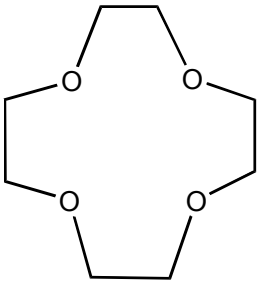
Use of an Oxidation-Resistant Macrocyclic Ligand for the Preparation of a Cu(III) Complex[1]

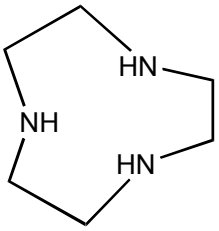
Inorganic Chemistry I, Spring 2004

This experiment illustrates a number of modern inorganic chemistry concepts: (1) use of an oxidation-resistant macrocyclic ligand to stabilize an unusually high metal oxidation state [Cu(III)], (2) use of a low-nucleophilicity amine base, (3) use of large organic cations to precipitate large inorganic anions, and (4) the development of metal-based oxidation catalysts for "green" chemistry applications such as the activation of hydrogen peroxide as an oxidant for use in industrial processes. In addition, the compound is structurally interesting, in that the Cu(III) center is of square planar geometry and is diamagnetic (low-spin $3d^8$).

Macrocyclic (large-ring) ligands, due to their high degree of pre-organization, are especially powerful complexing agents for metals. For "hard" metal ions, such as Na^+ or K^+, hard ligands such as crown ethers are highly effective complexing agents. Complexing agents for transition metal ions, which are, in most cases, "softer," need correspondingly softer ligand atoms, such as nitrogen, phosphorus, or sulfur. Examples of both types of ligand are illustrated below.

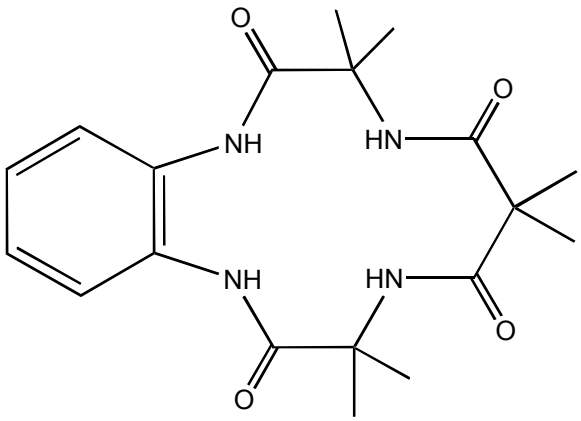


12-crown-4
a hard macrocyclic ligand



1,4,7-triazacyclononane (TACN)
a softer macrocyclic ligand

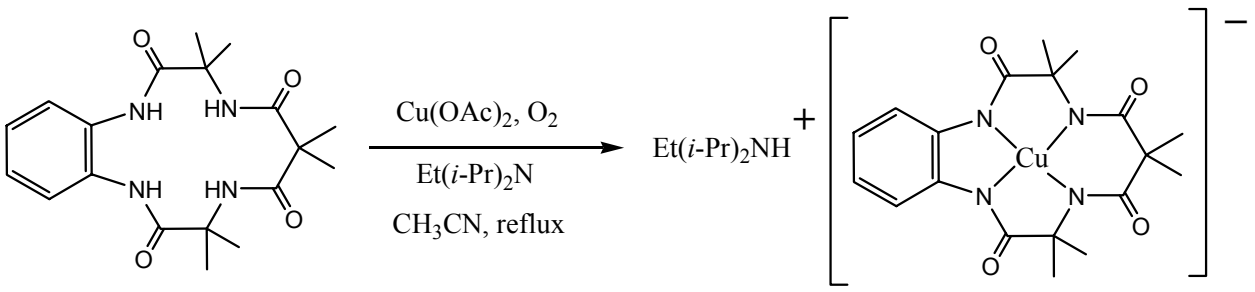
The ligand TAML®, illustrated below, is an example of a group of macrocyclic ligands that are highly oxidation-resistant, and thus able to form complexes with metals in unusually high oxidation states. We will be using TAML to facilitate formation of a Cu(III) complex.



TAML®
an oxidation-resistant macrocyclic ligand

The first step of the experimental procedure accomplishes three things: (1) deprotonation of TAML® to form a tetraanion, (2) insertion of copper into the ligand, and (3) oxidation of Cu(II) to Cu(III). The oxidation is done by oxygen in the air.

