Chem242. Int. Inorg. Chem. Spring, 2007 UMass-Amherst

Experiment 1

Hard-Soft Acids and Bases: Altering the Cu^+/Cu^{2+} Equilibrium with Nitrogen, Oxygen, or Halide Ligands

*Parts of the experiment are based on C. E. Ophardt & G. Wollaston, *J. Chem. Ed*. **1991**, *68*, 248-49.

Pre-Lab Assignment

In your lab notebook, write out *both* the balanced chemical reaction and the net ionic equation that you would expect for the two complexation reactions (**A**, **B**), the two reduction reactions (**C**, **D**), and the two oxidation reactions (**E**, **F**). Both charge and mass balance must be satisfied. The expected chemical products are: **A** – $Cu(NH_3)_4^{2+}$**;** **B** – $Cu(en_2)^{2+}$**;** **C** – CuCl**;** **D** – CuI**;** **E** – $Cu(NH_3)_4^{2+}$**;** **F** – $Cu(en_2)^{2+}$

Introduction

One of the more useful and interesting properties of most transition metals is their ability to adopt a variety of oxidation states, each with their own set of properties. For example, manganese is commonly found in oxidation states ranging from Mn^{2+} to Mn^{7+}. A very general qualitative concept related to oxidation state stabilization is the hard and soft (Lewis) acid-base model, which allows predictions about the stability of different oxidation states to be made.

In a nutshell, hard bases stabilize hard acids and soft bases stabilize soft acids. Oxygen and fluorine electron-pair donors are hard bases, nitrogen and chlorine donors are intermediate bases, and carbon, phosphorous, sulfur, bromine, and iodine donors are soft bases. Copper(II) is a borderline acid and copper(I) is a soft acid. Thus, we anticipate that in the aqueous world about us, copper(II) is the “normal” form of oxidized copper, but in situations where soft donors can compete with water, copper(I) might be the more stable form. A listing of hard and soft acids and bases is shown on the final page of this handout.

Related to the HSAB concept is the change in reduction potentials observed for a metal as the surrounding ligands change. Reduction potentials are related to thermodynamic stability by the equation $\Delta G = -nFE$. Recall that reduction potentials are related to reaction equilibrium constants (K_{eq}) and the non-equilibrium reaction quotient (Q) according to the following equations, where E^0 is the redox potential, R is the gas constant, n is the number of electrons transferred, and F is the Faraday constant:

$$E^0 = \frac{-RT}{nF}\ln K_{eq} \ (\textit{equilibrium}) \qquad \text{and} \qquad E = E^0 - \frac{RT}{nF}\ln Q \ (\textit{non-eq., Nernst eqn.})$$

A few selected reduction potentials for copper are shown on the next page to demonstrate this trend. In brief, softer bases stabilize Cu(I), leading to a more positive redox potential. The 1-electron reduction potential for Cu(II) in aqueous solution (where the Cu(II) is surrounded by water molecules at pH = 0) is +0.15 volts (relative to the standard hydrogen electrode), while in the presence of chloride ions this potential increases to +0.54 volts and in the presence of iodide ions this potential increases to +0.86 volts. In each case a solid CuX halide is produced.

Another type of reaction involving Cu(II) and Cu(I) is a disproportionation, in which 2 equivalents of Cu(I) react to form 1 equivalent of Cu and 1 equivalent of Cu(II), Eq. 1.

$$2Cu^+ \quad \leftrightarrows \quad Cu^{2+} + Cu \qquad (1)$$

By combination of the individual redox couples for each half-reaction, it can readily be shown that very little copper(I) can exist in acidic aqueous solution (remember, E^0 is for 1M H^+ concentration) unless it is complexed by a soft donor ligand, since it would very readily disproportionate to copper metal and Cu(II).

Oxidation:	Cu^+	$\leftrightarrows$	$Cu^{2+} + e^-$	$E^0 = -0.15V$	(2)
Reduction:	$Cu^+ + e^-$	$\leftrightarrows$	Cu	$E^0 = +0.52V$	(3)
Net:	$2Cu^+$	$\leftrightarrows$	$Cu^{2+} + Cu$	$E^0 = +0.37V$	(4)

Conversion of this value by the above equations leads to the conclusion that only about 0.1% of the copper in solution is in the form of aqueous copper(I) ions at reasonable laboratory concentrations ($K_{eq} = 10^{-6.6}$), even in the presence of excess copper metal. However, the analogous copper(I) chloride data results are quite different, as Cl^- helps to stabilize the softer Cu(I) more than the hard O-donor of water.

