

Synthesis and Decomposition Kinetic Studies of Bis(lutidine)silver(I) Nitrate Complexes as an Interdisciplinary Undergraduate Chemistry Experiment

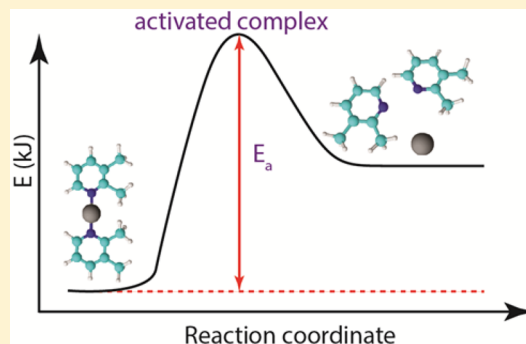
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S Supporting Information

ABSTRACT: Interdisciplinary experiments are being offered in upper-division chemistry laboratory courses in an attempt to encourage students to make a connection between techniques learned in one discipline to affirm chemical principles that form the basis of chemical reactions in another chemistry discipline. A new interdisciplinary experiment is described in which students synthesize bis(lutidine)silver(I) nitrate complexes, where the position of the methyl groups on the pyridine ring varies. The stability of these metal complexes is evaluated as a function of basicity of the ligand by studying the rate of decomposition of the metal complex through isothermal thermogravimetric analysis. An Arrhenius plot is used to determine activation energies for the decomposition reaction, and the data are used to establish the positive correlation between the activation energy with the basicity of the lutidine ligand.

KEYWORDS: Upper-Division Undergraduate, Interdisciplinary/Multidisciplinary, Laboratory Instruction, Synthesis, Coordination Compounds, NMR Spectroscopy, Kinetics, Thermal Analysis, Acids/Bases



INTRODUCTION

As a result of recent curriculum changes at our institution, an upper-division chemistry laboratory course is offered in the third year as an integrated course with experiments in all the chemistry disciplines. In addition to discipline-specific experiments, new interdisciplinary experiments are being designed and offered that combine two or more chemistry disciplines under the umbrella of one experiment. One such experiment is described herein that combines inorganic metal complex synthesis with physical chemistry analysis (kinetic studies) to measure the stability of the metal complexes using isothermal thermogravimetric analysis (TGA). Students use ^1H NMR spectroscopy as a tool to verify the progress of the reaction and purity of the product and are introduced to TGA to obtain information about the composition and stability of the metal complex. The relationship between the ligand's basicity and strength of the metal–ligand bond is assessed. It is expected and found that a higher activation energy (E_a) for the decomposition of the complex is positively correlated with an increasing basicity of the ligand.¹

Dimethyl-substituted pyridines (lutidines) were chosen as the ligands for this experiment. Lutidines have six positional isomers based on the relative position of the two methyl groups: 2,3-lutidine, 2,4-lutidine, 2,5-lutidine, 2,6-lutidine, 3,4-lutidine, and 3,5-lutidine (Figure 1). These compounds are used as chemical intermediates in many industrial processes such as the production of insecticides, pharmaceuticals, and

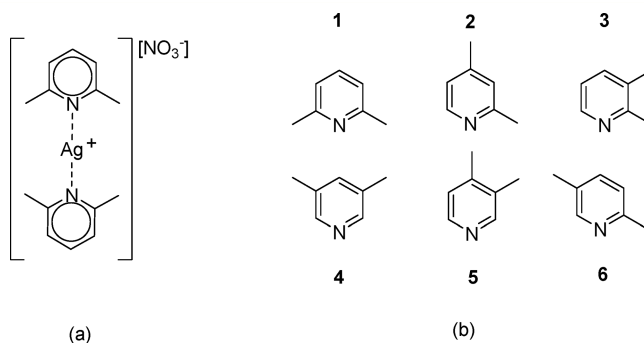


Figure 1. (a) Bis(2,6-lutidine)silver(I) nitrate. (b) Chemical structures of all the lutidines. 2,6-Lutidine (1); 2,4-lutidine (2); 2,3-lutidine (3); 3,5-lutidine (4); 3,4-lutidine (5); 2,5-lutidine (6).

