**Molecular Orbitals of Transition Metal Complexes**

**Objective: Become familiar with modeling transition metal cation complexes**

1. Define the terms *transition metal cation complex*, *crystal field splitting, metal-centered d-orbitals, sigma antibonding geometry, pi antibonding geometry*, *doubly degenerate*, and *triply degenerate*.
2. Describe shape and energy differences between *n-d-MO, σ\*-d-MO,* and *π\*-d-MOs*, with an example.
3. Describe qualitatively how sigma and pi antibonding affect the crystal field splitting (Δo) and the wavelength of absorbed light (λ).
4. Set up and run electronic structure calculations of transition metal complexes.

Introduction

Building intuition about how and why substances are colored is something chemists are very interested in. This has a practical side, in that if you understand why something is colored, you are in a position to predict and make new colored substances. Such intuition also has a fundamental side, though: it’s nice to know how things work at a molecular level.

One class of colored substances are *transition metal complexes*. Transition metal complexes are made up of a *transition metal* (often a cation) that is bound to some number of other molecules called *ligands*. A typical number of ligands is six; in that case, we say the stoichiometry of the complex is *ML6*, and we call the complex “octahedral”.

But *why* are transition metal complexes colored? One clue is that transition metal cations, by themselves, are generally *not* colored. The ligands are essential to the color! A second clue is that the interaction between the metal and the ligands is well described by Lewis acid/base theory, in which the transition metal cation is the Lewis acid and the ligands are bases. Moreover, it’s the *d-orbitals* of the transition metal cation that play a key role in this. We’ll take these ideas up one by one.

*d-orbitals of transition metal cations*. You probably already know about the shape of d-orbitals: there are five of them, mostly double-dumbell shaped (see the figure at right1). Transition metals, even if they have lost a few electrons (and therefore are transition metal cations) typically have a few electrons in these orbitals.

*Metal-centered d-orbitals of transition metal cations.* If you recall your Lewis acid/base theory, the usual situation is that the Lewis acid provides an empty orbital, and the Lewis base provides a fully occupied one. The resulting, stabilized molecular orbital (MO) is where the electrons originally from the base end up, forming a dative bond (see Fig. 1).



**Figure 1**. Molecular orbitals involved in a Lewis acid/base reaction2.

But what about that other, destabilized MO? In the case shown in Fig. 1, there are no electrons in that MO, so we don’t have to worry about it much. But transition metal cations have *partially filled d-orbitals*. That means, when a transition metal cation forms a dative bond with a ligand (or several ligands) to form a transition metal complex, it still has those same electrons. Where do those electrons go? They stay in the now-destabilized d-orbitals!

We call these new, destabilized orbitals *metal-centered d-orbitals*, or *d-MOs*. *d-MOs* in two transition metal complexes are circled in Fig. 2.

|  |  |
| --- | --- |
| (a) | (b) |
|  |  |

**Figure 2**. MO diagram of transition metal complexes. Circles indicate metal-centered d-orbitals, or *d-MOs*. Adapted from Blauch3.

You’ll notice in Fig. 2 that there are different types of *d-MOs*. One set is labeled “n orbitals”; we’ll refer to these as *n-d-MOs*. *n-d-MOs* have the same energy as bare metal d-orbitals because they’re the least destabilized by ligands. You can easily recognize *n-d-MOs* from their shape, because they look almost exactly like regular atomic d-orbitals.

A second set of *d-MOs* circled in Fig. 1 are labeled “π*\* orbitals”;* we’ll call them *π\*-d-MOs*. These are definitely destabilized (have higher energy) compared to the *n-d-MOs*. The mechanism of destabilization is destructive interference with ligand orbitals, via a geometrical arrangement called *pi antibonding*.

A third set of *d-MOs* in Fig. 2 are labeled “*σ\* orbitals”;* we’ll call these *σ\*-d-MOs.* They are destabilized even more because of destructive interference with ligand orbitals. This destabilization occurs in a geometrical arrangement called *sigma antibonding*.

Now, back to the reason why transition metal complexes are colored. You’ll notice in Fig. 2 that there is an energy gap labeled . This energy gap is called the *crystal field splitting*, and it is key to understanding the color of a transition metal complex. Here’s how it works: suppose an electron is initially sitting in one of the *n-d-MOs* (see Fig. 2(a)). Now a photon passes by. If the energy of the photon exactly equals , the electron can absorb the photon; the electron ends up in the higher-energy, *σ\*-d-MO*, as a result. If the photon that got absorbed was a visible photon (i.e., wavelength between 400 and 750 nm), the result would be that the complex is colored! A similar story would apply to an electron initially sitting in one of the *π\*-d-MOs* (see Fig. 2(b)).

