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Geometric Isomerism in Octahedral Complexes: Synthesis, Characterization, and Reaction of *Trans*-Dichlorobis(ethylenediamine)cobalt(III) Chloride

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Abstract The synthesis of the coordination complex *trans*-dichloro*bis*(ethylenediamine)cobalt(III) chloride is a classic experiment and can provide an opportunity for inclusion of diverse concepts if additional activities are incorporated. This laboratory experiment outlines the use of modern instrumentation such as UV-Vis spectrophotometer for thermal ligand substitution monitoring, and the magnetic susceptibility balance for confirmation of the electron configuration of the cobalt(III) center in *trans*-dichloro*bis*(ethylenediamine)cobalt(III) chloride.

Keywords Geometric isomerism, Octahedral cobalt(III) complexes, Aquation, Ligand substitution, Oxidation-reduction

1. Introduction

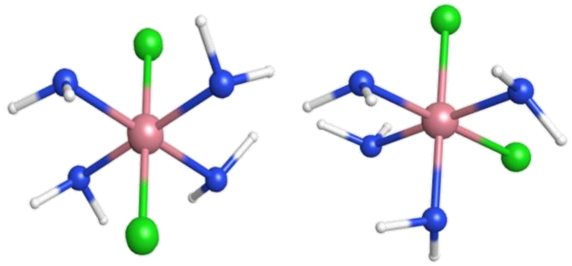

Figure 1. Example of geometric isomers with octahedral geometry

Disubstituted planar and octahedral complexes exhibit both cis and trans stereochemistry. **Figure 1** shows an example of octahedral geometric isomers. Octahedral cobalt(III) complexes that are low-spin d^6 configuration are diamagnetic and considered stable, [1] having a filled t_2g subshell. Due to the relative inertness of octahedral cobalt(III) metal centers, [1] their ligand substitution and isomerization reactions are slow compared to the complexes of many other transition metals. This allows us to monitor the substitution of chloride by water in the green *trans*-dichloro*bis*(ethylenediamine)cobalt(III) chloride, *trans*-$[Co(en)_2Cl_2]Cl$ complex. The aquation product, $[Co(en)_2Cl(H_2O)]Cl_2$, is purple in color and has cis geometry. [2]

This laboratory experiment introduces inorganic chemistry undergraduate students to the synthesis and characterization of coordination compounds, geometric isomerism, ligand substitution, magnetism and d^n electron configuration, and the use of UV-Vis spectroscopy for monitoring reaction progress. It also provides students the opportunity to see the energy and stability difference of geometric isomers.

This is a two-week laboratory experiment. The synthesis of trans complex will be done during the first meeting, then characterization of *trans*-$[Co(en)_2Cl_2]Cl$ and aquation will be on the second week. Upper level undergraduate students can be asked to calculate the rate constant for the ligand exchange reaction of water for a chloride ion in *trans*-dichlorobis(ethylenediamine)cobalt(III) ion, with the assumption of a pseudo-first order rate law. [3]

2. Experimental Section

Customized side arm test tubes (**Figure 2**) were fabricated at Illinois College Department of Chemistry by the laboratory manager, Andy Stice. Alternatively, these can be purchased from several manufacturers such as Eisco labs, Haines Educational, and OnlineScienceMall, among others. Reagents were obtained from commercial sources and used as received. Thermal monitoring of the ligand substitution was carried out using Cary-60 UV-Vis spectrophotometer. The cuvette is immersed into hot water bath and transferred every 2 minutes to the UV-Vis spectrophotometer for a wavelength scan.

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Students were provided with an experimental handout and asked to answer the following prelab questions:

1) Draw the structure of the complexes, *trans*-$[Co(en)_2Cl_2]Cl$ and *cis*-$[Co(en)_2Cl(H_2O)]Cl_2$.
2) Balance the oxidation-reduction reaction involved in the synthesis of *trans*-$[Co(en)_2Cl_2]Cl$.

$$Co^{2+} + H^+ + H_2O_2 \rightarrow Co^{3+} + H_2O$$

Which species is the oxidizing agent? Which is the reducing agent?