Procedure

SAFETY NOTES:* *Goggles are required. Prepare the solutions containing aqueous ammonia (ammonium hydroxide) and ethylenediamine in the hood.

Complexation of Copper(II) by Nitrogen Donors.

A. Add about 1mL of 0.03 *M* copper(II) chloride solution a small test tube and *in the hood* add 1 mL of 6 *M* aqueous ammonia. Record your observations (color? solubility? Gas? Explosion?)

B. Add about 1mL of 0.03 *M* copper(II) chloride solution to a small test tubes and *in the hood* add 1 mL of 25 % aqueous ethylenediamine (abbreviated “en”) to the other. What happens when these solutions are mixed?

Reduction of Copper(II) to Copper(I).

The preparation of copper(I) chloride and $[CuCl_n]^{1-n}$, where n = 2 or 3, takes advantage of the relative softness of the chloride ions as exemplified in reduction potentials (2) & (6) and the complexation of extra chloride ions to the “soft” CuCl.

C. Pour 10 mL of 0.03 *M* copper(II) chloride solution into a small Erlenmeyer flask. Add 1 g of ammonium chloride to the solution and stir or swirl to dissolve. Note any changes. Then, heat the solution to boiling to expel oxygen and add an excess of clean copper wire (3” of heavy gauge wire is more than enough), or (ca. 0.1 g) of clean copper turnings, and continue heating. Note what happens as this slow heterogeneous reaction proceeds and record the results.

> [*Hint:* Cu(II) exhibits colors in the visible spectrum, Cu(I) does not exhibit visible colors, and Cu(0) is a red metal.]

D. The preparation of CuI uses potentials (1) & (3). Take a small test tube and add about 2 mL of 0.03 *M* copper(II) chloride solution. Add an equal amount of 0.1 *M* potassium iodide solution. Note what happens and record the results.

Oxidation of Copper(I) to Copper(II).

E. Divide the material in the test tube from procedure step **D** into two equal parts (it should be CuI). *In the hood,* add about 1 mL of 6 *M* aqueous ammonia to one part and carefully record your observations.

F. *In the hood,* add about 1 mL of 25% ethylenediamine to the other part saved from **D**. This reaction proceeds differently than reaction **E**. Note the differences and explain them in your write-up.

G. Synthesize the Schiff-base bis(salicylidene)ethylenediamine (or "salen") by taking 3 mL of 95% ethanol in a test tube that also has a small magnetic stirring bar. Heat the ethanol to boiling in an oil bath on a magnetic stirrer/hotplate. Immediately, with continued heating and stirring, add 0.30 mL (2.8 mmol) of salicylaldehyde and then 0.10 mL (1.4 mmol) of ethylenediamine (98%). Stir the solution for 3 to 4 min and then cool in an ice-water bath to precipitate the yellow salen. Weigh your product and determining your %yield.

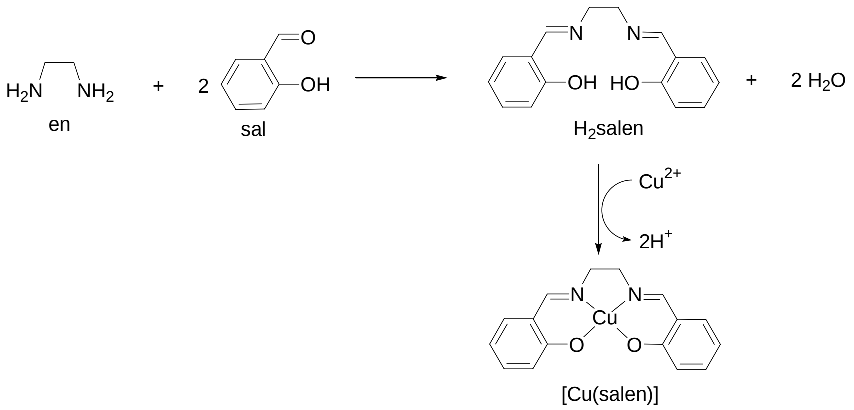


Figure 1. Synthesis of H_2salen, and formation of the [Cu(salen)] complex.

Develop an experimental scheme to test the equilibria of the three oxidation states of copper when ligated by salen. For example, your could show that Cu(II)salen is not easily reduced to copper(I) by copper metal (Eq. 5), or that Cu(I)salen spontaneously disproportionates to Cu(0) and Cu(II) (Eq. 6).

$$[\mathrm{Cu}^{2+}\mathrm{salen}] + \mathrm{Cu}(0) \leftrightarrows 2\,[\mathrm{Cu}^{1+}\mathrm{salen}]^{-} \qquad (5)$$

$$2\,[\mathrm{Cu}^{1+}\mathrm{salen}]^{-} \leftrightarrows [\mathrm{Cu}^{2+}\mathrm{salen}] + \mathrm{Cu}(0) + \mathrm{salen}^{2-} \qquad (6)$$

Show your scheme to a TA for approval before attempting your procedure. Carry out your scheme and record your results.