Practically speaking, the crystal field splitting is often given in *eV units*. To calculate the wavelength of an absorbing photon, you would first convert  from eV to Joules (1 eV equals 1.60e-19 joules), then use

 (1)

where *h* is Planck’s constant, and *c* is the speed of light to get the wavelength of light absorbed. The resulting value will be in meters; chemists usually convert to nanometers by multiplying by 109.

In this activity, you’ll construct two transition metal complexes, solve their electronic structures, and inspect the resulting *MOs* to identify which are *n-d-MOs, σ\*-d-MOs,* or *π\*-d-MOs*. Then you’ll construct an MO diagram like the part that is circled in Fig. 2. From there, you’ll be able to determine which of the two complexes is likely to absorb light at a longer wavelength.

What to do in prepration for this activity

For this lab, we will be concerned with the transition metal *Cr*, and its complexes *[Cr(H2O)6]3+* and *[Cr(NH3)6]3+*. Set aside a page for each of these three in your lab notebook. On each page, write the appropriate number of d-electrons.

In-lab activities

1. *Characterizing d-orbitals of atomic Chromium*. Use Spartan to solve the electronic structure of Cr at the B2LYP/6-31\*G level. Don’t forget to specify six unpaired electrons.

*Analysis.* When the calculation is finished, bring up the orbital energy display and find the d-orbitals. Sketch these in your comp notebook, and annotate your sketches with the orbital energies and the coloring you see.

1. *Characterizing metal-centered d-orbitals of the Chromium cation in [Cr(NH3)6]3+*. Use Spartan to solve the electronic structure of *[Cr(NH3)6]3+* at the B2LYP/6-31\*G level. Don’t forget to specify three unpaired electrons and a net 3+ charge.

*Analysis.* Bring up the orbital energy display and identify the five metal-centered d-orbitals (*d-MOs*). This will take some sleuthing, since some of them might appear to have leaked considerable electron density onto the ligands as well; the key feature is to look for *MOs* that, in the immediate vicinity of the metal, look a lot like the d-orbitals you found in step 1. Another hint that you’ve found them is that their energy grouping will be characteristic of the pattern shown in Fig. 1a: three *d-MOs* will be *triply* *degenerate* (have the same energy), and two more will be *doubly degenerate*. Finally, remember that these are not bonding *MOs*: you’re looking for orbitals with a color change (node) between the metal and the ligand.

Once you’ve identified the five *d-MOs*, your next task is to characterize them as *n-d-MO,* *σ\*-d-MO,* or *π\*-d-MO.* The upper-energy, doubly-degenerate set is easy: these are always *σ\*-d-MO*. But the lower-energy, triply-degenerate set will require some judgment. The question is, do these *d-MOs* look like they are interacting substantially with ligands, or more like isolated atomic d-orbitals?

Your third analysis task is to find the crystal field splitting, , between the lower-energy triply-degenerate set and the *σ\*-d-MOs*. Use this result to calculate the wavelength (nm) of a photon of light having that energy.

1. *Characterizing metal-centered d-orbitals of the Chromium cation in [Cr(H2O)6]3+*. Use Spartan to solve the electronic structure of *[Cr(H2O)6]3+* at the B2LYP/6-31\*G level. Don’t forget to specify three unpaired electrons and a net 3+ charge again.

*Analysis*. When the calculation is finished, do a similar analysis as in step 2.

1. *Constructing an MO diagram.* Based on your results in steps 2-3, construct MO diagrams corresponding to the circled parts of Fig. 1. Make a note of which complex corresponds more closely to Fig. 1(a), and which to Fig. 1(b).

After class

Write a brief summary of the analyses you carried out in the in-class activities, and your responses to self-assessment items 1-3 at the top of this document.

References

1. Wikipedia. High School Chemistry/Shapes of Atomic Orbitals - Wikibooks, open books for an open world. at <en.wikibooks.org/wiki/High\_School\_Chemistry/Shapes\_of\_Atomic\_Orbitals>

2. UC Davis. Lewis Concept of Acids and Bases - Chemwiki. at <http://chemwiki.ucdavis.edu/Physical\_Chemistry/Acids\_and\_Bases/Acid/Lewis\_Concept\_of\_Acids\_and\_Bases>

3. Blauch, David. Ligand Properties. (2009). at <www.chm.davidson.edu/vce/coordchem/Ligands.html>