

Harding University

Scholar Works at Harding

Honors Theses

Honors College

Spring 4-29-2022

Synthesis and Characterization of Silver Thione Complexes

Audrey V. Lawrence

Harding University, alawrence1@harding.edu

Follow this and additional works at: <https://scholarworks.harding.edu/honors-theses>

 Part of the [Inorganic Chemistry Commons](#)

Recommended Citation

Lawrence, Audrey V., "Synthesis and Characterization of Silver Thione Complexes" (2022). *Honors Theses*. 16.

<https://scholarworks.harding.edu/honors-theses/16>

This Thesis is brought to you for free and open access by the Honors College at Scholar Works at Harding. It has been accepted for inclusion in Honors Theses by an authorized administrator of Scholar Works at Harding. For more information, please contact scholarworks@harding.edu.





HARDING UNIVERSITY
HONORS COLLEGE
Undergraduate Thesis Certification

This form is to certify that the undergraduate thesis prepared

By Audrey Lawrence

Entitled

Synthesis and Characterization of Silver Thione Complexes

Is dually approved by the Harding University Honors College and the student's thesis advisor(s) with input from the entire thesis advisory committee.

Thesis Advisory Committee:

Jaime M. Murphy, Ph.D.

Cindy White, Ph.D.

Michael G. Gutierrez, Ph.D.

This thesis, to the best of our knowledge, was published with the highest standards of academic integrity as outlined in the [Harding University Academic Integrity Policy](#) and in the use of any materials that are copyrighted.

Thesis Advisor(s):

Jaime M. Murphy, Ph.D.

Honors College Representative:

James L. Huff, Ph.D.

2022 Audrey Lawrence
Copyright © _____: The author assigns to Harding University a perpetual, non-exclusive, worldwide, royalty-free, sublicense agreement to 1) deposit and store electronic versions of your work in Scholar Works at Harding; 2) publish and make the work available to view and download for free and to use for non-commercial, research, educational or other academic purposes; 3) create back-up copies of the work for security and preservation purposes; and 4) Convert the work, without changing the content, to any other format or medium necessary for preservation, storage and use of the work.

Synthesis and Characterization of Silver Thione Complexes

*Audrey V. Lawrence**

Department of Chemistry, Harding University, Box 12272, Searcy, AR 72149.

alawrence1@harding.edu

ABSTRACT

Coordination polymers are repeating units of a coordination complex that have applications as catalysts, conductors, and magnets. In this work, silver (I) was the metal of choice because it behaves similarly to copper (I), which has been studied much more extensively and thione ligands were chosen due to their potential for forming coordination polymers. These coordination complexes with silver were synthesized by combining silver nitrate with thioacetamide, N,N'-diphenylthiourea, and 2-mercapto-1-methylimidazole. These complexes were characterized via IR spectroscopy, elemental analysis, and X-ray crystallography. Silver thioacetamide was determined to form a coordination complex through the sulfur to form a trigonal crystal lattice while silver methimidazole was determined to form a coordination polymer using sulfur as a bridging atom.

KEYWORDS *Silver. Coordination complexes. Coordination polymers.*

INTRODUCTION

Coordination compounds are the backbone of inorganic chemistry and have applications in materials, synthetic, and engineering chemistry. Coordination polymers are of interest to study due to their variable applications as catalysts, conductors, and magnets. These polymers form complex networks that have enough room in them to allow the transition metal to act as a catalyst in a given system without losing the metal ion to the system. Polymers also allow for the potential to maintain magnetism permanently with some metals by maintaining the unpaired spins of the electrons. Conductivity (which is a huge part of materials chemistry) can also be affected by the polymeric structure of a coordinating species, where the identity of the ligand involved can boost or hinder conductivity. However, not just any ligands can be used to build a coordination polymer. For coordination polymers to form, multidentate or bridging ligands are needed to connect metal atoms and the monomeric units of a polymer¹.

Copper is a metal known to form coordination complexes and has been studied extensively due to its conductive properties²⁻⁷. It's an entertaining metal to work with due to its color shifts, however, it is also difficult to achieve stable and consistent complexes due to its dual oxidation states. Copper reaction environments must be strictly controlled to maintain homogenous and stable complexes. With the behavioral similarities Cu (I) and Ag (I) have, silver is an ideal metal to try to synthesize coordination polymers without having to deal with unintentional oxidation. Silver (I) only has one oxidation state with an electron configuration of $5s^0 4d^{10}$, which makes it a much more stable metal to work with. It's not UV active due to the lack of d-d electron transitions, however it is diamagnetic, so silver complexes can be analyzed via NMR. This allows for an additional characterization tool that copper lacks in its Cu (II) state. Silver has also been seen to form coordination polymers, however, it is much less extensively studied⁸⁻¹¹. Some of silver's notable qualities are its antibacterial and anticancer

properties. Silver has been known to efficiently kill bacteria¹²⁻¹⁴, and it has also been implicated to successfully reduce tumor growth in some anticancer research^{8,15}.

The identity of the source of silver in the reaction has drastic impact on the final structure and whether or not it will form a coordination polymer. Differing metal to ligand ratios can be achieved in complexes by using AgCl or AgNO₃^{16,17}. AgCl tends to slip the Cl⁻ ions into the crystal structure as bridging points due to their smaller size which incorporates their electronic effects into the final complex^{1,11,16,18}. Using AgNO₃ to supply the silver reduces the tendency to include the counterion in the crystal structure¹⁹.

