INORGANIC CHEMISTRY CUMULATIVE EXAM
NOVEMBER, 2016
Donald J. Wink

The Mechanical Bond and Inorganic Chemistry

The 2016 Nobel Prize in chemistry was given for the study of molecular machines. A **machine,** for the purposes of the concept of a molecular machine, is an assembly of **parts** that carry out a **task** through each part interacting with a **particular function**. We are of course familiar that molecules (and many other things) are made of parts—specifically atoms held together by interatomic interactions we call bonds. What makes a **molecular machine** is the idea that a molecule can be a part of a larger assembly. And what better way to build assemblies than with a metal ion at the center of the construction?

1. (30 points). Copper and nitrogen ligands: A key coordination switch.

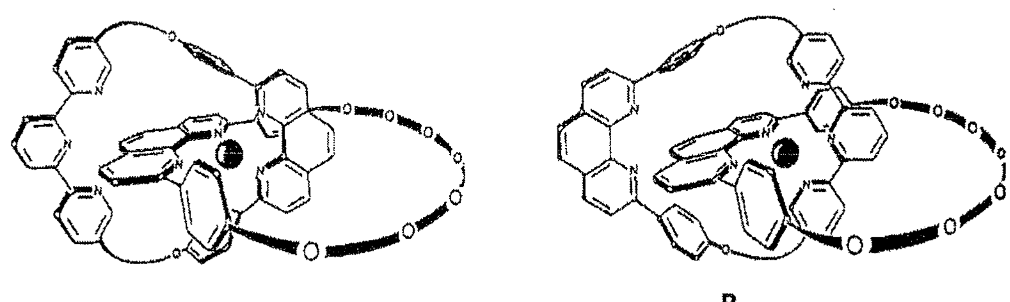
Jean-Pierre Sauvage, one of the recipients, has done extensive work based on tying molecules together around a metal center (Acc. Chem. Res. **1998,** 31, 611-619). The heart of much of the work is the propensity for some transition metals to have coordination stoichiometries and structures for different oxidation states.

(a) 10 points. One of Sauvage's favorite metals is copper, because of the geometric differences exhibited by Cu(I) and Cu(II). What differences do you expect for the coordination chemistry of these two ions? Specify both the **stoichiometries** and **structures** you expect. Assume you **only** have "L" type ligands to work with.

(b) 10 points. Sauvage does like "L" ligands, for example built from bipyridyl—bipy, terpyridyl—terpy, or phenanthroline—phen systems. Which is the most reasonable of the following pair of molecules? **Explain** your answer based on your reasoning in (a).

$$Cu(phen)_2^{2+} \text{ vs. } Cu(phen)_2^{+}$$
$$Cu(phen)_2^{2+} \text{ vs. } Cu(phen)(terpy)^{+}$$

(c) 10 points. The reasoning you just presented is the key to one of Sauvage's innovations: a redox-induced molecular motion. In 1994 he and coworkers (*JACS* **1994**, *116,* 9399-9400) reported a copper complex shown below. It has two binding modes. Based again on your reasoning for the acyclic systems in (a) and (b), which of these two forms is more stable? Why? And what will happen if the Cu^{2+} is reduced to Cu^{+}?



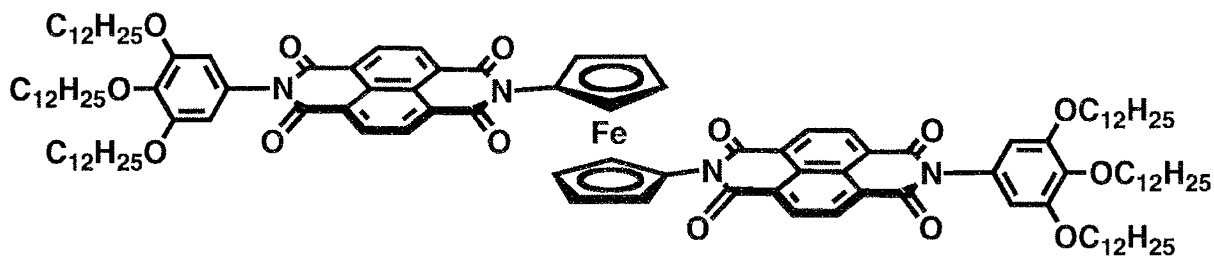
A B

In the figure, the black ball is a Cu^{2+} ion. The O—O links are a polyether ring that is not important in this question.

