis to be larger (i.e. thicker) than the torus. Henceforth, the d orbitals will be designated by their subscripts (i.e. $xy = d_{xy}$).

Crystal Field Effects: Octahedral Symmetry

In your mind's eye imagine 6 ligands interacting with a d^1 metal ion. As I hope you will see, if this works for a d^1 metal ion, it will work for any transition metal atom or ion. How do we arrange the ligands? If you think “VSEPR,” they lie on opposite ends of the coordinate axes, at an infinite distance from the origin. The transition metal ion resides at the origin.

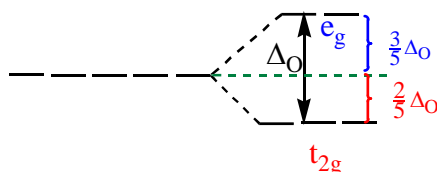
Where is the transition metal d electron? It spends 1/5 of the time in each orbital in the absence of an outside interaction. What happens as we bring the ligands towards the metal ion? Two opposing things: (i) M^+ -ligand attraction lowers the energy of d -orbitals and (ii) electron-electron repulsion raises the energy of the d -orbitals. Let's start with point (ii).

As the ligands approach the ion, their electrons repel the metal d electron. Repulsion is greatest in orbitals lying along the x , y , and z axes (z^2 , x^2-y^2) and less in the orbitals directed between the axes (xy , xz , yz). Thus, the orbitals are split in relative energies.

As you might guess, the electrons in all orbitals are repelled; so all orbitals increase in energy. When factor (i) is added in, all orbitals lower in energy. Now let's step back for a minute. Instead of 6 discreet ligands, imagine the pairs of electrons as smeared out in a spherical shell around the metal atom. If the shell were contracted all 5 orbitals would increase in energy at exact equal rates. Now, the 6 ligands described above are distributed spherically. (i.e. They come as close as 6 ligands can to simulating a spherical distribution.) As a result, the average energy of the d orbitals in the real complex is the same as the average energy of the d orbitals in the hypothetical complex

(called the barycenter).

So what does this mean? When the metal-ligand electrostatic attractions are figured in, the xy , xz , and yz orbitals go down in energy relative to the average and the z^2 and x^2-y^2 go up. Importantly, the total energy decrease of the xy , xz , and yz orbitals exactly equals the total energy increase of the z^2 and x^2-y^2 . Individually, xy , xz , and yz orbitals drop below the average by $2/5 \Delta_o$ and z^2 and x^2-y^2 increase by $3/5 \Delta_o$. This can be seen pictorially as:



Finally, these groups of degenerate orbitals are “named” t_{2g} for the lower energy orbitals and e_g for the higher energy orbitals. The labels come from group theory. To generate the labels, begin with the molecular point group O_h . Since there are three equal energy orbitals, they must belong to a “T” irreducible representation (T_{1g} , T_{2g} , T_{1u} , and T_{2u} exist for O_h). Then, treating the three orbitals as a group, perform the various symmetry operations and keep track of the results. They will generate a set of characters identical to one of the irreducible representations, in this case t_{2g} .

Crystal Field Stabilization Energy

Now that we see that the d orbitals split in energy and why they do so, we need to explore how the orbitals fill. All of the examples in this section possess an octahedral coordination geometry.

In the case of a one electron (d^1) atom or ion, the answer is simple: the electron drops into the t_{2g} set. This electron is more stable than in the free ion by $0.4\Delta_o$. This stabilization is called the crystal field stabilization energy (CFSE). Δ_o is measured from the electronic spectrum (UV-visible) where the $t_{2g} \rightarrow e_g$ transition is observed.

Likewise in d^2 and d^3 complexes, the second and third electrons go into the t_{2g} set with CFSEs of $0.8 \Delta_o$ and $1.2 \Delta_o$, respectively. So far this is just like filling the $2p$ orbitals from boron through nitrogen. Now things get interesting.

What happens with d^4 ? The electron may go into either the t_{2g} or e_g set depending on the magnitude of Δ_o . We will talk about this more later, but, in a nutshell, ligands with strong associations/attractions to metal ions have larger Δ_o s than those with weaker associations. We'll discuss the nature of these associations shortly (Factors Affecting the Magnitude of Δ_o). If Δ_o is greater than the spin pairing energy, P , the electron goes into the t_{2g} set. Conversely if $P > \Delta_o$ the electron goes into the e_g . $\Delta_o > P$ is called the strong field or low spin case and $P > \Delta_o$ is the weak field or high spin case. We begin with the latter scenario.