Both thioamides and thioureas have been found to form coordination polymers and complexes. For many of these, the sulfur is the primary coordination site²⁰⁻²³ however some complexes will bind to both the nitrogen and the sulfur¹⁹, or to both nitrogens²⁴. The sulfur is also known to act as a bridging atom, and combined with the multidentate qualities of the ligands, they work well for forming coordination polymers. There are heterocyclic thiourea ligands (such as 2-thiobarbituric acid) that are known to form stable coordination polymers with silver, so there is an open area of research¹⁰. Thus, all the ligands selected for this research are thiourea or thioamide derivatives.

This work is focused on discovering how successful thiones are at forming silver coordination complexes. With the three ligands that do not have proposed silver nitrate structures (thioacetamide, thiocarbanilide, and methimazole), it is desired to generate these structures for analysis and quantify the unique properties such as conductivity and antibacterial strength.

EXPERIMENTAL METHODS

General Information

AgNO₃ was acquired commercially and was combined with selected ligands in a soluble solvent. The ligands thioacetamide (**I**), 2-thiobarbituric acid (**II**), thiocarbanilide (N,N'-diphenylthiourea) (**III**), thiosemicarbazide (**IV**), and methimazole (2-mercapto-1-methylimidazole) (**V**) were used for this research (Figure 1). The resulting solutions were dried to isolate silver complexes and the solids were characterized via infrared spectroscopy, elemental analysis, and x-ray crystallography.

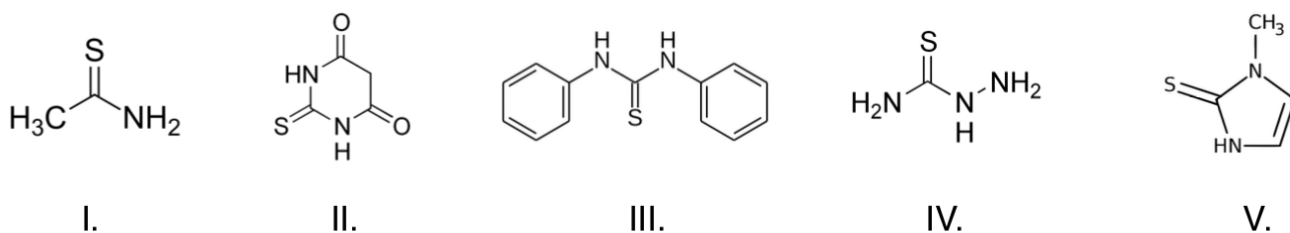
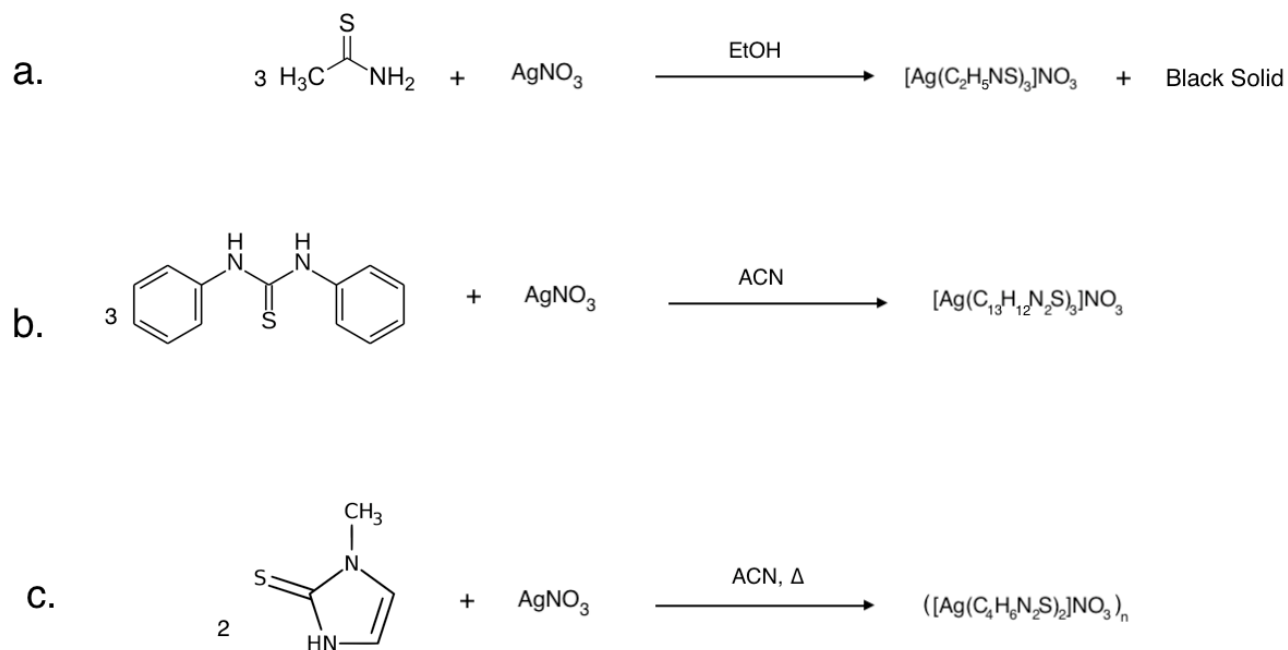


Figure 1: Ligands utilized in silver complex formation. **I:** thioacetamide. **II:** 2-thiobarbituric acid. **III:** thiocarbanilide. **IV:** thiosemicarbazide. **V:** methimazole.

