

PREPARATION OF COPPER GLYCINE COMPLEXES

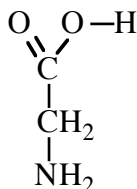
Purpose

There are two main objectives for this experiment:

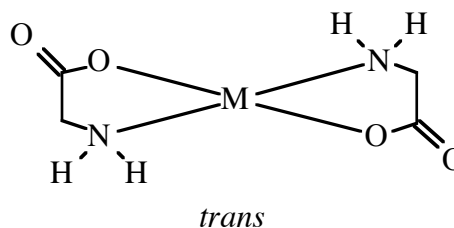
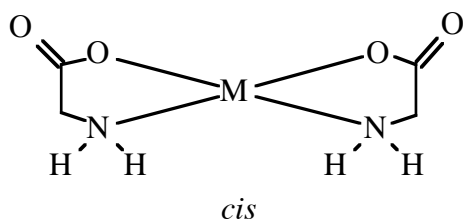
1. The preparation of both copper glycine complexes—*cis* and *trans*.
2. The analysis of the compounds to verify which complex is the kinetic product and which one is the thermodynamic product.

Background

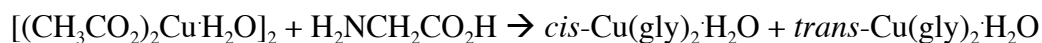
Like the more familiar acetylacetone, the amino acid glycine, below, dissociates to form an anion (gly) [and cation (H^+)], which can coordinate to a wide variety of metal complexes.



One major difference is that the glycine anion is not symmetric and structural isomers can arise depending on the relative orientation of the ligands.



In this experiment, the *cis* and *trans* copper glycinates are prepared. The direct reaction of copper(II) acetate monohydrate and glycine results in an equilibrium mixture of the two isomers.



One isomer precipitates much more quickly than the other, leading to a shift in the equilibrium away from the other, producing only the one isomer. The first isomer (kinetically favored product) is converted to the other (thermodynamically favored product) simply by heating.

Safety

Copper(II) acetate monohydrate (CAS No. 66923-668): This compound is harmful if swallowed, inhaled, or absorbed through the skin.

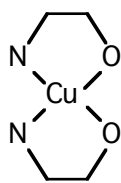
Glycine (CAS No. 56-40-6): No toxicity data is available for this compound, but it would be prudent to follow normal safety precautions.

Experimental

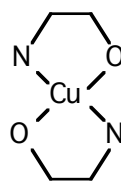
Preparation of Bis(glycinato)copper(II) Monohydrate (first isomer): Copper(II) acetate monohydrate (2.0 g) is dissolved in 25 mL of hot distilled water. Then 25 mL of ethyl alcohol is added and the solution is kept hot. Dissolve 1.5 g of glycine in 25 mL of hot water. Mix the two solutions while hot (ca. 70°C). When the solution is cooled on ice, a needle-like precipitate of the first isomer should be obtained. Vacuum filter this mixture into a clean flask, so that the filtrate may be preserved. Wash the solid with ethanol and air dry.

Preparation of Bis(glycinato)copper(II) Monohydrate (second isomer): Place around 10 mL of the filtrate from the previous preparation in a small round-bottom flask along with approximately three quarters of the solid product. Add 1.0 g of glycine and heat under reflux for 1 hour. Stirring with a magnetic stirrer under the heating mantle helps give a gentle reflux. **Be careful to avoid bumping. Material can bump out of the flask through the condenser if you are not careful.** Filter off the solid from the hot solution and air dry.

Characterization of Products: Obtain the IR spectrum of both products. Perform a group theoretical analysis to confirm the identity of both products. To begin this analysis, determine the point groups of the *cis* and *trans* isomers.