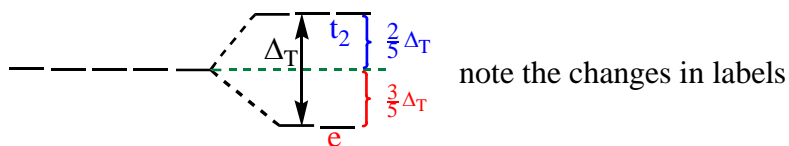
The filling for d^4 is $\uparrow \uparrow \uparrow _ _ _$ ($t_{2g}^3 e_g^1$). Thus, $CFSE = (3 \cdot 0.4\Delta_o - 1 \cdot 0.6\Delta_o) = 0.6\Delta_o$. For d^5 , $CFSE = 0$ because the fifth electron also goes into the e_g . For d^6 , the next electron goes into t_{2g} so $CFSE = 0.4\Delta_o$. For d^7 , $CFSE = 0.8\Delta_o$. Let's stop here and go back to the low spin case. (It merges with the high spin configuration at d^8 .)

The d^4 case looks like $\uparrow \downarrow \uparrow \uparrow _ _$, so $CFSE = 1.6\Delta_o - P$. For d^5 , $CFSE = 2.0\Delta_o - 2P$. d^6 yields a result that is a little surprising at first glance. It's $CFSE = 2.4\Delta_o - 2P$. Why not $-3P$? For the same reason you do not subtract $1P$ from the high-spin d^6 case. Remember we are measuring CFSE relative to the unsplit case. In the unsplit case d^6 would have one spin paired anyway, so only the additional paired spins are counted. (The book is in error here.) For d^7 $CFSE = 1.8\Delta_o - P$ ($6 \cdot 0.4\Delta_o - 1 \cdot 0.6\Delta_o$).

Once eight electrons are placed in the orbitals, the low-spin and high-spin configurations are identical and the labels no longer are relevant. Thus, high and low spin applies only to d^4 - d^7 . In d^8 complexes $CFSE = 1.2\Delta_o$, d^9 : $CFSE = 0.6\Delta_o$, d^{10} : $CFSE = 0$.

Tetrahedral Symmetry

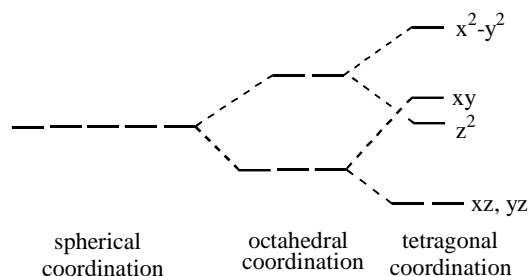
We can use the same approach here as for octahedral symmetry. The ligands are placed on alternating corners of a cube and are then brought in towards the metal ion. If the coordination axes are passed through the faces of the cube, then the incoming ligands will interact more strongly with the xy , xz , and yz orbitals than z^2 and x^2-y^2 orbitals. Thus, the splitting will be reversed.



Note that because the point group is now T_d , the labels have changed slightly. The presence of only four ligands causes Δ_T to be smaller than Δ_O under almost all conditions. That the ligands do not exactly align with the orbitals, also reduces the value of Δ_T versus Δ_O . This causes tetrahedral complexes to be almost exclusively high spin.

Tetragonal Symmetry: Square Planar Complexes

The book mentions the Jahn-Teller effect here, we both will put it off for a while. The easiest way to think about square complexes is as octahedra with one pair of *trans* ligands removed. Mathematically, it is easiest to remove the two ligands on the z -axis. When this happens, orbitals with a z component drop in energy. To maintain the barycenter, those without a z component increase in energy by an equal amount.



The spacing of energy gaps is somewhat different for square planar complexes than for the two previous cases. One might conclude from the discussion on tetrahedral complexes that the top-to-bottom gap would be small because there are only 4 ligands. That is only partially true. For the four orbitals that don't point at the ligands (xy , xz , yz , z^2) the splitting is indeed small (see Table 11.5, p. 405 for details). The x^2-y^2 orbital, however, bears the full brunt of the repulsion in the complex and is therefore elevated in energy by a significant amount. Furthermore, since there are now four energy levels the gaps between any two tend to be fairly small.

Factors Affecting the Magnitude of Δ

All of these factors will have something in common: the stronger the M^{n+} -L interactions, the

larger will be Δ .

