University of Massachusetts Boston
Department of Chemistry
Chemistry Doctoral Program
Green Chemistry Track

June 25, 2010

Written Qualifying Exam: Inorganic Chemistry

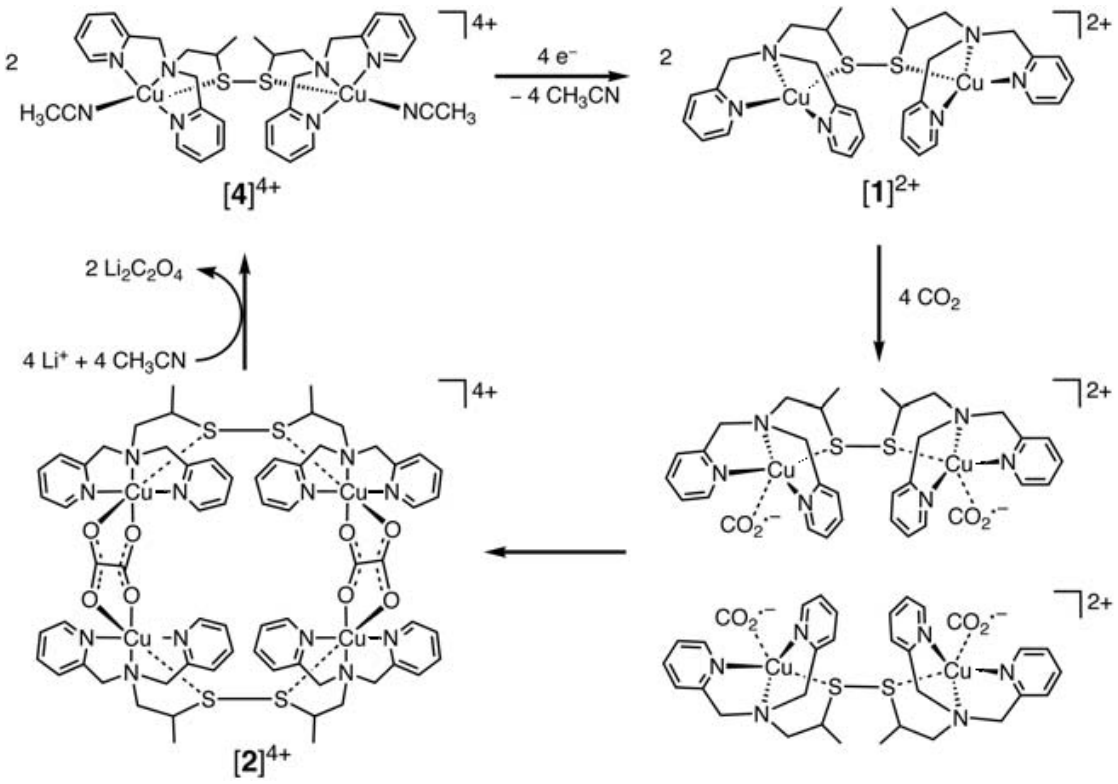
Questions are based on the following article:
Angamuthu R.; Byers P.; Lutz M.; Spek A. L.; Bouwman E. Electrocatalytic CO_2 Conversion to Oxalate by a Copper Complex, *Science* **2010**, 327, 313–315.

1. Angamuthu et al. cite the use of lithium, sodium and calcium hydroxides for the stoichiometric transformation of CO_2 to carbonate salts as well as the use of organic amines which bind irreversibly with CO_2 through the formation of carbamates. Write balanced equations for the formation of (i) a carbonate salt and (ii) a carbamate with CO_2 through the use of calcium hydroxide and ammonia respectively. Discuss briefly any similarities/differences between both reactions and how they differ from the catalytic process described in the article.

   (2 points)

2. For the catalytic cycle proposed by Angamuthu et al. (below) indicate the formal oxidation state of copper in each case and identify which complex is considered the "active" catalyst in the cycle (*hint: oxidation states and coordination geometries can be used as a guideline*).

   (3 points)

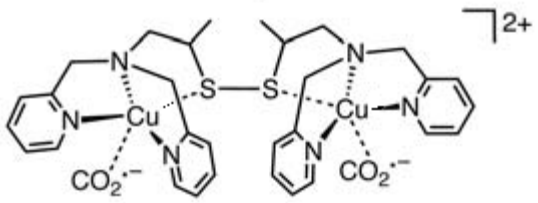


3. Copper complexes **[3]**$^{4+}$ or **[4]**$^{4+}$, when reduced electrochemically to complex **[1]**$^{2+}$ show a disappearance of their characteristic *d-d* electronic transition absorption band observed by UV-Vis spectroscopy. Explain this observation based upon the formal oxidation states of the copper ions in **[4]**$^{4+}$ and **[1]**$^{2+}$ (see previous question for structures of **[4]**$^{4+}$ and **[1]**$^{2+}$)

(2 points)

4. In the article by Angamuthu et al., reductive coupling of CO_2 to form oxalate is accomplished by electrochemical methods. What is most impressive about this system is its selectivity over O_2 reduction. The electrochemical reduction of CO_2 to its anion radical $CO_2^{\bullet-}$ occurs at E = -1.97 V vs. NHE, whereas the reduction of [Cu]-CO_2 to [Cu]-$CO_2^{\bullet-}$ reported by Angamuthu et al. occurs at E = -0.03 V vs. NHE ([Cu] = copper catalyst). The proposed intermediate below was not structurally characterized due to its high reactivity – suggest a possible binding mode of the CO_2 molecule to the copper center. Discuss how any suggested binding mode may be responsible for the reduced overpotential required for catalytic CO_2 reduction?

(3 points)



5. ***(Green Chemistry Question)*** In the opening sentence of this article the authors state that "Global warming concern has dramatically increased interest in using CO_2 as a feedstock for preparation of value-added compounds, thereby helping to reduce its atmospheric concentration." To the best of your ability discuss the motivation behind this statement and the role inorganic catalysts such as the copper system here studied may play in our future energy economy.

(2 points)