Student-Directed Explorations To Learn about Ligands in an Inorganic Chemistry Course

Marion E. Cass
Department of Chemistry, Carleton College, Northfield, MN 55057; *mcass@carleton.edu*

As an instructor of an advanced inorganic chemistry course and a person who has strong interests in the field of bioinorganic chemistry, I have a deep appreciation of the overwhelmingly large number of diverse ligands that have an impact on the chemistry of metal species. Both naturally occurring and synthetically-designed ligands affect metal ion selectivity, coordination number, coordination environment and geometry, metal oxidation state, complex stability, stereochemistry, and reactivity. Where do we have the time, however, in a term or even a semester course in inorganic chemistry to teach about this large and significant field within inorganic chemistry?

Over the past several years I have developed a "ligand-of-the-week" exercise for my junior–senior-level advanced inorganic chemistry course at Carleton College. Every week, beginning in week three of the 10-week term, each student is instructed to examine a different "ligand-of-the-week", selected from a specified category. In the first week of this exercise (see Ligand Assignment 1 in Figure 1), students are asked to search reference materials or the recent literature for

Ligand-of-the-Week Assignments

Ligand Assignment 1: Find one ligand that binds to transition metal ions through nitrogen (only through N, no mixed ligands) and answer Questions 1–5 on the "Ligand-of-the-Week" Questions (that will apply to all subsequent ligand assignments). A list of resources of where you might look is shown below. You may use any of these resources but are not limited to this list. Sign up for a ligand on our course folder so that there are no duplicates. Place the name of your ligand and a structure (using ChemDraw) in the file labeled "N Ligands." Hand in your answers to the questions and give a full citation for your source(s). For every ligand assignment, several of you will take 2–5 minutes each to present your ligand. This first set of presentations will be given by the first three students on the course registration list.

Ligand Assignment 2: Ligands that bind through oxygen (Questions 1–6).

Ligand Assignment 3: Chelating ligands (Questions 1–6 and 10).

Ligand Assignment 4: Ligands that bind through sulfur (Questions 1–10).

Ligand Assignment 5: Ligands that bind through phosphorus (Questions 1–10).

Ligand Assignment 6: Ligands that impose tetrahedral geometry (Questions 1–10).

Ligand Assignment 7: Ligands that bind through carbon (Questions 1–11).

Ideas for Additional Ligand Assignments (given time):
Ligands that impose trigonal prismatic symmetry
Ligands that impose square planar geometry
Macrocyclic ligands that show preorganizational entropy
Bridging ligands (that bridge two or three metals)
Naturally occurring ligands that bind to copper
Ligands that favor binding to high oxidation state metals
Et cetera: The possibilities seem endless to me!

Suggested Resources:
1. *Comprehensive Coordination Chemistry;* Pergamon Press: New York, 1987; Vol. 7.
2. Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry,* 6th ed.; (as well as earlier editions); John Wiley and Sons: New York, 1999.
3. *Nomenclature of Inorganic Chemistry. Recommendations 1990* (International Union of Pure and Applied Chemistry); Issued by the Commission on the Nomenclature of Inorganic Chemistry, Leigh, G. L., Ed.; Blackwell Scientific Publications: Cambridge, MA, 1990.
4. Journals available in our library: *Inorganic Chemistry, Journal of the American Chemical Society, Journal of the Chemical Society, Dalton Transactions, New Journal of Chemistry (Nouveau Journal de Chemie), Inorganic Biochemistry,* and *Organometallics.*

Figure 1. Ligand-of-the-week assignments for a term.

a ligand that binds through the nitrogen atom. Students sign up individually for their ligand on a first-come-first-served basis. Early in my teaching career my students wrote their chosen ligand on a list taped to my office door. With the modern technologies available, each student now signs up for a ligand on a list that is made available in a course folder on the college server. A list of student-selected ligands that bind through nitrogen from one year is shown in Figure 2. For each ligand, the students have a list of questions they must answer, which becomes increasingly more complex as the term goes on. The questions for the first week and the questions added in subsequent weeks are shown in Figure 3. A typical list of ligand types that might be covered over the course of the term is shown in Figure 1.

Student Presentations

The most important learning from this exercise comes from the in-class presentations on the student-chosen ligands. In a rotation cycle of three to four students each week, students present their ligands in a session that takes approximately 15 minutes of class time for the entire group of students. During the first five minutes, all of the assigned students go to the board and draw their ligand along with any other information they want to present (a name, a metal complex of that ligand, charges, symmetry of the complex, etc.). In a spontaneous few minutes, a variety of interesting topics (and some more mundane but necessary topics) can be addressed. During the term, every student presents a ligand at least once and in years with smaller enrollments, every student presents two ligands.