food additives.^{2,3} Because of their extensive use, some of the lutidines pose an environmental concern as the methyl group slows down the biodegradation process considerably.² Lutidines are interesting compounds to study in the undergraduate laboratory as pyridine derivatives that can be easily functionalized, and they have a range of closely related compounds with varying basicity.^{1,4,5} Lutidine coordinates as

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a sigma-donor, monodentate ligand with most metal ions.^{6–8} The electronics and steric hindrance of the molecule varies with the position of the methyl groups. Steric hindrance is significant when the methyl groups are in the 2 and/or 6 position, whereas the presence of the methyl group at the 4 position decreases resonance stabilization of the compound when considering π back-bonding from the metal ion.

This project was developed with all six lutidines and their respective silver(I) complexes (Figure 1). However, the undergraduate experiment is designed such that a pair of students only works with two lutidines at a given time. This is done to provide variability so that two groups of students could be attempting two variations of the same experiment with a different set of lutidines. This experiment has been carried out by 22 students in a third-year laboratory course and is completed over two, 4-h laboratory periods. In the first part, students synthesize and characterize two silver complexes with positional isomers of lutidines that vary in the position of one of the methyl groups (Scheme 1). The bis(lutidine)silver(I)

Scheme 1. Synthesis of Bis(lutidine)silver(I) Complexes



nitrate complexes are characterized by ^1H NMR spectroscopy since $\text{Ag}(\text{I})$ is a d^{10} diamagnetic ion. The second laboratory period is used for the kinetic analysis of the product where each of the complexes is subjected to isothermal TGA with a predetermined controlled temperature. The TGA data are used to analyze the decomposition reaction of the complex, a first-order kinetic process.¹ The availability of six-ligand-isomers provides the opportunity to use group work and pooled results to explore the effect of substituent position on the experimental outcome. The pedagogical goals of this experiment are

- (1) To introduce students to a new technique, isothermal TGA, for collecting kinetic data for a decomposition reaction.
- (2) To teach students how to use ^1H NMR spectroscopy as a tool to characterize their product, a metal complex in this case.
- (3) To study the effect of basicity on the stability of a metal complex as the position of a substituent is varied.
- (4) To highlight the interdependence of concepts taught in different subdisciplines of chemistry. Students are typically familiar with assessing the stability of metal complexes using thermodynamic parameters; however, in this experiment, kinetic studies provide an alternative method to access the same results.

Interdisciplinary experiments were recently introduced into a traditional mix of experiments, and students were surveyed about the effect of this practice on their acquired knowledge. Student feedback indicated that this approach to interdisciplinary learning in chemistry laboratories was beneficial in their final-year undergraduate research (thesis) projects, in which they are required to integrate knowledge from multiple fields to achieve desirable results. In this experiment, specifically, they were able to utilize the data obtained from the physical techniques to infer information about the relative stability of an inorganic coordination complex.

EXPERIMENTAL OVERVIEW

Synthesis and Characterization

Students work in pairs. Each group chooses two lutidines that vary in the position of one of the methyl groups, for example, 1 and 2, 3 and 4, etc. Lutidine (2 equiv) is added to a solution of AgNO_3 in a minimum quantity of ethanol, water, or a mixture of water and ethanol, and the pure crystalline product is obtained by cooling the solution. The metal complexes are characterized by melting point and ^1H NMR spectroscopy (in CDCl_3). In the ^1H NMR spectra, the peaks corresponding to the protons in coordinated lutidine appear more downfield as compared to those in the unbound ligand.

Thermogravimetric Analysis

Students determine the desired temperature for isothermal TGA by analyzing a thermal degradation plot; a known amount of the complex is subjected to increasing temperature with a constant rate of heating. On the basis of the degradation pattern, the temperature at which the ligand dissociates from the complex is determined. These data are collected for students by teaching assistants. With the help of an instructor/teaching assistant, students determine the desired temperature range for the isothermal TGA experiment. In isothermal TGA, a substrate sample is subjected to constant temperature under positive flow of nitrogen to monitor the degradation of the compound as a function of time; it is repeated at two other temperatures (10 °C apart). Because of time constraints in a given laboratory period, students run their sample only at one temperature and are provided with the data for two other temperatures by an instructor. Rate constants for the decomposition reaction are determined by isothermal kinetic analysis of data from all three temperatures. These data points are used to prepare an Arrhenius plot to obtain an activation energy for the decomposition of the complex. A detailed experimental procedure is in the Supporting Information.

