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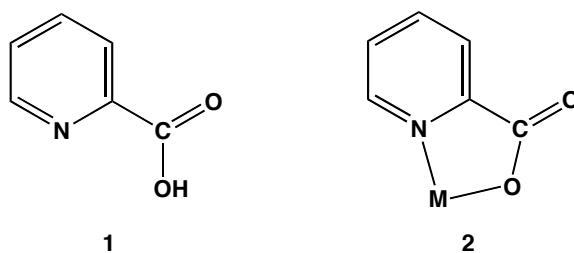
Inorganic Chemistry Laboratory

Preparation and Spectroscopic Characterization of the Classical Coordination Compounds Copper(II) and Silver(II) Picolinate. A Comparison of a First and a Second Transition-Series Element in the Same Family

*Thomas J. Smith
Department of Chemistry
Kalamazoo College
Kalamazoo, Michigan 49006-3295
tsmith@kzoo.edu*

Introduction

This experiment involves classical transition-metal coordination compounds. The purpose of the exercise is to compare the physical and chemical properties of coordination complexes containing copper(II) and silver(II) ions bound to the anion of pyridine-2-carboxylic acid, also known as picolinic acid, picH **1**. The metallic elements copper and silver are in the same family in the periodic table (named the coinage metals along with gold), but their chemical properties are quite different. Although Cu(II) is the stable oxidation state in aqueous solution, Ag(II) is powerfully oxidizing in water. The conjugate base of picH, pyridine-2-carboxylate or picolinate ion, acts as a ligand or Lewis base toward the metal ions. This ligand typically binds to metal ions in chelating mode through the pyridine ring nitrogen atom and one of the carboxylate oxygen atoms as seen in **2**.



The compounds are synthesized in water at room temperature. In both cases picolinic acid is deprotonated to give picolinate ion, which then binds to Cu²⁺ and Ag²⁺, yielding products formulated as M(pic)₂. For silver, Ag⁺ must be oxidized to Ag²⁺. Molecular and electronic structural characterization will be accomplished through infrared, electronic absorption, and electron spin resonance (ESR) spectroscopy and density functional calculation. Molecular structures will be explored using the Cambridge Structure Database.

Procedure

1. *Preparation of Cu(pic)₂*. Prepare in separate beakers aqueous solutions (deionized water) of Cu₂(CH₃CO₂)₄(H₂O)₂ (0.200 g in 20 mL) and picH (0.247 g in the minimum volume of water) with gentle heating and stirring. Add the Cu²⁺ solution to the picH solution with stirring;

rinse the Cu^{2+} beaker with a small amount of water into the reaction vessel. The resulting suspension should be stirred at room temperature for 20 min after which it should be placed in an ice bath for 20 min. Filter the suspension through a filtering funnel. Wash the solid product with cold water and 95% ethanol and dry under vacuum overnight. Determine the yield. Place the dried product in vial and attach a label with the compound name, student partner names, the yield, and the date written on it. One or two pairs of students will recrystallize this compound.

2. *Preparation of $\text{Ag}(\text{pic})_2$.* Prepare aqueous solutions of AgNO_3 (0.200 g in 20 mL), picH (0.290 g in the minimum volume of water), Na_2CO_3 (0.250 g in 20 mL), and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.158 g in 20 mL) each in a beaker, with stirring. (CAUTION: do not allow AgNO_3 to make contact with your skin; it will turn the skin black. This lasts for only a few days and causes no irritation.) Add the Ag^+ solution to the picH solution with stirring, followed by the Na_2CO_3 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solutions. The resulting suspension should be stirred at room temperature for 5 min. Filter the suspension through filtering funnel. Wash the solid product with water and dry it under vacuum overnight. Determine the yield. Place the dried product in a vial and attach a label with the compound name, student partner names, the yield, and the date written on it.
3. *Physical Measurements.* Record the solid-state infrared spectrum of $\text{Cu}(\text{pic})_2$ and $\text{Ag}(\text{pic})_2$ as KBr (vacuum dried) pellets or mineral-oil mulls on NaCl plates using the Midac M-Series FTIR spectrometer. An atmospheric background should be obtained at 4-cm^{-1} resolution and with 25 scans for the background correction. Acquire the spectra in the range $4000\text{-}500\text{ cm}^{-1}$ (to 600 cm^{-1} for the mull) under the same instrument settings used for the background. Print the spectra both with and without the band wavenumbers marked and save them to a flash drive or e-mail them to both partners.

Acquire the electronic absorption spectrum of both compounds using a mineral-oil mull of the compound on filter paper using a Cary 300 spectrophotometer. The baseline correction should be recorded with mineral oil only on filter paper in both the sample and reference compartments. The spectra should be recorded in the range $900\text{-}300\text{ nm}$ at 60 nm/min scan rate and 0.1 nm data interval. Print the spectra in the range $900\text{-}300\text{ nm}$ with and without the band wavelength maxima marked and save them to a flash drive or e-mail them to both partners. One or more pairs of students will acquire the aqueous solution spectra for both products.

The ESR spectra for both compounds will be provided.

4. *Density Functional Calculation.* A density functional calculation on $\text{Cu}(\text{pic})_2$, employing Spartan software will be done as an in-class exercise; details will be provided. The silver compound has too many electrons to be done with the available software.
5. *Cambridge Structure Database Search.* The search for reported molecular and crystal structures of the $\text{M}(\text{pic})_2$ compounds will also be done in class; details will be provided.

Discussion

1. Provide complete, balanced reaction equations for each step of the syntheses of $\text{Cu}(\text{pic})_2$ and $\text{Ag}(\text{pic})_2$.

2. Draw the molecular structure of the $M(\text{pic})_2$ compounds, using a computer drawing program such as ChemDraw (*not* a photocopied or downloaded figure). The figure should clearly indicate the molecular geometry in correct spatial perspective. Provide name for the structure. Note that picolinate produces a moderately strong ligand field.
3. Assign the infrared spectra in as much detail as you can, employing literature precedents. Include your spectral assignments in a separate table. Is the organic ligand present in both products?
4. Assign the electronic spectra in the visible and near ultraviolet regions in as much detail as you can, employing literature precedents. Include your spectral assignments in a separate table. Assign specific transitions(s) to the band(s) using an orbital energy diagram. For these molecules interelectronic repulsions can be ignored (explain why) so that the orbital energy ordering may be employed directly. What is the likely origin(s) of the high intensity ultraviolet bands?
5. See the directions for the calculation of the ESR g -value and spin-only magnetic moment for the $M(\text{pic})_2$ compounds. Explain the significance of your μ_{SO} results in terms the number of unpaired electrons in each complex and the oxidation state of Cu and Ag.
6. Interpret the observed higher energy MOs obtained in the density functional calculation. Relate the axial symmetry of the experimental ESR spectra to the computed HOMO.
7. Compare the results of the CSD search for the $M(\text{pic})_2$ compounds with the symmetry of the electronic structure suggested by the ESR spectra.
8. Account for the non-existence of gold(II) picolinate.

General References

1. F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th Ed., Wiley, 1999.
2. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Part B, 6th Ed., Wiley, 1997.