Metal ion oxidation state - Δ increases with oxidation state, higher charged ions draw ligands in closer.

Nature of M^{n+} - Δ increases down a group for M^{n+} with constant charge. Probably because there is more overlap with larger d -orbitals. (Note that this trend is opposite to what occurs for main group elements.)

Number and Geometry of Ligands - Δ increases with increasing number of ligands - as discussed previously

Nature of Ligands - memorize the basic outline of the spectrochemical series $I^- < Br^- < Cl^- < F^- < O^{2-} < H_2O < N \text{ compounds} < \text{alkyls/aryls} < CN^- < CO$. This ordering is generally true although there are exceptions depending on the metal. Note this is the reverse from what is expected in crystal field theory. We will talk about why later.

Applications of Crystal Field Theory - Skip, pp. 408 – 413 (top)

Molecular Orbital Theory

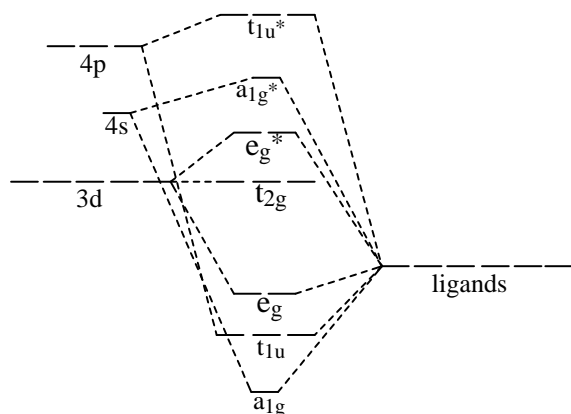
The notion that metal-ligand interactions are purely ionic is clearly inaccurate (c.f. electroneutrality, *vide supra*). In fact, for most ligands the interactions are primarily covalent (e.g. neutral ligands) and there is significant experimental evidence consistent with this assertion. In fact, the spectrochemical series is essentially backwards from what it should be for a reasonable prediction based on the assumptions of crystal field theory. The book discusses this briefly. Read it on your own.

Octahedral Complexes

The MO diagram of an octahedral complex probably seems like it would be very difficult to construct. In fact, it is not so hard to generate. The first question to ask is: what orbitals are involved? The 6 ligand σ donors and the $3d$, $4s$, and $4p$ orbitals on the metal (this is for a first-row transition metal with six 2-electron donor ligands).

The ligands can be treated in terms of ligand group orbitals (see pp. 175 - 182 to review).

We've already seen that the metal d orbitals can be broken into e_g and t_{2g} sets. The $4s$ orbital is spherically symmetrical and will be described by the A_{1g} irreducible representation (with a sphere any operation will give back a sphere, therefore all characters in the reversible representation will be 1). Given the high symmetry of an octahedron, it's a good bet that the p orbitals would be treated together. They yield a T_{1u} irreducible representation (think a sphere with one half-positive, the other half negative). The lobes on the ligands used to donate to the metal may have positive or negative signs on the wave function. These signs are used to make up the group orbitals. The ligands generate a reducible representation that can be broken into A_{1g} , E_g , and T_{1u} irreducible representations. The LGOs are displayed on p. 416.



Note here the t_{2g} set does not change in energy. This is because there is no net σ bonding with the ligand orbitals (see p. 415, Fig. 17). These are non-bonding orbitals.

When filling the MO diagram remember the ligands will contribute 12 electrons ($6 \times 2e^-$) so the a_{1g} , t_{1u} , and e_g sets will always be filled. Filling of the t_{2g} and e_g^* will depend on the number of the metal d electrons. A result is that the same final d orbital pattern is generated as existed for crystal field theory. The crystal field e_g orbitals become e_g^* orbitals in molecular orbital theory. Be sure to remember this distinction.

Tetrahedral and Square Planar complexes

Read this section on your own. You are not required to memorize these MO diagrams, but understand how they are constructed.

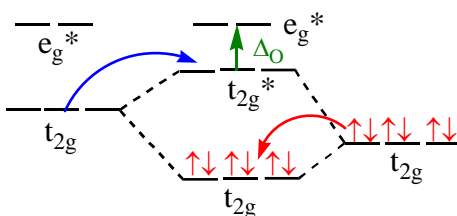
Pi Bonding and MO Theory

Your book only looks at an octahedral system but π -bonding also exists for tetrahedral and square planar complexes. The MO treatment for these systems is very similar to what is observed for an octahedral system.