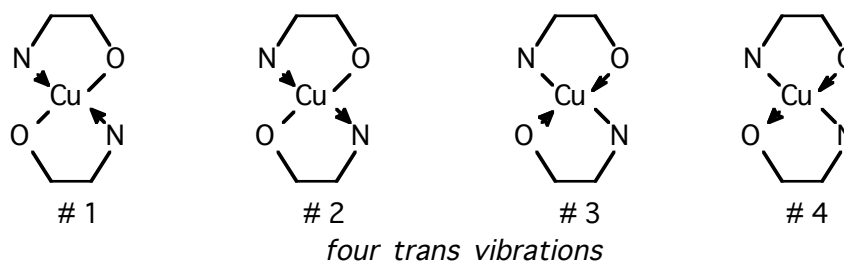
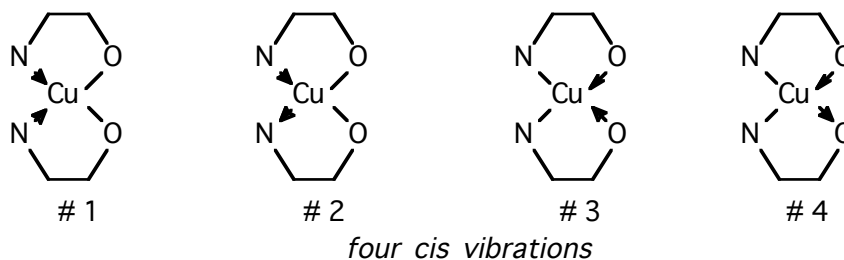
cis



trans

Use the character tables in an inorganic text to help with your analysis. When you have determined the point groups, check your answer with me if you are unsure.

Now consider the stretching vibrations of the *trans* and *cis* isomers, which are shown below. The arrows on the bonds indicate the direction the outer atom is moving. The copper is stationary.



- Using the point group corresponding to each isomer, determine the symmetries of each stretching vibration.
- Check if each stretching vibration is IR active. How many stretching vibration peaks would you expect to see in the IR spectrum of the *cis* isomer? What about the *trans* isomer?
- Look at the given IR spectra in the region 200-600 cm^{-1} . The Cu-N bond stretches occur in the region 450-500 cm^{-1} and the Cu-O bond stretches lie in the region 250-350 cm^{-1} . In both spectra you will see a single peak at 390 cm^{-1} : ignore it, because it does not correspond to a Cu-N or Cu-O stretch.
- Think about your group theoretical analysis. How many stretches did you expect to see for the *cis* isomer? For the *trans* isomer? Does this help you establish the identity of the two isomers you have prepared?
- Obtain mull spectra of both isomers and look at the fingerprint region between 800 and 1200 cm^{-1} . The *trans* isomer is centrosymmetric (has a center of inversion symmetry) whereas the *cis* isomer is not. Does there appear to be any difference between the complexity of spectra of centrosymmetric complexes compared to those of noncentrosymmetric complexes.

HINT: One of the isomers fits this point group

C_{2h}	E	C_2	i	σ_h	
A_g	1	1	1	1	x^2, y^2, z^2, xy
B_g	1	-1	1	-1	xz, yz
A_u	1	1	-1	-1	z
B_u	1	-1	-1	1	x, y

Thoughts/Reflections

1. Considering the conditions for your syntheses, comment on which isomer is produced under kinetic control and which isomer is produced under thermodynamic control.
2. Why is the IR spectrum of the trans compound much simpler than that of the *cis*, especially in the fingerprint region (800-1200 cm^{-1})?

References (in addition to any Inorganic textbook)

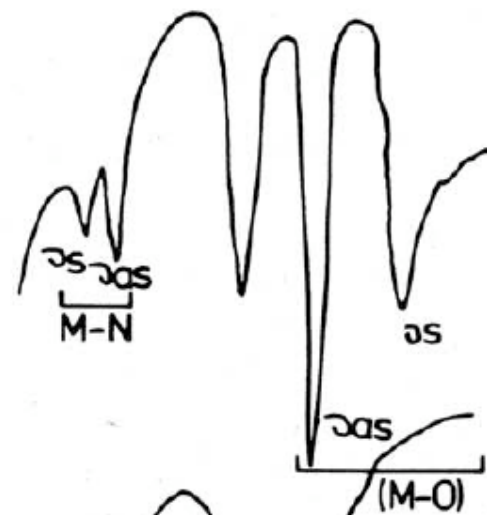
1. O'Brien, P. J. *Chem. Educ.* **1982**, *59*, 1052.

Assignment

An experimental synopsis (including an abstract, experimental data, and the answers to the thoughts/reflections above) is due **Oct 19**.

GEOMETRIC ISOMERS OF BIS-GLYCINATO COPPER(II)

ISOMER 1



ISOMER 2