HAZARDS

Standard personal protective equipment is required while performing the experiment. Dimethylpyridines (or lutidines) are odorous, flammable liquids that may be harmful if the vapors are inhaled or the liquid is ingested. While dispensing the liquid, nitrile gloves should be worn, and the reaction must be carried out in a fume hood to avoid inhalation. Silver nitrate is a toxic, oxidizing material and can cause skin damage if absorbed. Deuterated chloroform is a volatile liquid that can cause irritation in the respiratory tract. Hence, the NMR samples with deuteriochloroform are prepared in a fume hood with nitrile gloves to avoid inhalation and skin contact. Temperatures on a TGA instrument are maintained below 200 °C to minimize the formation of silver byproducts that adhere to the surface of the crucible in a TGA instrument. Although hazards for $\text{Ag}(\text{I})$ complexes are not known, students are told to assume that these compounds retain the hazards of the starting materials and should be handled in a similar manner.


RESULTS AND DISCUSSION

All six lutidine silver(I) nitrate complexes ($(\text{AgL}_2)\text{NO}_3$) can be synthesized by a procedure adapted from a study¹ that describes the synthesis of silver(I) complexes with many substituted pyridines including some of the lutidines. However, the third-year undergraduate laboratory experiment was

designed such that a pair of students was given only two of the lutidines to synthesize the complexes and to perform TGA studies. This ensured novelty in the experiment as two pairs of students may attempt this experiment simultaneously, but they can work with a different set of lutidines and, hence, have a variable collection of properties to discuss based on their results. The set of lutidines chosen for an experiment was varied in the position of only one of the methyl groups (e.g., **1** and **4** or **2** and **5** would be paired together). This limitation was chosen so that students encountered only one factor that varied the electronics of the ligand, and students were able to discuss the effects of this change on the coordination chemistry of the corresponding silver(I) complex. The overall student yields ranged from 30–85% based on the solubility of the complex. Ethanolic solutions were used to synthesize the complexes except for the synthesis of the **1** and **5**, which were synthesized in deionized water due to their higher solubility in ethanol compared to the other four complexes. The melting points of the synthesized complexes agreed well with literature values, which ranged from 115–203 °C.¹

The ¹H NMR spectrum of each complex (Supporting Information) clearly showed only one set of peaks, shifted downfield as compared to the uncomplexed ligand, indicating the purity of the products obtained. This verified that the coordinate bond to the silver ion resulted in the deshielding of electrons around the hydrogens of lutidine. The NMR peak assignments agreed with recent studies where 1D and 2D NMR data were published for some lutidines and silver(I) lutidine complexes.^{6,8} Student data for 2,4-lutidine (Table 1) show that

Table 1. Change in ¹H NMR Chemical Shift of 2,4-Lutidine when Coordinated to Silver Nitrate^a

Ligand	Compounds	H _a	H _b	H _c	H _d	H _e
	2,4-lutidine	2.43	6.88	2.21	6.81	8.26
	Bis(2,4-lutidine)silver(I) nitrate	2.69	7.17	2.38	7.08	8.51

^aNMR spectra at 300 MHz in CDCl₃ with reference of CHCl₃ at 7.270 ppm. All numbered values in ppm.

the complexing of the lutidine results in a downfield chemical shift (deshielding) for the protons around the aromatic ring. The chemical shift analysis for all of the complexes is provided in the Supporting Information.