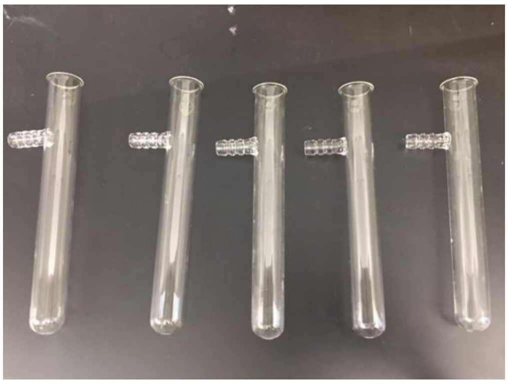

Figure 2. Customized side arm test tubes

2.1. Synthesis of *Trans*-Dichloro*bis*(ethylenediamine)co-balt(III) Chloride

A modified procedure from Szafran, Pike, and Singh [4] for the synthesis of *trans*-dichloro*bis*(ethylenediamine) cobalt (III) chloride, *trans*-$[Co(en)_2Cl_2]Cl$, was performed. $CoCl_2{\cdot}6H_2O$ (300 mg, 1.26 mmol), water (2.5 mL), and 10% ethylenediamine (1 mL) were added to the side arm test tube. Dropwise addition of 0.300 mL of a 30% H_2O_2 solution was then done, followed with dropwise addition of 0.600 mL of concentrated HCl. A Pasteur pipet was inserted through a rubber stopper with a drill hole, to serve as air inlet, **Figure 3**. The test tube was then clamped in a hot water bath. Air was drawn slowly and continuously through the solution by connecting the side arm of the test tube to a vacuum source (aspirator or hood vacuum) by way of a water trap using appropriate tubing, **Figure 4**. The reaction was heated and oxidized until green crystals were apparent. Additional water should be added if the test tube is almost dry but has no formation of green crystals. The mixture was cooled in ice bath and then filtered by suction. The green crystals were washed twice with 2-mL portions of cold methanol, and then two 2-mL portions of cold diethyl ether. The filtrate that contains the HCl co-solvate (additional crystalline product) was discarded. The crystals were placed on a small watch glass and heated in an oven at 110°C until the next lab session.

The balanced chemical equation for the synthesis of *trans*-$[Co(en)_2Cl_2]Cl$ is as follows:

$$2CoCl_2{\cdot}(H_2O)_6 + H_2O_2 + 2\,HCl + 4\,en \rightarrow 2\,[Co(en)_2Cl_2]Cl + 14\,H_2O$$

2.2. Characterization

The green *trans*-$[Co(en)_2Cl_2]Cl$ compound was weighed, and the percentage yield was obtained. The product was characterized by IR and UV-Vis spectroscopy.

The IR spectrum of the product, **Figure 5**, was acquired using the Varian 640-IR FT-IR spectrophotometer. The molar extinction coefficient of *trans*-$[Co(en)_2Cl_2]Cl$ was determined by preparing 5 mL aqueous solutions of 0.02, 0.04, 0.08, 0.12, 0.16 M *trans*-$[Co(en)_2Cl_2]Cl$. The UV-Vis spectra were obtained from 700 to 300 nm using the Cary-60 UV-Vis spectrophotometer.

The magnetic moments of *trans*-$[Co(en)_2Cl_2]Cl$ and the starting material, $CoCl_2{\cdot}(H_2O)_6$, were determined by the Gouy technique. The calibration constant of the instrument was determined using mercury tetrathiocyanatocobaltate(II) as the standard reference material. Students were introduced and provided with the formula of the magnetic moment (μ_{eff}), as well as diamagnetic corrections for the ligands, [5] for positive reading (paramagnetic case).