First, there are four plausible L-M π -interactions: $p_{\pi}-d_{\pi}$, $d_{\pi}-d_{\pi}$, π^*-d_{π} , σ^*-d_{π} . The book gives examples of each in Table 11 on p. 421. The $p_{\pi}-d_{\pi}$ interaction involves ligand-to-metal π donation while the other three are metal-to-ligand π donations. π -bonds will involve the t_{2g} set, not the e_g^* . This is because the e_g^* orbitals point directly at the ligands and are set up for σ overlap. See pictures on p. 420.

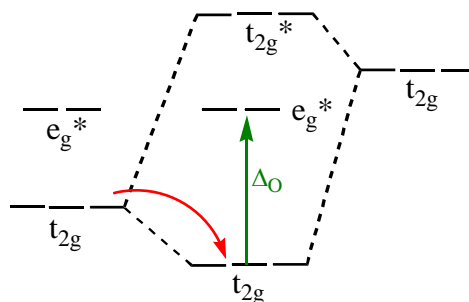
The direction of electron donation and the energy levels of ligand π -bonding orbitals will have a pronounced effect on molecules. We will consider a molecule with six π -donor ligands (e.g. halide ions) and then 6 π -acceptor ligands (e.g. CO).

MX_6^n : The halide p orbitals are lower in energy than the metal d orbitals and they are filled, while metal d orbitals may or may not contain electrons. Thus:



When the MOs form the ligand p electrons fill the t_{2g} orbitals, thus metal t_{2g} electrons go into the t_{2g}^* MOs. The result of this type of interaction is a small Δ_o .

$M(CO)_6$: The CO π^* orbitals are empty and are high in energy (remember CO bond energy).



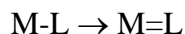
Since the CO π^* orbitals are empty, the t_{2g} MO is filled with metal t_{2g} electrons and promotion is

then a relatively high energy process.

These diagrams explain the relative placements of the halides and CN⁻/CO in the spectrochemical series. In an electrostatic model, the reverse would be expected.

Experimental Evidence For Pi Bonding

So what evidence is there for π -bonding (i.e. what do we look for)? We begin by asking what would the interaction look like without π -bonding? Then, what happens with full π -bonding:



Since the bonding between metal and ligand changes between these forms, bonding within the ligand must change (see the figures on p. 2 of these notes). If electron density is fed into a π or σ orbital on the metal, a bond within the ligand will be weakened. The strongest evidence for π -bonding comes from metal-carbonyl complexes.

Crystallography - The greater the extent of π -backbonding, the more M=C character there will be and the more C \equiv O will resemble C=O. The difference in C \equiv O and C=O bond lengths is about 0.1 Å and should be useable for quantification. Unfortunately, this has not been observed. In contrast, M-C bond lengths do change.

Consider the complexes Cr(CO)₆ and Cr(CO)₅(PR₃). In the absence of π -backbonding the Cr-C bond lengths should be the same. If it does occur, then the bond lengths should be shorter in Cr(CO)₅(PMe₃). Why? Two reasons: PMe₃ is at best a very poor π -acceptor so only 5 COs are competing for electron density from the metal, not 6; and PR₃ is a very good σ donor, CO is not. Thus, the Cr has more electron density to share with fewer acceptors. One other trend is expected. The Cr-C(O) bond *trans* to PR₃ should be shorter than those *cis*. This is because the *trans* CO will bind to the same *d*-orbital as the PR₃ and the effect will be greatest there. As can be seen in Table 12, p. 427 all of this is observed.

Infrared Spectroscopy

Evidence for C=O character is most clearly seen in IR spectroscopy. $\nu(\text{CO})$ for C \equiv O is about 2150 cm⁻¹, while in R₂C=O $\nu(\text{C=O})$ is about 1700 cm⁻¹. Thus, the greater the extent of backbonding the lower the expected $\nu(\text{C}\equiv\text{O})$. This is seen dramatically for two series of complexes

$M(\text{CO})_6^{n+/-}$ and $M(\text{CO})_4^{n+/-}$ in Table 13 on p. 428. This can also be seen when a CO is substituted for by another ligand as seen in crystallography. The only problem with using this technique is that the CO stretching band is almost always split into several components making interpretation difficult. Read the section in the book on IRs of substituted complexes. Skip the subsection on photoelectron spectroscopy (pp. 431 - 433).