AgNO₃ was combined with ligands **I**, **III**, and **V** in a 1:4 ratio by mass. 0.30 g of AgNO₃ was dissolved in 20 mL of the respective solvent and then 0.120 g of the ligand was added (scheme 1). The reaction was stirred via magnetic stirring for 1 hour and then the stir bar was removed. For **I**, a black precipitate formed and settled to the bottom of the flask. For crystallization, the supernatant solution was transferred to a diffusion chamber with diethyl ether. The ether was then allowed to evaporate to dry the crystals. In the case of **V**, crystals began to form when removed from heat, so the remaining solution was removed via vacuum filtration to leave behind the dried crystals. **III** was prepared in the same manner, however crystals did not form through evaporation. Recrystallization was unsuccessfully

attempted with acetone and ACN and diffusion with diethyl ether produced an unknown white precipitate. Dried silver thiocarbanilide was scraped off the bottom of the reaction flasks for analysis.

Silver barbituric acid is a coordination polymer that has been previously published and the structure has been illustrated¹⁰. Silver thiosemicarbazide has also been published, and the IR data were reported¹⁷. However, the previous syntheses of these complexes in the literature were vague and difficult to understand, so synthesis in this work was done to match the ligands **I**, **III**, and **V** as a comparison tool. 0.30 g of AgNO₃ were dissolved in 20 mL of hot methanol, and then 0.120 g of **II** and **IV** were added. 10 drops 0.1 M sodium hydroxide were added to **II** to aid in dissolution. The reactions were stirred for 1 hour and the resulting precipitants were dried via vacuum filtration.



Scheme 1: reaction conditions for experimental complexes. a. thioacetamide, b. thiocarbanilide, and c. methimazole.

Infrared Radiation Analysis

IR spectra of the ligands and complexes were acquired in the range 4000–550 cm⁻¹ via the tabletop iD5 Diamond ATR FTIR. IR peaks were compared to literature values of the **I**, **III**, **IV**, and **V** ligands to identify the amine and thione peak locations.

Elemental Analysis

Solid samples were dried fully and massed into 6 mg aliquots. These were sent to Atlantic Microlab Inc. for elemental analysis. Resultant percentages were used to calculate metal:ligand:counterion ratios.

X-ray Crystallography

Crystalline samples of silver thioacetamide and silver methimazole were sent to Dr. McMillen at Clemson University for X-ray crystallography. The X-ray intensity data were measured and the structure was solved and refined using the Bruker SHELXTL Software Package.

RESULTS AND DISCUSSION

Infrared Spectroscopy

When compared to the ligand, shifts were expected to occur at the nitrogen and sulfur peaks, based on the IR data of the ligands²⁵⁻²⁷. The shifts and their locations would be indicative of where coordination was occurring and potentially what type of coordination was occurring.

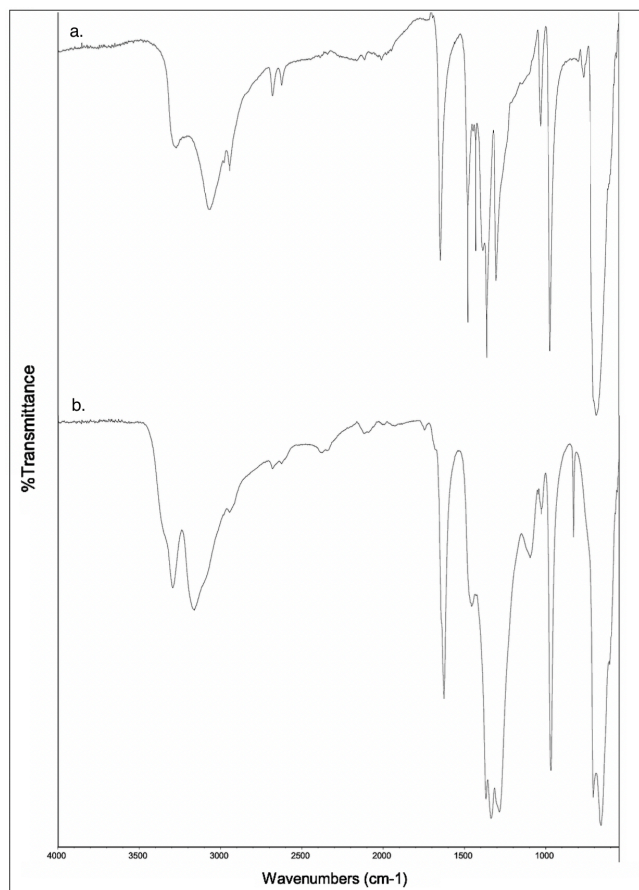


Figure 2: comparative IR spectra of a. thioacetamide and b. silver thioacetamide in cm^{-1}

For the thioacetamide, few changes are seen overall (figure 2), however shifts were seen in the amine region, as well as the thione region when coordinated with the silver. The amine peaks were identified to be 3069 cm^{-1} and 3290 cm^{-1} , which was compared with literature values of 3165 cm^{-1} and 3290 cm^{-1} ²⁶. These peaks shifted up to 3160 cm^{-1} and 3293 cm^{-1} respectively when coordination with the silver occurred (table 1). The higher shift seen in the amine region is attributed to a shortening of the N-H bond, which is likely occurring because of the hydrogen bonding happening between the ligand and the nitrate counterion. The thione peak is seen to decrease in wavenumber, shifting from 718 cm^{-1} to 702 cm^{-1} . The decrease in wavenumber is attributed to a lengthening of the C=S bond and is indicative of coordination through the sulfur.