As the relative position of the methyl group is varied, the basicity and steric factors of lutidine as a ligand also vary.¹ Consequently, the strength of the Ag–N bond and, thus, the overall stability of the metal complex are affected by the basicity of the ligand; the more basic the ligand, the stronger the metal–ligand bond. Although steric factors do not have a direct effect on the values of the stability constants, the crystallization of the product from the synthesis clearly showed a preference for lutidines with a more electronegative and accessible nitrogen. While there are many methods available for comparing the stability of the metal complexes,⁸ studying the rate of decomposition of the complex was chosen so that students were able to relate kinetics of the decomposition reaction and the thermodynamic stability of the complex as a characteristic of the metal–ligand bond strength. Similar studies have examined the stability of related metal complexes.^{9,10}

The activation energy required to break the metal–ligand bond is directly correlated to the strength of the bond. TGA was used to provide information about the composition and stability of a complex in the solid state. The analysis of thermal degradation plots indicated that silver(I) lutidine complexes tended to decompose and produce undesired byproducts beyond a certain temperature. Hence, the temperature range was varied between 90 and 130 °C depending on the lutidine chosen. To determine the activation energy for dissociation of the ligand, isothermal TGA was performed on each complex at three different temperatures that were 10 °C apart. The variable temperature range compensated for the occurrence of side reactions that sometimes obscure the reaction kinetics at higher temperatures.¹¹ An advantage of this experiment was that students were exposed to the imperfections of kinetic studies, and hence, they were encouraged to think critically about their results.

A known amount of the silver(I) lutidine complex was heated at a constant temperature for 40 min to 1 h, and the rate constant (*k*) was derived from the slope of a plot of the negative natural log of the fractional molar amount remaining ($-\ln(1 - \alpha)$) against time (Figure 2) (see Supporting

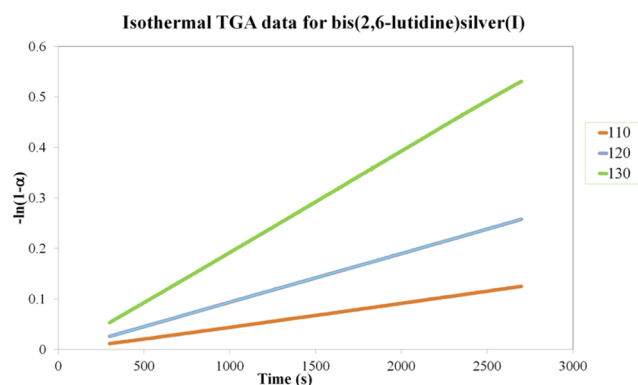


Figure 2. Isothermal TGA to determine rate constants for the decomposition of bis(2,6-lutidine)silver(I) nitrate at three different temperatures (110, 120, and 130 °C). (Note: Because of a large number of data points for each set of data, error bars have not been included.)

Information for details). Kinetic data were analyzed as described in literature,^{11,12} and plots for zero-, first-, and second-order, as well as the residual plots, were obtained. On the basis of the data analysis, it was concluded that, under the given conditions for this experiment, these complexes experienced pseudo-first-order kinetics for their degradation in this range of temperatures. The *k* values obtained from these data were used to prepare an Arrhenius plot to determine the activation energy for this decomposition reaction.

An Arrhenius plot (Figure 3) for bis(2,6-lutidine)silver(I) nitrate complex at 110, 120, and 130 °C gave an activation energy of 119.7 ± 4 kJ/mol for decomposition of this complex. Detailed kinetic data can be found in the Supporting Information.

Activation energies for the Ag(I) lutidine complexes and p*K*_a values for the six lutidines (Table 2) are comparable to the corresponding values reported previously.¹ As expected, the Arrhenius activation energies showed a direct association to the basicity of the pyridine ligand. A higher p*K*_a resulted in a

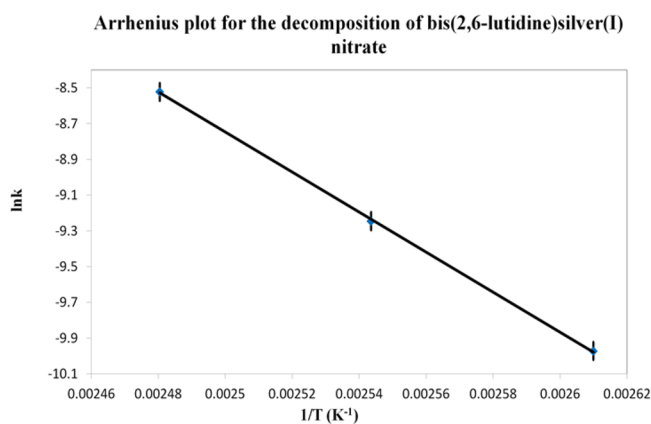


Figure 3. Arrhenius plot for the decomposition of bis(2,6-lutidine)-silver(I) nitrate at 110, 120, and 130 °C. The activation energy for this complex is 119.7 ± 4 kJ/mol.