2. (15 points) Molecular motors—gears in the inorganic realm.

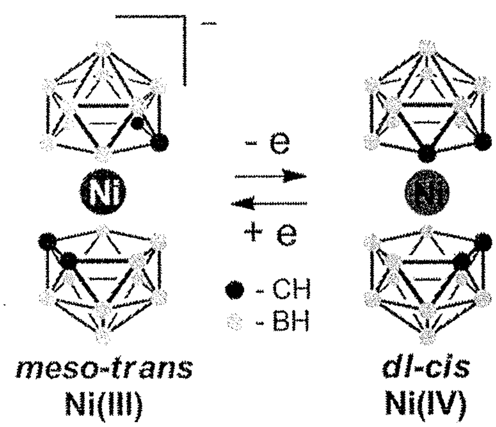
Another laureate, Ben Feringa, started out in the field of molecular catalysis (see question 4 later). He and his coworkers migrated to the area of molecular motors, in which light-induced *cis-trans* isomerism is used to exploit photo-induced C=C double bond rotation into molecular motion. Of course, that is organic chemistry, but versions of this kind of conformational flexibility are actually well known in inorganic chemistry.

One inorganic gear may be developed is based on metallocene frameworks, where a molecule like ferrocene can act as a molecular hinge also (*J. Am. Chem. Soc.*, 2016, 138 (35), pp 11245–11253).



(a) 10 points. What is it that makes the metallocene (or other bis-π-aromatic systems) have the potential to act as a **gear**? What may limit these?

(b) 10 points. One gear example has being developed by Fred Hawthorne and his colleagues (e.g., *Inorg. Chem.*, 2014, 53 (19), pp 10045–10053). They observed that a nickel bis(carborane) complex, shown below, underdoes a form of cis-trans isomerization based on the redox sate of the nickel ion.



How does the ligand in this case, with two carbons and three boron atoms forming the π-system that bonds to the metal, capable of forming *cis-trans* isomers?

3. (15 points). The mechanical bond:

As one part of the development of this chemistry, one of the other prize recipients, J. Fraser Stoddart, suggested a new kind of bond: one that forms the basis of a machine—hence, the concept of a 'mechanical bond' in which, "two or more molecular components become mechanically interlocked, one with another, and so on, in some manner or another." (*Chem. Soc. Rev.*, **2009,** *38*, **1802-1820).**

(a) 10 points. Sauvage's molecules (see question 1) provide one such example of a mechanical bond. Comment on how the copper works as the center of a mechanical bond in Stoddart's definition.

(b) 10 points. The π-compolexes in question 2 would not be considered as having a mechanical bond in themselves. What might be done to "mechanically interlock" substituents on a ferrocene?

4. 20 points. Molecular machines and organometallic catalysis.

Arguably, *any* molecular system that carries out a transformation of another system without underoing a net change in its own structure is a molecular machine. Hence, *all catalysts* are molecular machines. Given an example of a metal-catalyzed reaction and explain how it may meet the definition of a "molecular machine" given in the opening paragraph. You are encouraged to use examples from UIC chemistry labs.

5. 20 points. In 1987, the Nobel prize went to three individuals who are credited with opening up applications in the field that became key to molecular machines. They are associated with host-guest chemistry. Name the three persons (hints—UCLA, Strasbourg, and duPont) and give an example of one of their molecular innovations.