This trend is also seen in the thiocarbanilide ligand, where the amine peaks of 3035 cm^{-1} and 3202 cm^{-1} shift to 3040 cm^{-1} and 3211 cm^{-1} . This could again be due to hydrogen bonding to the N-H group on the thiocarbanilide, but the amines on this ligand are secondary instead of primary. There is not a crystal structure to check with yet to conform. The thione region shifts from 700 cm^{-1} to 690 cm^{-1} , which is once again a good indicator that the complex is coordinating through the sulfur. These trends

match the increases and decreases seen in the amine and thione region of the IR of the silver thiosemicarbazide data¹⁷.

The methimazole complex is more difficult to determine where coordination is occurring through just the IR, due to the aromaticity of the heterocyclic ring, and the final bonding state of the sulfur. The resonance of the methimazole can elongate the double C=S bond into a single C-S bond. Additionally, the final structure of the silver methimazole has a sulfur coordinating to two silver atoms, which changes its bond length to 1.72 Å. As such, there is no peak on the experimental spectrum that reflects a known C-S or C=S peak²⁴, and other data are relied on to determine the coordination of the complex.

	Ligand N-H peak	Complex N-H Peak	Ligand C=S peak	Complex C=S peak
Thioacetamide	3069	3160	718	702
	3290	3293		
Thiocarbanilide	3035	3040	700	690
	3202	3211		
Thiosemicarbazide	3120	3117	803	789
	3218	3228		
Methimazole	3010	3012	664	-
	3103	3103		

Table 1: Significant IR shifts seen in the amine and thione regions. All values in cm⁻¹. Thiosemicarbazide data from the literature¹⁷.

Elemental Analysis

Elemental analysis data came back as percentages and are shown in table 2. The values were mathematically analyzed to determine the ratio of silver to ligand to nitrate counterion based on the mass of each element detected. These ratio data are shown in table 3, and are compared to the known ratios of thiobarbituric acid and thiosemicarbazide^{10,17}.

Complex	Analysis: found (calculated %)			
	C	H	N	S
Ag(thioacetamide) ₃	18.41 (18.23)	3.75 (3.83)	14.10 (14.18)	24.57 (24.33)
Ag(thiocarbanilide) ₃	54.57 (54.79)	4.43 (4.25)	11.48 (11.47)	11.51 (11.25)
Ag(methimazole) ₂	24.33 (24.12)	2.85 (3.04)	17.56 (17.59)	16.18 (16.10)

Table 2: average percent composition data from elemental analysis (n=2). All values in percent mass

Ligand	Ag:Ligand:NO3
Thioacetamide	1:3:1
Thiocarbanilide	1:3:1
Methimazole	1:2:1

Table 3: calculated ratios of silver to ligand to nitrate counterion for newly synthesized complexes

The thioacetamide and thiocarbanilide were both found to have the same ratio of 1:3:1. These ratios are different from the comparable silver thiosemicarbazide complex, which had a ratio of 2:3:2¹⁷

With elemental analysis being the most advanced form of analysis for thiocarbanilide, it could be assumed that thiocarbanilide adopts a similar structure to thioacetamide, however more data would be needed to back this claim. This hypothesis is supported by the IR data, where the thiocarbanilide is seen to coordinate through the sulfur.

Methimazole adopts a 1:2:1 ratio which is different from the heterocyclic comparable molecule (thiobarbituric acid with 1:1:1)¹⁰, but it is comparable to a copper methimazole complex (figure 3), indicating likelihood that it could be a coordination polymer⁵.

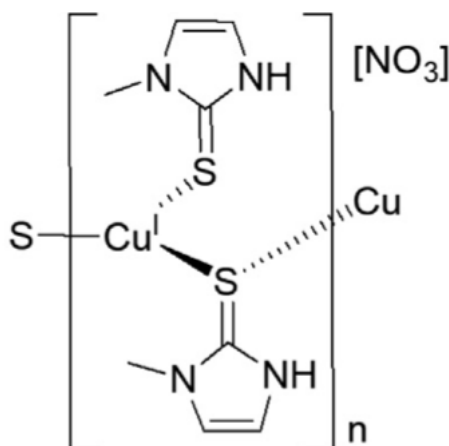


Figure 3: copper methimazole coordination polymer with 1:2:1 copper:methimazole:nitrate ratio⁵

X-Ray Crystallography

X-ray diffraction data were collected for the silver thioacetamide and silver methimazole crystals. With the thioacetamide, it was found to be a coordination complex where one silver atom is coordinating with three thioacetamide molecules through the sulfur (figure 4).