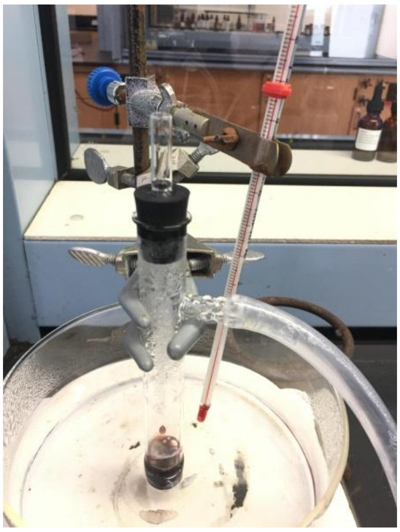

Figure 3. A Pasteur pipet was inserted through a rubber stopper with a drill hole, to serve as air inlet

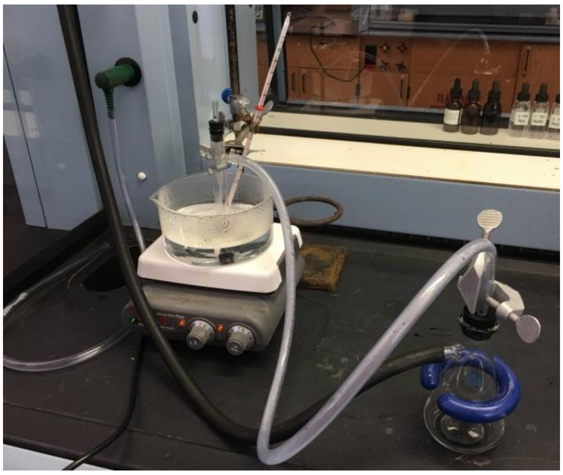

Figure 4. Microscale synthesis of *trans*-$[Co(en)_2Cl_2]Cl$ complex using a test tube with side arm attached to water-trap then vacuum source

2.3. Aquation of *trans*-[Co(en)$_2$Cl$_2$]Cl: Synthesis of *Cis*-Dichloro*bis*(ethylenediamine)cobalt(III) Chloride

UV-Vis spectrophotometer was used to observe the isomerization/aquation process at 80°C.

A glass cuvette was filled with a few milliliters of 0.016 M aqueous *trans*-[Co(en)$_2$Cl$_2$]Cl solution. The cuvette was placed in a hot water bath then transferred to the UV-Vis sample holder for wavelength scan from 700 to 300 nm, in 2-minute intervals. Chloride substitution with water is complete once the solution turns purple permanently. The resulting solution contains the *cis*-[Co(en)$_2$Cl(H$_2$O)]Cl$_2$ complex. The UV-Vis spectra display the absorption maxima for *trans*-[Co(en)$_2$Cl$_2$]Cl and *cis*-[Co(en)$_2$Cl(H$_2$O)]Cl$_2$, **Figure 6**.

The aquation reaction [6] involved is:

$$[Co(en)_2Cl_2]^+ + H_2O \rightarrow [Co(en)_2Cl(H_2O)]^{2+} + Cl^-$$

Students can be asked to completely evaporate the water from the aqueous purple solution using the roto-evaporator. This step will show students the more stable isomer in the solid state.