Outcome

In the presentations and followup discussion, an example of an interesting topic that comes up every year is electronically "non-innocent" ligands that have one or more states with respect to charge and number of total electrons. A more mundane topic is nomenclature. I never spend planned time in lecture talking about nomenclature and find that this topic takes on new significance when a student is trying to understand a name rather than merely proceeding through a systematic list of rules. Names and symbols for bridging ligands, ligands with names specifying hapticity, multidentate ligands, and chiral ligands always come up. Humorously we occasionally encounter a situation where two students unknowingly selected the same ligand by assigning the ligand different names. We also have experienced cases where one student has chosen a ligand in a neutral form whereas a fellow student selected the same ligand in a charged form (example: pyrazole versus pyrazolate).

One question in the assignment is always, "Is there anything particularly interesting about this ligand or the metal complexes it forms?" Sometimes I am disappointed by the "nothing interesting" answer; more often however, this opens the door for a brief discussion of a wide variety of topics such as ligands that are used for detoxification agents, ligands that force a certain geometry, or ligands that model the active site of an enzyme. In addition, I find that some students will seek the simplest ligand (ammonia for a ligand that binds through nitrogen, water for a ligand that binds through oxygen), how-

Ligands That Bind through Nitrogen

1. pyrazolate
2. cadaverine
3. 1,2-diaminobenzene
4. phenathroline
5. aziridine
6. 4,4-bi-1,2,4-triazdyl
7. adenine
8. dimethylglyoxime
9. propylenediamine
10. protoporphyrin IX
11. ethylenediamine
12. ammonia
13. 1,4-di(2'-pyridyl)aminopthlalazine
14. 2,2-bipyridyl
15. imidazole
16. trifluoroacetonitrile
17. putrescine

Figure 2. Student sign-up sheet for N ligands. Students that chose ligands 3, 14, and 15 made a short presentation to the class.

Questions for Ligand-of-the-Week Assignments

1. Give the name of the ligand and the name of one complex that it forms with a selected metal.
2. Draw the Lewis structure of the ligand and determine the geometry and hybridization of each atom in the ligand.
3. Is it charged or neutral (determine if it can or will deprotonate when it binds)?
4. Is it a chelating or monodentate ligand?
5. Is there any other interesting chemistry associated with this ligand?

New Questions to add (as time goes on and we cover the relevant topics in the course)

6. What is the symmetry of your metal–ligand complex?
7. Is it a strong, medium, or weak field ligand? Why do you classify it as such?
8. Is it a hard or soft Lewis base?
9. What types of metals (or metal ions) does it bond to?
10. Does the ligand impose a certain structure on the complex?
11. Can you describe the ligand orbitals used in bonding to the metal ion?

A Culminating Question that Could be Used on an Exam or Final Ligand Assignment

12. Given the following ligands (taken from your collected assignments) rank them in the spectrochemical series. Predict the π-donating or π-accepting capability of each ligand and then classify each ligand as hard or soft.

Figure 3. Questions used in the ligand-of-the-week assignments.

ever many students will seek out the most odd or complex ligand they can find and, as the term progresses, the students tend to favor the latter.

There are many reasons why I love this exercise. I find that students take greater ownership in the class even at times when we are not focused on ligands per se. Student presentations are concise, full of useful information, and require advance preparation. Often students come to see me prior to their presentation and we spend time counting electrons or generating a reasonable name for a complex. (If you are an instructor who favors more structure in class, a required meeting for presenters could give you time to collect information to supplement the in-class discussions.) Student presentations drive the discussion of a variety of topics not necessarily covered systematically during the scheduled lectures. Finally, my students are forced to use reference materials that support the field and, as they become more sophisticated, the students often move to the most current literature to find examples.

Conclusion

I find that the ligand-of-the-week assignment is a win–win exercise. I win by having interesting and fun topics introduced into the class and the students win by feeling more ownership in the class. Furthermore, the students can contribute in a relatively informal fashion and we all have the opportunity to learn about the amazing variety of ligands that have an impact on the field of inorganic chemistry. Finally, the variations on this theme are endless and can be adapted to fit the vastly different ways that instructors teach inorganic chemistry.