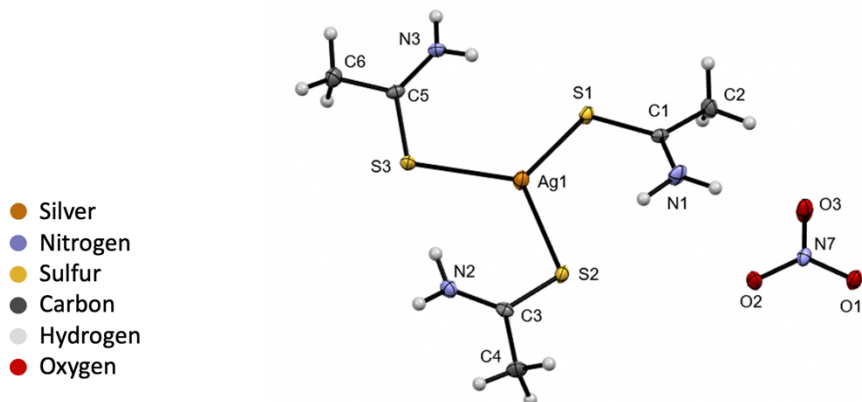


Figure 4: crystal structure diagram of silver thioacetamide

The complexes form a sheet that is held together via hydrogen bonding of the amines to the nitrate counterions (figure 5). The complex sheets stack vertically with the silver ions directly above each other to form a trigonal crystal structure (figure 6). Selected bond distances and angles are included in table 4.

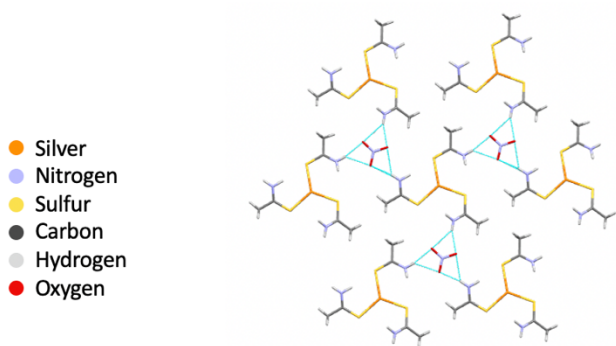


Figure 5: trigonal planar arrangement of thioacetamide ligands around silver, stabilized by nitrate.

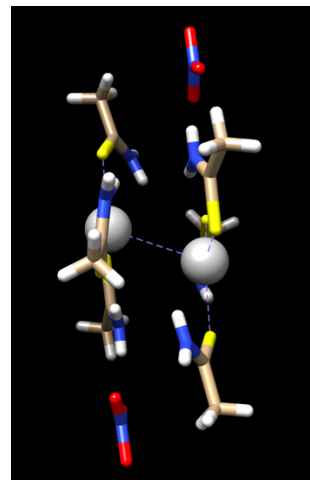


Figure 6: vertical arrangement of thioacetamide ligands showing silver-silver bond.

Ag1-S1	2.4863
Ag1-S2	2.4869
Ag1-S3	2.4999
Ag1-Ag2	3.2846
S1-Ag1-S2	121.25
S1-Ag1-S3	118.25
S2-Ag1-S3	119.11
S1-Ag1-Ag2	79.55
S2-Ag1-Ag2	92.69
S3-Ag1-Ag2	85.99
Ag1-S1-C1-C2	173.4
Ag1-S2-C3-C4	176.9
Ag1-S3-C5-C6	160.2

Table 4: selected bond lengths (Å) and angles (°) of silver thioacetamide

The silver thioacetamide complex has some distortion from the trigonal planar geometry, as seen in the torsional angles of table 4. This distortion has been attributed to the relativistic effects of the silver atom and shown in the Gaussian calculations for the optimized geometry of the complex (figure 7). The optimized geometry shows some twisting of the ligands from a planar arrangement, however the optimized geometry aligns with the trigonal planar arrangement seen in the X-ray crystallography data. It is worth noting that the optimized calculations were performed assuming a gaseous state while all other data were collected in a solid state. These calculations were performed with the RB3LYP method under the basis set LANL2DZ.

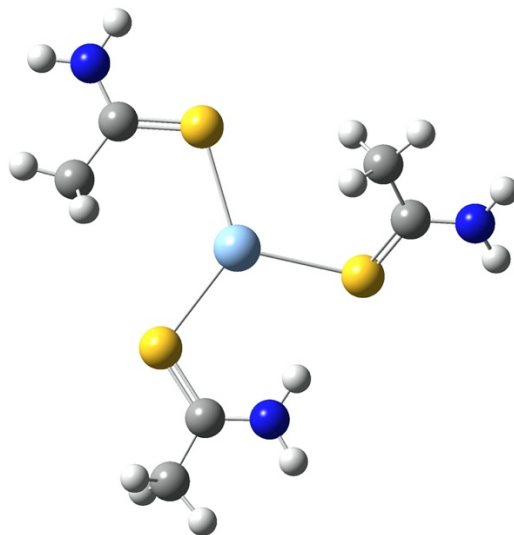


Figure 7: Optimized geometry of silver thioacetamide, calculated with Gaussian

X-ray crystallography revealed that the silver methimazole complex is a coordination polymer. The repeating unit is one silver coordinating to two methimazole ligands and the nitrate acts as a stabilizer between polymer chains (figure 8).