[Note: Metal deactivators in gasoline include a similar Schiff-base with 1,2-diaminopropane as the diamine. The Schiff-base prevents copper(I) catalyzed gum formation.]

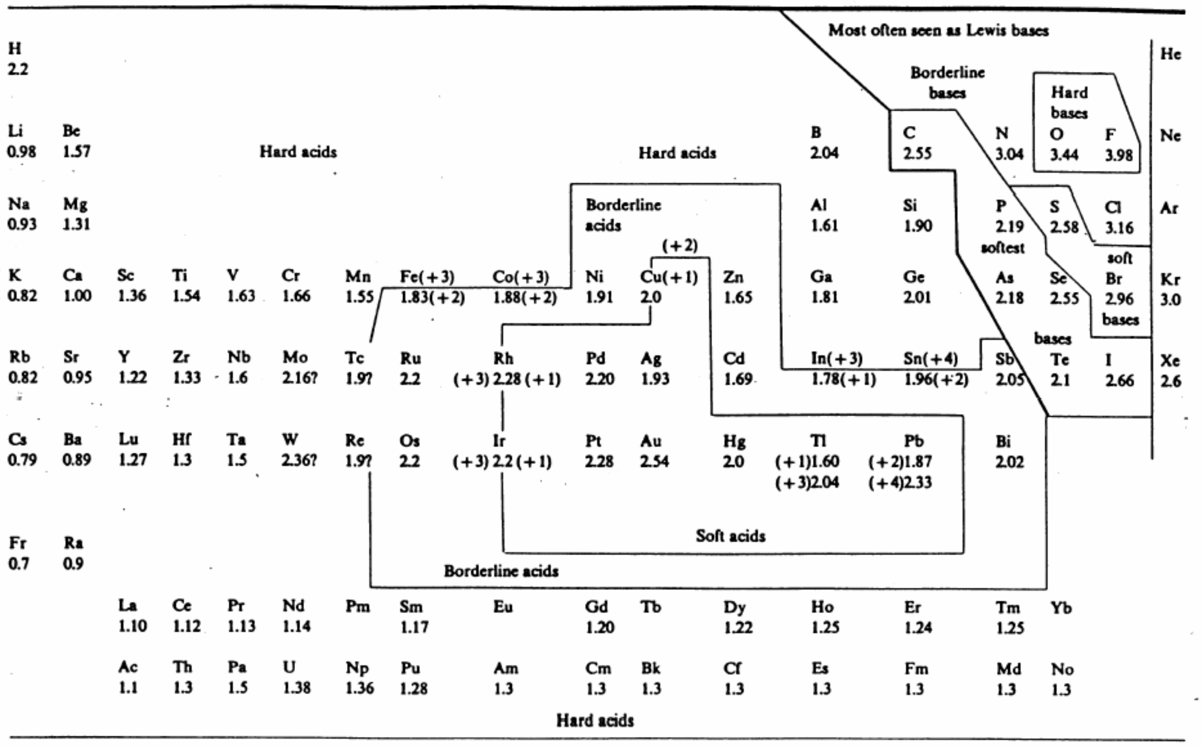
Questions

1. Making use of Table 1, write out individual redox half-reactions (and their balanced sum, including the overall potential) that describe the net chemical reactions in procedures (**A-F**). Use the associated potentials to account for your observations and results. *Hints*: Potentials (5) and (7) are relevant to **A**, (1) and (3) to procedure **D**, while procedure **E** requires three half reactions. In each case, the half-reactions should sum to the net ionic equation, with no e^- left over.
2. Calculate the voltage (E°) for the preparation of copper(I) chloride from Cu(II) and Cu(0) using the standard reduction potentials at the end of this handout. How does it compare to the potential for the analogous process in the absence of chloride ion (equation 4) in the introduction?
3. Use your result from the previous problem to calculate the free energy change (ΔG) for the preparation of CuCl from copper(II) and Cu(0) in the presence of aqueous chloride ions. How does it compare to the free energy chance in the absence of Cl? Under which conditions is Cu(I) the most stable?
4. Is the presence of the halogen affecting the stability of just the Cu(I) ion or is it affecting the stability of the Cu(II) ion as well? If you assume that the stability of metallic Cu(0) is unchanged by the presence or absence of halogens, you can use it as a baseline and discuss how the stability (in Volts) of Cu(I) and Cu(II) changes relative to Cu(0).
5. In what ways do the experimental conditions vary from the conditions used to calculate the standard reduction potentials in the table below. Roughly speaking, will the actual potentials have large or small variations from the ideal potentials (from the Nernst eqn.)?
6. Why is Cu(I) colorless, while Cu(II) tends to be colored (green or blue)? Think about electron configurations.