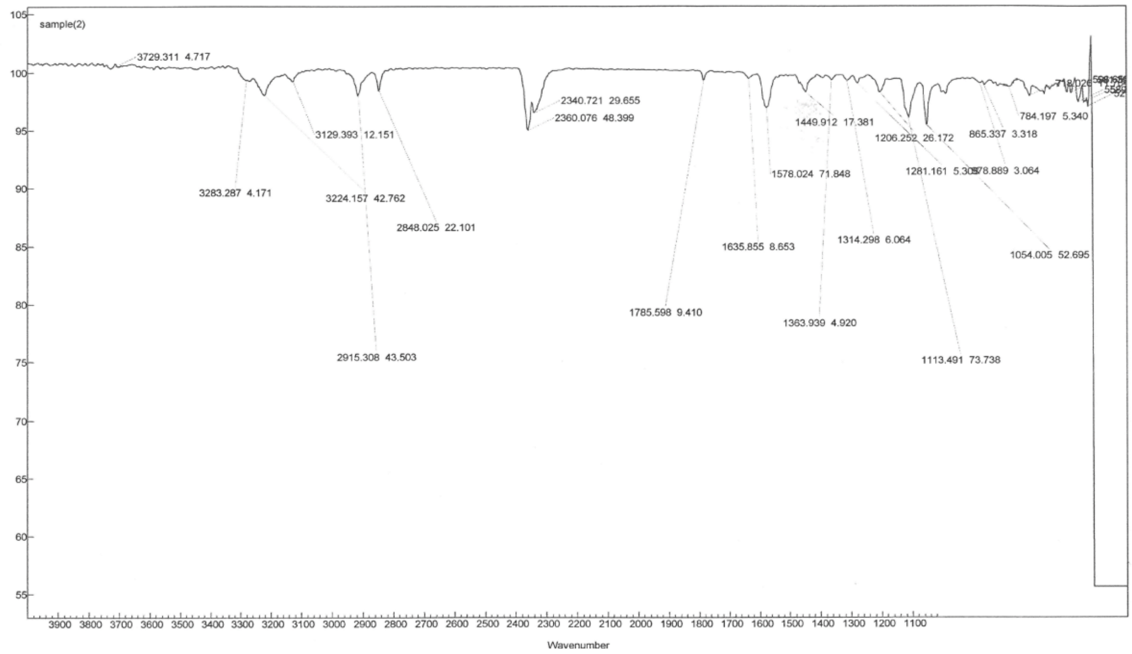

Figure 5. IR spectrum of *trans*-[Co(en)$_2$Cl$_2$]Cl

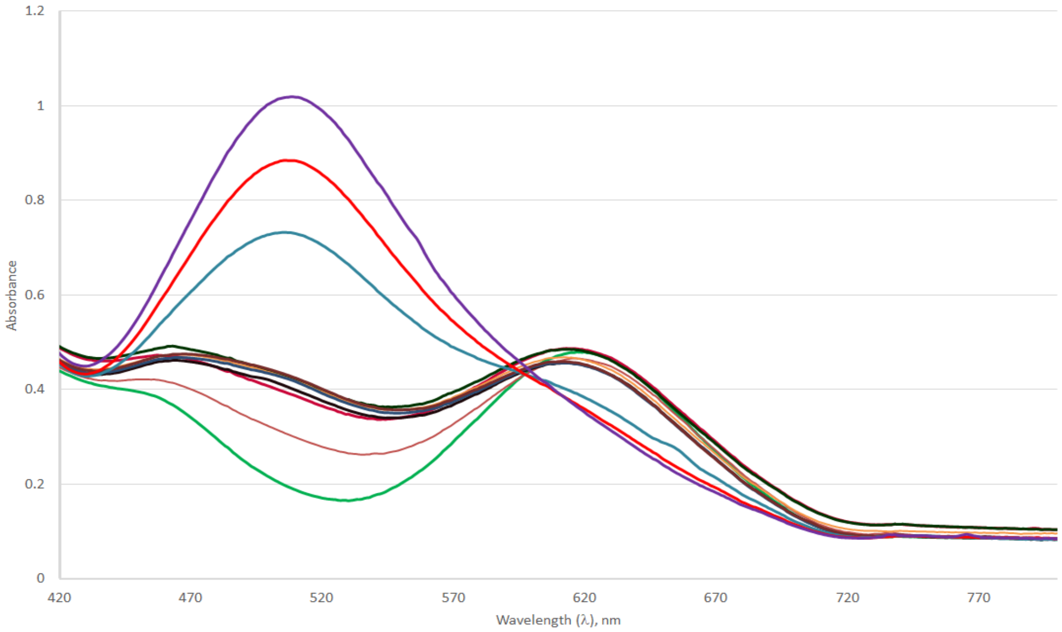

Figure 6. UV-Vis spectra for the water substitution of chloride in *trans*-[Co(en)$_2$Cl$_2$]Cl

3. Results and Discussion

The set-up for the microscale synthesis of *trans*-$[Co(en)_2Cl_2]Cl$ is shown in **Figure 4**. The initial and final colors of the mixture are shown in **Figure 7**. The final product *trans*-$[Co(en)_2Cl_2]Cl$ obtained after filtration during the first lab meeting is shown in **Figure 8**. Typical student yields for the synthesis of *trans*-$[Co(en)_2Cl_2]Cl$ were in the range of 45 to 50%.