Table 2. Relationship between pK_a of Uncomplexed Lutidine against the Experimentally Obtained Student E_a Values for the Decomposition of the Corresponding Complexed Lutidine Silver Complex

complex	pK_a of lutidine ^a	activation energy (kJ/mol) ^b
bis(2,5-lutidine)silver(I) nitrate	6.18	96.0
bis(3,5-lutidine)silver(I) nitrate	6.34	104.1
bis(2,3-lutidine)silver(I) nitrate	6.57	114.9
bis(2,6-lutidine)silver(I) nitrate	6.75	119.7
bis(3,4-lutidine)silver(I) nitrate	6.50	71.2
bis(2,4-lutidine)silver(I) nitrate	6.99	121.8

^a pK_a values from literature.^{1,4,5} ^bThe reported E_a values have an error of ± 4 kJ/mol.

stronger Ag–N bond. Hence, a higher activation energy was required to break the bond.

Further analyses of the data in Table 2 showed a positive correlation between E_a and pK_a values with two different trends (Figure 4): those lutidines with a methyl at the 4 position and those without a methyl at the 4 position. Complexes without a methyl group at the 4 position were more stable than complexes with a methyl group at the 4 position substituent, correlating to the basicity. This phenomenon of different trends was explained briefly in the literature.^{1,13} It was proposed that the presence of a methyl group at the 4 position weakened the

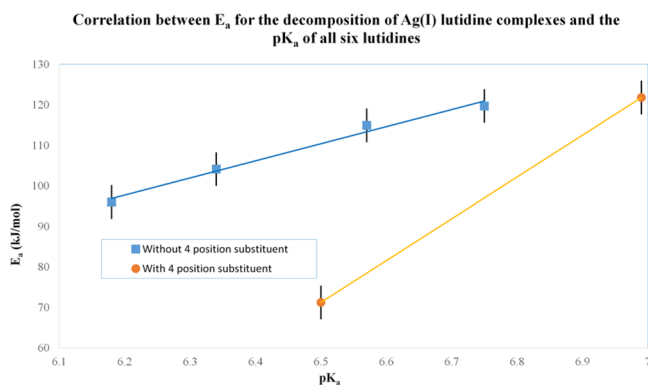


Figure 4. Graph of pK_a versus E_a (Table 2) showing a trend in the complexes with a methyl group at the 4 position and the complexes without a methyl group at the 4 position.

metal–ligand π back-bond because resonance forms of the pyridine ring would place the electron density from this bond on the carbon with the methyl group, which is not favorable (Figure 5). This is evident from the relative E_a values.

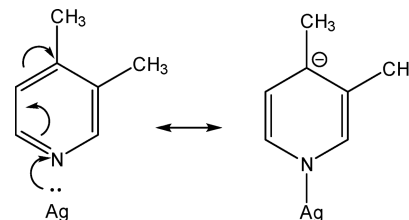


Figure 5. Resonance form of Ag(I) with 3,4-lutidine. Presence of the electron donating methyl group at the 4 position renders this association less favorable.

The E_a for the 3,4-complex was much lower than that of the 3,5-complex (Table 2) even though the basicities of the two ligands are comparable.

On the basis of the experimental results, the assessment of the pedagogical goals was established as follows:

- (1) The students successfully learned how to use a new instrument, TGA, and analyze the collected data to obtain E_a values.
- (2) The students used their ^1H NMR spectra to prove the purity of the obtained product. They also learned how to assess the change in the chemical shift (more downfield in the metal complex) when a ligand is coordinated to a metal ion.
- (3) The students were asked to assess the trend in the E_a values as a function of basicity of the coordinated ligand. They recognized the direct relationship between the stability of the complex and the activation energy required to decompose the complex.
- (4) Student discussions clearly indicated that they could see a correlation between thermodynamic stability and kinetic data.