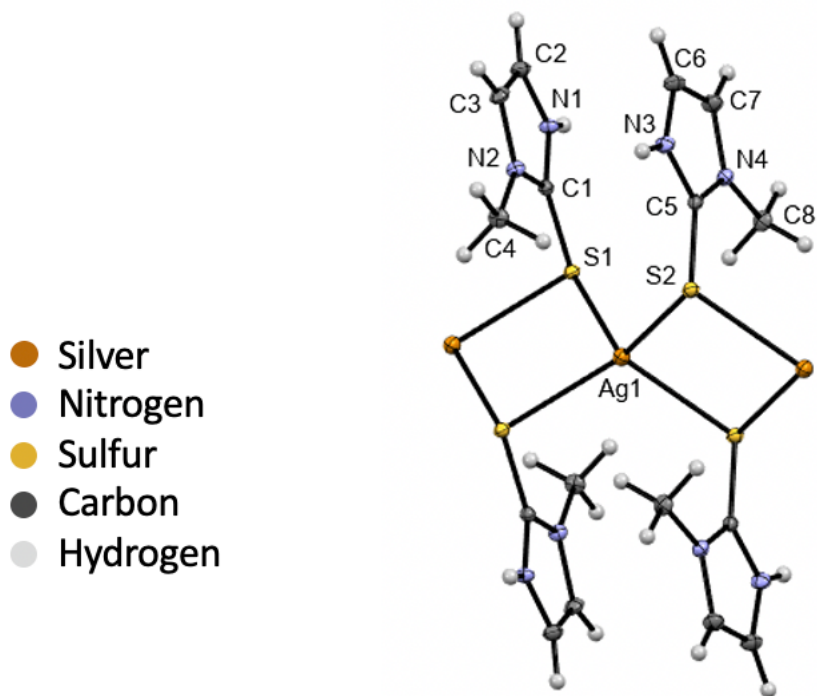


Figure 8: structural arrangement of silver methimazole polymer

The polymer chains are at odd angles with each other and end up forming a monoclinic crystal structure (Figure 9). In this polymer, the sulfur-silver bond length ends up being longer than in the silver thioacetamide, due to its role as a bridging ligand. The sulfur-silver-sulfur bond angles also have a wider range due to the changing orientation of the methimazole ligands, which are large and place some steric strain on the system. These values are reflected in table 5.

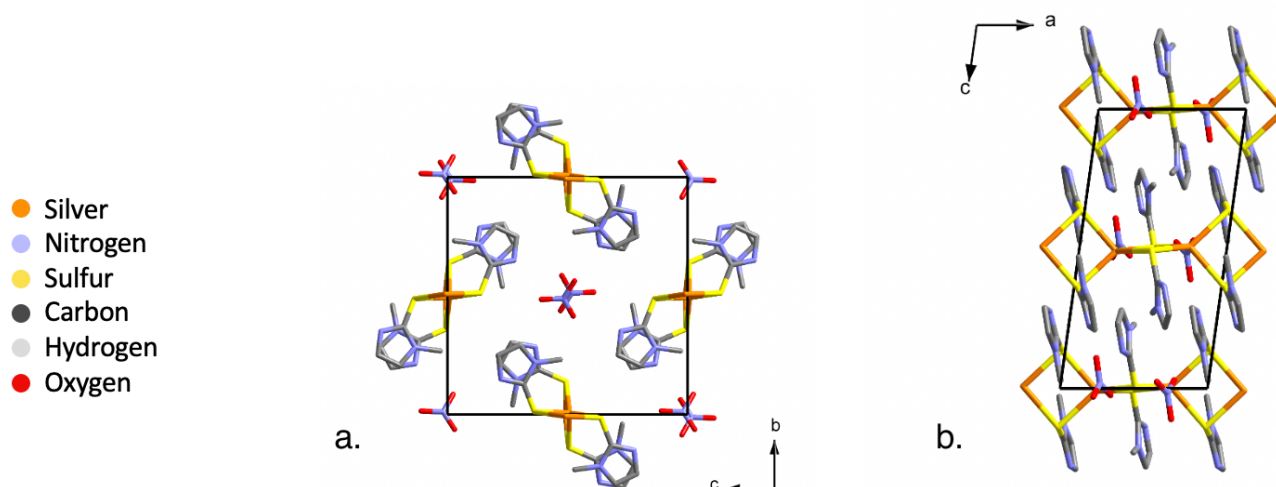


Figure 9: structural arrangement of polymeric chains within a silver methimazole cell from a. the top of the cell and b. the side of the cell.

Ag1-S1	2.5871
Ag1-S2	2.5937
S1-Ag1-S2	129.772
S2-Ag1-S1	114.44
S2-Ag1-S2	92.544
S1-Ag1-S1	92.273
S1-Ag1-S2	113.66
S1-Ag1-S2	116.038

Table 5: selected bond lengths (Å) and angles (°) of silver thioacetamide and silver methimazole.

CONCLUSION

With these data, it can be concluded that synthesis with silver nitrate and thioacetamide can result in a coordination complex by binding with the sulfur. Thiocarbanilide is thought to coordinate in a similar manner based on the elemental analysis and IR shifts. Synthesis of silver nitrate with methimazole can result in a coordination polymer, using the sulfur as a bridging point.

Future work in this project would center around testing the antibacterial and conductive potential most notably of the silver methimazole polymer, but also of the silver thioacetamide complex. Given data in these areas, it would aid in the applications of the polymer. It could potentially be applied in biomedical engineering to layer on materials and combat bacterial growth, or used in electronics that need to be kept biologically clean. Given the antibacterial properties of silver that would be maintained in a coordination polymer, the applications to biomaterials and bioelectronics would be of interest to pursue.

ACKNOWLEDGMENTS

The author thanks Dr. Jaime Murphy for advising this project, Dr. Colin McMillen for X-ray crystallography contributions, Dr. Michael Gutierrez for Gaussian calculations, Professor Chantelle Taylor for microscopy work, and the Harding University department of Chemistry and Biochemistry for funding this research.

REFERENCES

- (1) Janiak, C. Engineering Coordination Polymers towards Applications. *Dalton Trans.* **2003**, No. 14, 2781. <https://doi.org/10.1039/b305705b>.