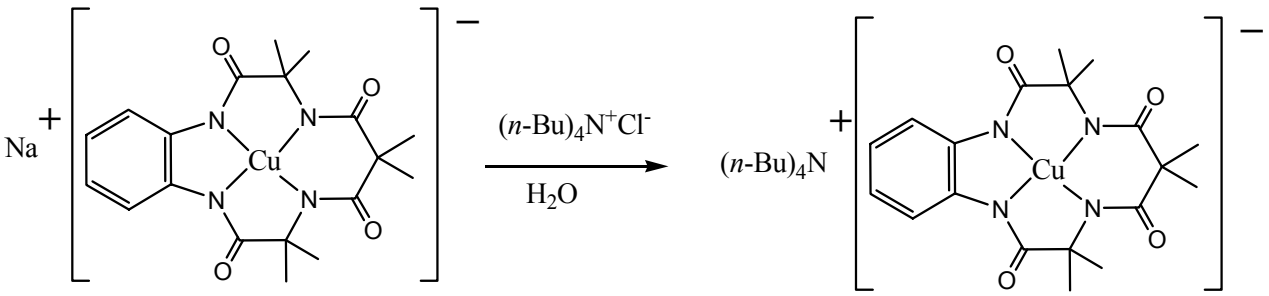
Steps (1) and (2) probably occur more or less in parallel, since coordination of Cu(II) to the neutral ligand will probably occur, leading to acidification of the amido hydrogens. Deprotonation is done with a highly hindered base (ethyldiisopropylamine, Hünig's base). Bases such as Hünig's base are slow to react with most electrophiles (such as alkyl halides or transition metal coordination complexes), due to steric hindrance. They are, on the other hand, reactive with acidic hydrogens, since the transition state for deprotonation is little affected by steric constraints. The overall conversion is illustrated below.



Preparation of $Et(i\text{-}Pr)_2NH^+CuL^-$ (L = TAML tetraanion)

The product is purified by column chromatography on silica gel. The organic groups on both the cation and the anion provide solubility in organic solvents, and acetone is used as the eluent. Less lipophilic byproducts remain on the column.

In the next step, the ethyldiisopropylammonium ion is exchanged for sodium ion to produce an aqueous solution of NaCuL. The complex anion is then re-precipitated by addition of tetra-*n*-butylammonium chloride solution to produce $n\text{-}Bu_4N^+CuL^-$. This operation provides an organic-soluble salt that contains no reactive N-H bonds (compare to the initial product).



Precipitation of $(n\text{-}Bu)_4N^+CuL^-$ (L = TAML tetraanion)

1. This preparation is adapted from: Uffelman, E. S.; Doherty, J. R.; Schulze, C.; Burke, A. L.; Bonnema, K. R.; Watson, T. T.; Lee, D. W., III *J. Chem. Ed.* **2004**, *81*, 182-185, and references therein.

Experimental Procedures

The preparation will be done as a microscale experiment, so as to illustrate relevant techniques and also to minimize the cost of the ligand, which is expensive.

1. Preparation of Et(*i*-Pr)$_2$NH$^+$CuL$^-$ (L = TAML® tetra-anion)

Place 6-8 mg of TAML® in a ******dry***** 10 mL microscale round-bottom flask, along with a magnetic stirring bar.

> ***NOTE: Before performing the next step, you must know that it is imperative that you replace the cap on the copper(II) acetate bottle. If the Cu(OAc)$_2$ becomes hydrated, the reaction will fail.***

Place 5 mg of anhydrous Cu(OAc)$_2$ in the flask. Measure, by syringe, 1.0 mL of acetonitrile and add it to the flask. Add four drops of ethyldiisopropylamine (Hünig's base).

Attach an air-cooled reflux condenser to the flask, and gently reflux the reaction mixture for 50 minutes. Run a TLC of the reaction mixture (silica gel plate, acetone eluent) so as to observe the chromatographic behavior.

Allow the reaction mixture to cool to room temperature.

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> ***The next two procedures MUST be done in a hood, due to the toxicity of acetonitrile vapor.***

Pour the reaction mixture into a small beaker.

Evaporate the solvent on a steam bath, heating mantle, or hot plate. Be careful not to overheat toward the end of the evaporation.

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Dissolve the residue in ca. 1 mL of acetone.

Place a glass wool plug in a 4 mL Pasteur pipet (MonstrPette®, the same type of pipet used in the acetylferrocene preparation), then add ca. 1.5 cm of silica gel.

Pass the solution of complex through the silica gel column, then run ca. 2 mL more acetone through the column. The Et(*i*-Pr)$_2$NH$^+$Cu(L)$^-$ should pass through as a brown band, leaving byproducts behind on the column.

2. Conversion of $Et(i\text{-}Pr)_2NH^+Cu(TAML)^-$ to $Na^+Cu(L)^-$

In a small test tube, dissolve the $Et(i\text{-}Pr)_2NH^+Cu(L)^-$ in ca. 1 mL of methylene chloride, then add 1 mL of 1 M aqueous NaOH and mix. Remove the methylene chloride layer by pipet, the rinse the aqueous layer with two successive 1 mL portions of methylene chloride. This provides a brown aqueous solution of $Na^+Cu(L)^-$.

3. Conversion of $Na^+Cu(TAML)^-$ to $(n\text{-}Bu)_4N^+Cu(L)^-$

Add a few drops of concentrated aqueous $(n\text{-}Bu)_4N^+Br$- to the aqueous solution of $Na^+Cu(L)^-$, so as to precipitate $(n\text{-}Bu)_4N^+Cu(L)^-$ as a brown solid. Centrifuge the mixture and discard the supernatant (be sure to balance the centrifuge with a similar test tube, containing a similar volume of water). Wash and centrifuge the precipitate two more times.

Dissolve the product in a small amount of methylene chloride and dry the solution with anhydrous magnesium sulfate. Filter off the drying agent and evaporate the solvent. Weigh your product, then turn it in to your instructor for spectral analysis.