Inorganic Chemistry Cumulative Exam
Thursday, October 1, 2020
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1. The 1983 Nobel Prize in Chemistry was awarded to Prof. Henry Taube "for his work on the mechanisms of electron transfer reactions, especially in metal complexes." The key set of data collected by Taube involved the general reaction in eq 1.

$$[Co(NH_3)X]^{2+} + [Cr(OH_2)_6]^{2+} + 5\ [H_3O]^{+} \rightarrow [Co(OH_2)_6]^{2+} + [Cr(OH_2)_5X]^{2+} + 5\ [NH_4]^{+} \quad \text{(eq 1)}$$

   a) The equation above is a redox reaction. Which elements are being reduced, and which are being oxidized?
   b) Provide a qualitative explanation for why the Co center prefers to bind NH_3 in the reactant but H_2O in the product.
   c) Taube was awarded the Nobel Prize for revealing the mechanism of inner-sphere electron transfer (ET) involved in eq 1. Describe the difference between inner-sphere and outer-sphere ET mechanisms.
   d) The rate constant for eq 1 is given in Table 1 as a function of X. Place the X ligands in their correct places from the following list: F^{-}, Cl^{-}, Br^{-}, I^{-}.

Table 1. Rate constant data for eq 1.

X	k ($dm^3\ mol^{-1}\ s^{-1}$)
	2.5×10^5
	6.0×10^5
	1.4×10^6
	3.0×10^6

   e) Explain the trend in Table 1 in the context of the standard inner-sphere ET mechanism.
   f) Another inner-sphere ET reaction is shown in eq 2, with corresponding reduction potential data in Table 2. Is the reaction spontaneous or not under standard conditions?

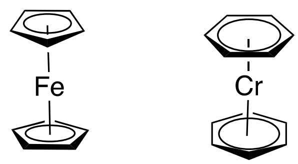
$$[Fe(CN)_6]^{3-} + [Co(CN)_5]^{3-} + H_2O \rightarrow [Fe(CN)_6]^{4-} + [Co(CN)_5(OH_2)]^{2-} \quad \text{(eq 2)}$$

Table 2. Reduction potential data for eq 2.

X	$E°$ vs. NHE
$[Fe(CN)_6]^{3-} + e^{-} \rightarrow [Fe(CN)_6]^{4-}$	+0.36 V
$[Co(CN)_5(OH_2)]^{2-} + e^{-} \rightarrow [Co(CN)_5]^{3-}$	–0.84 V

   g) The reaction in eq 2 is unique in that the binuclear intermediate formed during inner-sphere ET can be detected directly and characterized by spectroscopic methods. What is that intermediate's structure?
   h) Why does the Co center bind a water molecule in the product but not the reactant in eq 2?

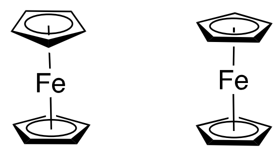
2. The 1973 Nobel Prize in Chemistry was awarded to Profs. E. O. Fischer and Geoffrey Wilkinson "for their pioneering work, performed independently, on the chemistry of the organometallic, so called sandwich compounds." Two of the molecules (**1** and **2**) studied by these two scientists are shown below.



1 **2**

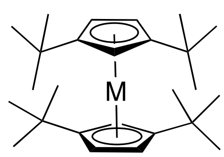
a. For each complex, provide the metal's formal oxidation state, the metal's *d*-electron count, and the metal's total valence electron count. Will either of these complexes have unpaired electrons (and therefore exhibit paramagnetism)?

b. For complex **1**, which is called "ferrocene" due to its high aromatic reactivity, there are two main conformations that differ based on whether the C_5H_5 rings are staggered or eclipsed (see below). Give the point group of each conformer.



"staggered" "ecplised"

c. While the energy barrier for staggered/eclipsed interconversion is small (< 10 kJ/mol) for ferrocene itself, substituted derivatives such as 1,1',3,3'-tetra(*t*-butyl)ferrocene (**3**) can have rotation barriers as high as 57 kJ/mol. Describe an experiment or series of experiments that you would use to measure the barrier to ring rotation in **3**.



3: M = Fe
4: M = Ru

d. Do you expect 1,1',3,3'-tetra(*t*-butyl)ruthenocene (**4**) to have a smaller or larger barrier to ring rotation compared to **3**? Why?

3. The 1976 Nobel Prize in Chemistry was awarded to Prof. William N. Lipscomb, Jr., "for his studies on the structure of boranes illuminating problems of chemical bonding." Among the boranes he studied, the simplest case is diborane, B_2H_6 (**5**). The surprising finding that two hydrogens bridge between two boron centers led to widespread acceptance of the three-center-two-electron (3c-2e) bond as a chemical concept. Another simple case of the 3c-2e bond is the bifluoride anion, $[HF_2]^-$ (**6**). Provide a molecular orbital diagram for **6**, highlight the orbitals involved in the 3c-2e bond, and explain how this model accounts for hydrogen connecting to two other atoms despite having a single 1*s* valence orbital.

4. The 1996 Nobel Prize in Chemistry was awarded to Profs. Robert F. Curl, Jr., Harold Kroto, and Richard Smalley "for their discovery of fullerenes". Fullerenes were found by these researchers as a new, crystalline allotrope of carbon.
   a. What is an allotrope?
   b. There are six other crystalline allotropes of carbon. Name two of them.

5. Nobel Prize trivia:

a. There are two people ever to be awarded Nobel Prizes in two different fields. Name them. (Hint: one of them won Nobel Prizes in Chemistry and Physics, and the other won in Chemistry and Peace.)
b. There is a single family that contains 4 Nobel Prize winners (and 5 total Nobel Prizes) collectively. Name the family. (Hint: Arguably, the most famous surname in the family was that of the matriarch.)
c. There are only 5 women that have ever won the Nobel Prize in Chemistry, the most recent being in 2018. Name two of these women.