- (2) Dias, H. V. R.; Flores, J. A.; Pellei, M.; Morresi, B.; Lobbia, G. G.; Singh, S.; Kobayashi, Y.; Yousufuddin, M.; Santini, C. Silver(I) and Copper(I) Complexes Supported by Fully Fluorinated 1,3,5-Triazapentadienyl Ligands. *Dalton Trans.* **2011**, 40 (34), 8569–8580. <https://doi.org/10.1039/c1dt10524h>.
- (3) Hollmann, K.; Oppermann, A.; Witte, M.; Li, S.; Amen, M.; Flörke, U.; Egold, H.; Henkel, G.; Herres-Pawlis, S. Copper(I) Complexes with Thiourea Derivatives as Ligands: Revealing Secrets of Their Bonding Scheme: Copper(I) Complexes with Thiourea Derivatives as Ligands: Revealing Secrets of Their Bonding Scheme. *Eur. J. Inorg. Chem.* **2017**, 2017 (9), 1266–1279. <https://doi.org/10.1002/ejic.201601547>.
- (4) Kimani, M. M.; Watts, D.; Graham, L. A.; Rabinovich, D.; Yap, G. P. A.; Brumaghim, J. L. Dinuclear Copper(I) Complexes with N-Heterocyclic Thione and Selone Ligands: Synthesis, Characterization, and Electrochemical Studies. *Dalton Trans.* **2015**, 44 (37), 16313–16324. <https://doi.org/10.1039/c5dt02232k>.
- (5) Murphy, J. M.; Gaertner, A. A. E.; Owen, A. M.; Struder, S.; McMillen, C. D.; Wetzler, M.; Brumaghim, J. L. Coordination Complexes of Methimazole with Copper: Controlling Redox Reactions and Sulfur Extrusion. *Inorganica Chim. Acta* **2020**, 507(119568), 119568. <https://doi.org/10.1016/j.ica.2020.119568>.
- (6) Stocker, F. B.; Troester, M. A. Crystal Structures of Two New Complexes Produced by Reaction of Copper(I) Cyanide with Thioacetamide. In Situ Formation of the Thiosulfate Anion. *Inorg. Chem.* **1996**, 35 (11), 3154–3158. <https://doi.org/10.1021/ic9502436>.
- (7) Stocker, F. B.; Staeva, T. P.; Rienstra, C. M.; Britton, D. Crystal Structures of a Series of Complexes Produced by Reaction of Copper(I) Cyanide with Diamines. *Inorg. Chem.* **1999**, 38 (5), 984–991. <https://doi.org/10.1021/ic970226b>.
- (8) Anastasiadou, D.; Geromichalou, E.; Tsavea, E.; Psomas, G.; Hatzidimitriou, A. G.; Kalogiannis, S.; Geromichalos, G.; Trafalis, D.; Dalezis, P.; Aslanidis, P. Silver Complexes with Heterocyclic Thioamide and Tertiary Arylphosphane Ligands: Synthesis, Crystal Structures, in Vitro and in Silico Antibacterial and Cytotoxic Activity, and Interaction with DNA. *J. Inorg. Biochem.* **2020**, 210 (111167), 111167. <https://doi.org/10.1016/j.jinorgbio.2020.111167>.
- (9) Corradi Bonamartini, A.; Fava Gasparri, G.; Ferrari Belicchi, M.; Nardelli, M. Ligand Configuration and Coordination Geometry in Silver(I)–Thiosemicarbazide Complexes. *Acta Crystallogr. C* **1987**, 43 (3), 407–413. <https://doi.org/10.1107/s010827018709557x>.
- (10) Palomino, L.; Metal Thiobarbituric Acid complexes. *Zhurnal Neorganicheskoi Khimii.* **1989**, 34 (11), 2901–2906.
- (11) Troyano, J.; Perles, J.; Amo-Ochoa, P.; Martínez, J. I.; Zamora, F.; Delgado, S. Reversible Recrystallization Process of Copper and Silver Thioacetamide–Halide Coordination Polymers and Their Basic Building Blocks. *CrystEngComm* **2014**, 16 (35), 8224–8231. <https://doi.org/10.1039/c4ce00480a>.
- (12) Onodera, A.; Nishiumi, F.; Kakiguchi, K.; Tanaka, A.; Tanabe, N.; Honma, A.; Yayama, K.; Yoshioka, Y.; Nakahira, K.; Yonemura, S.; Yanagihara, I.; Tsutsumi, Y.; Kawai, Y. Short-Term Changes in Intracellular ROS Localisation after the Silver Nanoparticles Exposure Depending on Particle Size. *Toxicol. Rep.* **2015**, 2, 574–579. <https://doi.org/10.1016/j.toxrep.2015.03.004>.
- (13) Park, H.-J.; Kim, J. Y.; Kim, J.; Lee, J.-H.; Hahn, J.-S.; Gu, M. B.; Yoon, J. Silver-Ion-Mediated Reactive Oxygen Species Generation Affecting Bactericidal Activity. *Water Res.* **2009**, 43 (4), 1027–1032. <https://doi.org/10.1016/j.watres.2008.12.002>.
- (14) Altaf, M.; Stoeckli-Evans, H.; Cuin, A.; Sato, D. N.; Pavan, F. R.; Leite, C. Q. F.; Ahmad, S.; Bouakka, M.; Mimouni, M.; Khardli, F. Z.; Hadda, T. B. Synthesis, Crystal Structures, Antimicrobial, Antifungal and Antituberculosis Activities of Mixed Ligand Silver(I) Complexes. *Polyhedron* **2013**, 62, 138–147. <https://doi.org/10.1016/j.poly.2013.06.021>.
- (15) Allison, S. J.; Sadiq, M.; Baronou, E.; Cooper, P. A.; Dunnill, C.; Georgopoulos, N. T.; Latif, A.; Shepherd, S.; Shnyder, S. D.; Stratford, I. J.; Wheelhouse, R. T.; Willans, C. E.; Phillips, R.