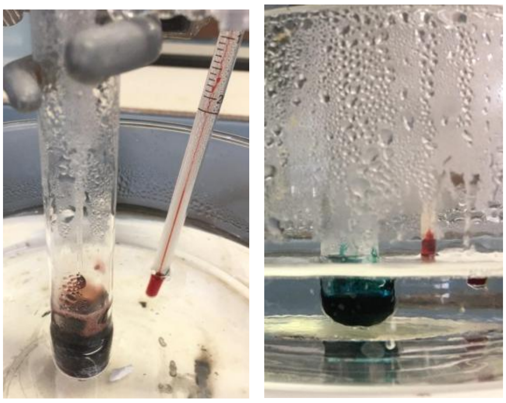

Figure 7. Initial and final color of the mixture

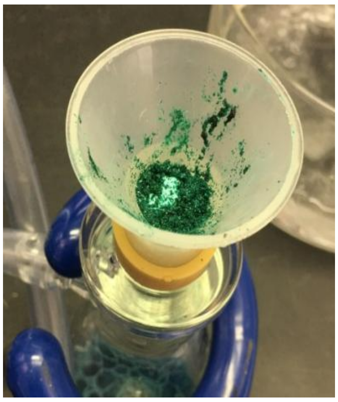

Figure 8. *Trans*-$[Co(en)_2Cl_2]Cl$

The IR spectrum of solid *trans*-$[Co(en)_2Cl_2]Cl$ (**Figure 5**) showed two absorption bands in the 3200 cm^{-1} region corresponding to the NH_2 stretching vibrations of the coordinated ethylenediamine; whereas, the absorption bands in the 1635 to 1578 cm^{-1} can be assigned to the NH_2 deformation frequencies.

Absorbance, at the maximum wavelength of 618 nm, as a function of concentration was plotted to determine the molar extinction coefficient ($\varepsilon = 37.00\ M^{-1}cm^{-1}$).

The formation of *cis*-$[Co(en)_2Cl(H_2O)]Cl_2$ was monitored at 80°C over time by UV-Visible spectroscopy in water, which shows the disappearance of the peak at 618 nm and the appearance of another peak at 509 nm, **Figure 6**. The initial green aqueous solution of *trans*-$[Co(en)_2Cl_2]Cl$ turned purple and was converted to *cis*-$[Co(en)_2Cl(H_2O)]Cl_2$, **Figure 9**.

The magnetic susceptibility balance reading of *trans*-$[Co(en)_2Cl_2]Cl$ (**Figure 10**) was determined to be negative, indicating the diamagnetic nature of the cobalt center.

Evaporation, using a roto-evaporator, of the resulting aqueous solution of *cis*-$[Co(en)_2Cl(H_2O)]Cl_2$ yielded green crystals.

Figure 9. *Cis*-$[Co(en)_2Cl(H_2O)]Cl_2$ complex

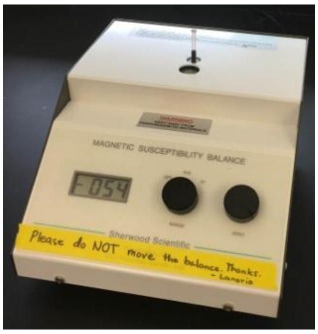

Figure 10. Negative reading from magnetic susceptibility balance for the *trans*-$[Co(en)_2Cl_2]Cl$ complex

4. Conclusions

This lab was successfully carried out by CH 332 Advanced Inorganic students in the Fall 2017 at Illinois College. The negative magnetic moment confirmed the successful oxidation of Co(II) to Co(III), and the d^6 electron configuration of the cobalt(III) center. The IR spectrum showed the NH_2 vibrational modes of the coordinated ethylenediamine ligand. The maximum absorption wavelengths obtained from UV-Vis spectral analysis of *trans*-$[Co(en)_2Cl_2]Cl$ and *cis*-$[Co(en)_2Cl(H_2O)]Cl_2$ are 618 nm and 509 nm, respectively. Students realized the importance of further use of modern instrumentation in monitoring reaction and determination of kinetic parameters, as noted in their lab reports.

ACKNOWLEDGEMENTS

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