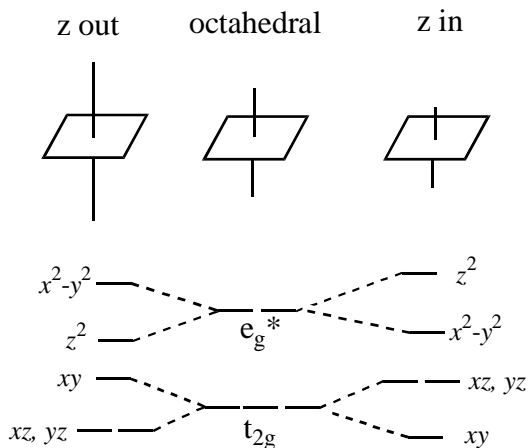
Electronic Spectra of Complexes/Tanabe-Sugano Diagrams - Skip pp. 433-447

Tetragonal Distortions from Octahedral Symmetry

The sections we just passed over, discussed how energy levels are affected by having different ligands bound to the central metal atom or ion. As I said earlier, this is more complex than we need to get into, however energy level distortions can occur even if the ligands are all the same.

The Jahn-Teller theorem predicts these distortions. It states that for a non-linear molecule in a non-degenerate state, the molecule must distort such that the symmetry of the molecule is lowered, the degeneracy is removed, and the energy of the molecule is lowered.

So what does this mean? First, a non-degenerate state is one in which all sets of orbitals are not full, empty, or half-full (e.g. 1 or 2 electrons in t_{2g} or 1 electron in e_g^*). Let's assume for a moment you have 1 electron in an e_g set. That electron spends 50% of the time in the z^2 and 50% of the time in the x^2-y^2 . Now what would happen if the two z-axis ligands were pulled slightly away from the metal? The x and y axis ligands would be pulled in a little closer to replace lost electron density. With the z^2 ligands further away the z^2 drops in energy. The x^2-y^2 will rise in energy by an equal amount because its ligands are drawn closer. The reverse may also happen. That is: z ligands move in and x, y ligands move out. There will also be an effect on the t_{2g} set (Fig. 47, p. 450). This is shown graphically below.



Note the average energy of each split set equals the energy of the unsplit set. These splittings are quite small and so do not affect pairings. Altering spin pairings could conceivably happen in a d^4 case where to avoid spin pairing energy the fourth electron moved into a lowered e_g^* orbital. However, the square planar geometry can be viewed as an extreme Jahn-Teller distortion with the z -ligands moved to infinite distance.

Finally, the number of electrons in a t_{2g} set will govern the type of distortion: $1e^-$, $4e^-$ (LS), or $6e^-$ (HS) z out and $2e^-$, $5e^-$ (LS), or $7e^-$ (HS) z in. What about the e_g^* set? This brings us to an important point about the Jahn-Teller theorem. It tells us neither the type, nor the size of the distortion, only that it will occur with the proviso that the center of symmetry will remain. For the e_g set, either distortion can occur, depending on the complex.

The book briefly discusses some experimental evidence for Jahn-Teller distortions. Read it.

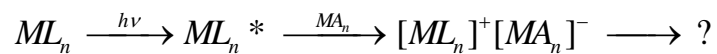
Charge Transfer Spectra

The previous discussion centered on $d-d$ transitions. That is, transferring an electron from one metal d based orbital to another (e.g. $t_{2g} \rightarrow e_g^*$). But other types of electron promotions can occur. For an electron in a metal-based MO excited to a ligand-based MO the electron is effectively moved from the metal to the ligands. This is called a metal-to-ligand charge transfer (MLCT). The converse is a ligand-to-metal charge transfer (LMCT).

LMCT are favored for metals in high oxidation states that are bound to electron-rich, low electronegativity ligands. MLCT is favored for electron metals bound to ligands with low-lying π orbitals (e.g. CO, heteroarenes (e.g. pyridine)). These complexes are frequently highly colored.

A functional use of these compounds is as photoreducing agents. Basically, an electron is promoted to a high-energy excited state by shining light on the compound, which then transfers the electron to another species. Following this, two things can happen: (i) the electron can return to the first molecule or (ii) if either molecule undergoes some irreversible rearrangement the

electron transfer becomes permanent.



When applicable, this method has advantages over traditional methods: (i) The reducing power can be varied by promoting into different energy levels. That is, the higher the electron is promoted, the more powerful the complex is as a reductant and (ii) the reaction can easily be stopped in progress by simply turning the light off.

August 25, 2014