- M. Preclinical Anti-Cancer Activity and Multiple Mechanisms of Action of a Cationic Silver Complex Bearing N -Heterocyclic Carbene Ligands. *Cancer Lett.* **2017**, *403*, 98–107. <https://doi.org/10.1016/j.canlet.2017.04.041>.
- (16) Gasparri, G. F.; Mangia, A.; Musatti, A.; Nardelli, M. The Crystal and Molecular Structure of Monothiosemicarbazidesilver(I) Chloride. *Acta Crystallogr. B* **1968**, *24* (3), 367–374. <https://doi.org/10.1107/s0567740868002384>
- (17) Ademola Adejumobi, J.; Goddard, D. R. The IR Absorption Spectra of Some Solid Metal Ion Complexes of Thio- and Seleno-Semicarbazide. *J. inorg. nucl. chem.* **1977**, *39* (5), 910–912. [https://doi.org/10.1016/0022-1902\(77\)80187-5](https://doi.org/10.1016/0022-1902(77)80187-5)
- (18) Lobana, T. S.; Sultana, R.; Butcher, R. J.; Jasinski, J. P.; Golen, J. A.; Castineiras, A.; Präpper, K.; Fernandez, F. J.; Vega, M. C. Heterocyclic-2-Thione Derivatives of Silver(I): Synthesis, Spectroscopy and Structures of Mono- and Di-Nuclear Silver(I) Halide Complexes. *J. Organomet. Chem.* **2013**, *745–746*, 460–469. <https://doi.org/10.1016/j.jorganchem.2013.08.020>.
- (19) Khalaji, A.; Shahsavani, E.; Feizi, N.; Kucerakova, M.; Dusek, M.; Mazandarani, R. Silver(I) Thiosemicarbazone Complex [Ag(Catsc)(PPh₃)₂]NO₃ : Synthesis, Characterization, Crystal Structure, and Antibacterial Study. *C. R. Chim.* **2017**, *20* (5), 534–539. <https://doi.org/10.1016/j.crci.2016.09.001>.
- (20) Thongtem, T.; Phuruangrat, A.; Thongtem, S. Characterization of Copper Sulfide Nanostructured Spheres and Nanotubes Synthesized by Microwave-Assisted Solvothermal Method. *Mater. Lett.* **2010**, *64* (2), 136–139. <https://doi.org/10.1016/j.matlet.2009.10.021>.
- (21) Mufakkar, M.; Isab, A. A.; Rüffer, T.; Lang, H.; Ahmad, S.; Arshad, N.; Waheed, A. Synthesis, Characterization, and Antibacterial Activities of Copper(I) Bromide Complexes of Thioureas: X-Ray Structure of [Cu(Metu)₄]Br. *Transit. Met. Chem.* **2011**, *36* (5), 505–512. <https://doi.org/10.1007/s11243-011-9496-9>.
- (22) Krzewska, S.; Podsiadły, H. Complexes of Ag(I) with Ligands Containing Sulphur Donor Atoms. *Polyhedron* **1986**, *5* (4), 937–944. [https://doi.org/10.1016/s0277-5387\(00\)80133-3](https://doi.org/10.1016/s0277-5387(00)80133-3)
- (23) Wallace, D.; Quinn, E. J.; Armstrong, D. R.; Reglinski, J.; Spicer, M. D.; Smith, W. E. Surface Science of Soft Scorpionates. *Inorg. Chem.* **2010**, *49* (4), 1420–1427. <https://doi.org/10.1021/ic9014898>.
- (24) Kuyper, J.; Keijzer, P. C.; Vrieze, K. S,N,N'-Substituted Sulfurdiimines as Ligands. *J. Organomet. Chem.* **1976**, *116* (1), 1–13. [https://doi.org/10.1016/s0022-328x\(00\)87191-0](https://doi.org/10.1016/s0022-328x(00)87191-0).
- (25) Balachandran, V.; Lakshmi, A.; Janaki, A. Ab Initio, DFT, HOMO–LUMO and Natural Bond Orbital Analyses of the Electronic Structure of 2-Mercapto-1-Methylimidazole. *J. Mol. Struct.* **2011**, *1006* (1–3), 395–401. <https://doi.org/10.1016/j.molstruc.2011.09.037>.
- (26) Ritchie, R. K.; Spedding, H.; Steele, D. A Spectroscopic Study of Thiourea Derivatives—(III). *Spectrochim. Acta A* **1971**, *27* (9), 1597–1608. [https://doi.org/10.1016/0584-8539\(71\)80214-3](https://doi.org/10.1016/0584-8539(71)80214-3)
- (27) Suzuki, I. Infrared Spectra and Normal Vibrations of Thioamides. II. Thioacetamide. *Bull. Chem. Soc. Jpn.* **1962**, *35* (9), 1449–1456. <https://doi.org/10.1246/bcsj.35.1449>.