Table 1. Reduction Potentials Involving Copper and Copper Compounds

	Couple			E° value
(1)	$Cu^{2+} + I^- + e^-$	$\leftrightarrows$	CuI	0.86V
(2)	$Cu^{2+} + Cl^- + e^-$	$\leftrightarrows$	$CuCl$	0.54V
(3)	$I_2 + 2e^-$	$\leftrightarrows$	$2I^-$	0.54V
(4)	$Cu^+(aq) + e^-$	$\leftrightarrows$	$Cu(s)$	0.52V
(5)	$Cu^{2+}(aq) + 2e^-$	$\leftrightarrows$	$Cu(s)$	0.37V
(6)	$CuCl + e^-$	$\leftrightarrows$	$Cu + Cl^-$	0.14V
(7)	$Cu(NH_3)_4^{2+} + 2e^-$	$\leftrightarrows$	$Cu + 4NH_3$	-0.12V
(8)	$Cu^{2+}(aq) + e^-$	$\leftrightarrows$	$Cu^+(aq)$	-0.15V
(9)	$CuI + e^-$	$\leftrightarrows$	$Cu + I^-$	-0.19V
(10)	$Cu(en)_2^{2+} + 2e^-$	$\leftrightarrows$	$Cu + 2en$	-0.50V [en =ethylenediamine]

Hard & Soft Acids & Bases (Table 8.1 from Wulfsberg, *Principles of Descriptive Inorganic Chemistry...*)



H 2.2												Most often seen as Lewis bases	Borderline bases		Hard bases		**He**
Li 0.98	**Be** 1.57				Hard acids					Hard acids		**B** 2.04	**C** 2.55	**N** 3.04	**O** 3.44	**F** 3.98	**Ne**
Na 0.93	**Mg** 1.31								Borderline acids			**Al** 1.61	**Si** 1.90	**P** 2.19 softest	**S** 2.58	**Cl** 3.16	**Ar**
K 0.82	**Ca** 1.00	**Sc** 1.36	**Ti** 1.54	**V** 1.63	**Cr** 1.66	**Mn** 1.55	**Fe(+3)** 1.83(+2)	**Co(+3)** 1.88(+2)	**Ni** 1.91	(+2) **Cu(+1)** 2.0	**Zn** 1.65	**Ga** 1.81	**Ge** 2.01	**As** 2.18	**Se** 2.55	soft **Br** 2.96 bases	**Kr** 3.0
Rb 0.82	**Sr** 0.95	**Y** 1.22	**Zr** 1.33	**Nb** 1.6	**Mo** 2.16?	**Tc** 1.9?	**Ru** 2.2	**Rh** (+3) 2.28 (+1)	**Pd** 2.20	**Ag** 1.93	**Cd** 1.69	**In(+3)** 1.78(+1)	**Sn(+4)** 1.96(+2)	**Sb** 2.05	bases **Te** 2.1	**I** 2.66	**Xe** 2.6
Cs 0.79	**Ba** 0.89	**Lu** 1.27	**Hf** 1.3	**Ta** 1.5	**W** 2.36?	**Re** 1.9?	**Os** 2.2	**Ir** (+3) 2.2 (+1)	**Pt** 2.28	**Au** 2.54	**Hg** 2.0	**Tl** (+1)1.60 (+3)2.04	**Pb** (+2)1.87 (+4)2.33	**Bi** 2.02			
Fr 0.7	**Ra** 0.9							Borderline acids			Soft acids						
		La 1.10	**Ce** 1.12	**Pr** 1.13	**Nd** 1.14	**Pm**	**Sm** 1.17	**Eu**	**Gd** 1.20	**Tb**	**Dy** 1.22	**Ho** 1.25	**Er** 1.24	**Tm** 1.25	**Yb**		
		Ac 1.1	**Th** 1.3	**Pa** 1.5	**U** 1.38	**Np** 1.36	**Pu** 1.28	**Am** 1.3	**Cm** 1.3	**Bk** 1.3	**Cf** 1.3	**Es** 1.3	**Fm** 1.3	**Md** 1.3	**No** 1.3		
									Hard acids								

NOTES: Numbers in parentheses are oxidation numbers. The number below each atomic symbol is the Pauling electronegativity of that element.