CONCLUSION

Feedback from students was that they really enjoyed this experiment as the NMR data gave them firm evidence that the reaction had gone to completion and the product was obtained as the pure complex. Their interest was intrigued by the discussion on the effect of moving a methyl substituent and the consequence of this substitution on the electronics and stability of the resulting complex. The students were also able to use activation energy as scientific evidence to study the stability of inorganic complexes while comparing the basicity of the ligands. Overall, this was a great experience for students and accomplished the goal of teaching students how to use a new technique to obtain evidence for an old, but crucial, concept of basicity and stability and to connect two chemistry subdisciplines in one experiment.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00243.

^1H NMR spectra and tables with peak assignments; plots for isothermal thermogravimetric data and Arrhenius

plots for determination of $\ln k$ and E_a ; notes for instructors; lab manual experiment for students with details of the synthetic procedure ([PDF](#), [DOCX](#))

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Akhvein, A.; House, J. E. Thermal studies on Solid Complexes of Silver Nitrate with Substituted Pyridines. *J. Inorg. Nucl. Chem.* **1970**, *32* (5), 1479–1484.
- (2) Scriven, E. F. V.; Murugan, R. Pyridine and Pyridine Derivatives. *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed.; John Wiley and Sons, Inc.: New York, 2005; Vol. 20, pp 1–33 and references therein.
- (3) Sims, G. K.; Sommers, L. E. Biodegradation of pyridine derivatives in soil suspensions. *Environ. Toxicol. Chem.* **1986**, *5* (6), 503–509.
- (4) House, J. E.; Strode, O. G. Kinetics of Decomposition of bis(2,5-dimethylpyridine)silver(I) nitrate. *Trans. Ill. State Acad. Sci.* **1968**, *61* (2), 356–359.
- (5) Handloser, C. S.; Chakrabarty, M. R.; Mosher, M. W. Experimental Determination of pK_a values by use of NMR chemical shift. *J. Chem. Educ.* **1973**, *50* (7), 510–511.
- (6) Sakharov, S. G.; Kovalev, V. V.; Gorbunova, Yu. E.; Kokunov, Yu. V. Structures of the silver complexes with lutidines according to the NMR data. Crystal structure of $[AgNO_3(3,5-Lut)_2]$. *Russ. J. Coord. Chem.* **2013**, *39* (2), 187–193.
- (7) Engelhardt, L. M.; Pakawatchai, C.; White, A. H.; Healy, P. C. Lewis-base adducts of group 1B metal(I) compounds. Part 12. Structural studies of some bis(methyl-substituted pyridine)-copper(I) and -silver(I) nitrates and perchlorates. *J. Chem. Soc., Dalton Trans.* **1985**, No. 1, 117–123.
- (8) Gift, A. D.; Stewart, S. M.; Kwete Bokashanga, P. Experimental Determination of pK_a Values by Use of NMR Chemical Shifts, Revisited. *J. Chem. Educ.* **2012**, *89* (11), 1458–1460.
- (9) Kruger, H.; de Waal, D. J. A. Ligand replacement at a square planar metal center: A kinetic experiment for the inorganic chemistry laboratory. *J. Chem. Educ.* **1987**, *64* (3), 262–265.
- (10) Sattar, S. Unified Kinetics and Equilibrium Experiment: Rate Law, Activation Energy, and Equilibrium Constant for the Dissociation of Ferriin. *J. Chem. Educ.* **2011**, *88* (4), 457–460.
- (11) Levine, I. N. *Physical Chemistry*, 5th ed.; McGraw Hill: New York, 2002; pp 532–533.
- (12) Elvas-Leitão, R.; Moreira, L.; Martins, F. Design of an Excel Spreadsheet To Estimate Rate Constants, Determine Associated Errors, and Choose Curve's Extent. *J. Chem. Educ.* **2006**, *83* (12), 1879–1883.
- (13) Murmann, R. K.; Basolo, F. The Stability of Silver(I) complexes of some 3- and 4- Substituted Pyridines. *J. Am. Chem. Soc.* **1955**, *77* (13), 3484–3486.