

9-25-2014

## Syntheses and characterization of three-and five-coordinate copper(II) complexes based on SNS pincer ligand precursors

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### Repository Citation

Miecznikowski, John R.; Lynn, Matthew A.; Jasinski, Jerry P.; Lo, Wayne; Bak, Daniel W.; Pati, Mekhala; Butrick, Elizabeth E.; Drozdowski, Anne Elise R.; Archer, Kerry A.; Villa, Christine E.; Lemons, Elise G.; Powers, Erin; Siu, Margaret; Gomes, Camile D.; Bernier, Nicholas A.; and Morio, Kaitlyn N., "Syntheses and characterization of three-and five-coordinate copper(II) complexes based on SNS pincer ligand precursors" (2014). *Chemistry & Biochemistry Faculty Publications*. 41.  
<https://digitalcommons.fairfield.edu/chemistry-facultypubs/41>

### Published Citation

Miecznikowski, J.R.; Lynn, M.A.; Jasinski, J.P.; Lo, W.; Bak, D.; Pati, M.; Butrick, E.E.; Drozdowski, A.E.R.; Archer, K.A.; Villa, C.E.; Lemons, E.G.; Powers, E.; Siu, M.; Gomes, C.D.; Bernier, N.A.; Morio, K.N. (2014). Syntheses and characterization of three-and five-coordinate copper(II) complexes based on SNS pincer ligand precursors. *Polyhedron* (invited: Special Issue dedicated to Prof. Vukadin Leovac), 80(25), pp.157-165. <https://doi.org/10.1016/j.poly.2014.03.020>

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Syntheses and Characterization of Five-Coordinate Copper(II) Complexes based on  
Tridentate SNS Pincer Ligand Precursors

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honoring the 70th birthday of Professor Vukadin Leovac.

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**Abstract:**

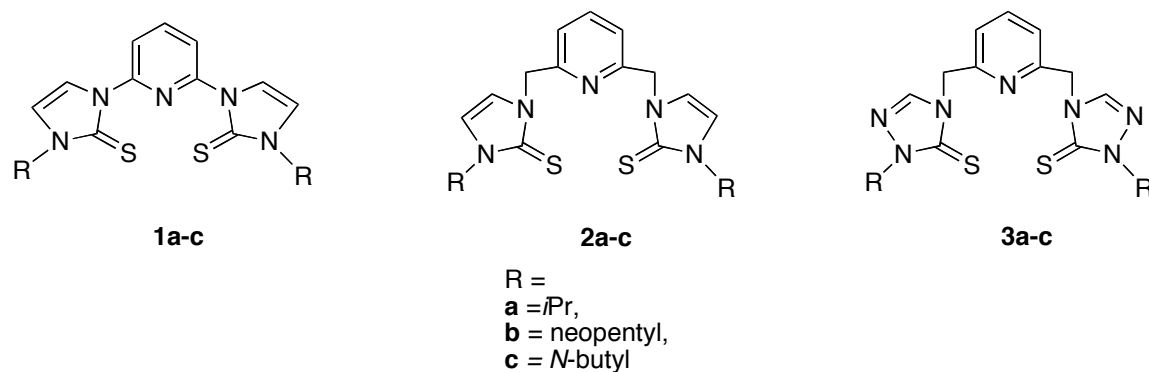
A series of tridentate pincer ligands, each possessing two sulfur- and one nitrogen-donor functionalities (SNS), based on a bis-imidazolyl precursor were metallated with  $\text{CuCl}_2$  to give new tridentate SNS pincer copper(II) complexes  $[(\text{SNS})\text{CuCl}_2]$ . These purple complexes exhibit a five-coordinate pseudo-square pyramidal geometry at the copper center. The  $[(\text{SNS})\text{CuCl}_2]$  complexes were characterized with single crystal X-ray diffraction, electrospray mass spectrometry, EPR spectroscopy, attenuated total reflectance infrared spectroscopy, UV-Vis spectroscopy, cyclic voltammetry, and elemental analysis. The EPR spectra are consistent with typical anisotropic Cu(II) signals with four hyperfine splittings in the lower-field region ( $g_{\parallel}$ ). Various electronic transitions are apparent in the UV-Vis spectra of the complexes and originate from d-to-d transitions or various charge transfer transitions. We performed computational studies to understand the influence that structural constraints internal to our tridentate SNS ligand precursors have on the oxidation state of the resulting bound copper complex. We have determined that a  $d^9$  copper(II) metal center is better situated than a  $d^{10}$  copper(I) center to bind our tridentate SNS ligand set when it does not contain an internal  $\text{CH}_2$  group. Without this methylene linker, the SNS ligand forces the N and S atoms into a T-shaped arrangement about the metal center.

## Keywords

SNS pincer ligand  
Mononuclear Cu complexes  
X-ray crystallography  
Cyclic voltammetry  
EPR Spectroscopy

## Introduction

Recently, we have prepared and reported a series of tridentate pincer ligand precursors, each of which possesses SNS donor atoms.[1-2] In our previous studies, we have used a variety of these ligand sets to prepare tetradentate zinc(II) and tridentate Cu(I) SNS pincer complexes. The SNS ligand framework can be constructed through the linking of two thioimidazolyl and thiotriazolyl heterocycles with one pyridinyl unit, resulting in an organic framework that is capable of tridentate chelation of a metal ion. Using 2,6-dibromopyridine as a starting material results in the binding of the thioimidazolyl groups directly to the pyridine moiety (**1a-c**), thereby generating a stiff ligand system in which rotation about the C-N bond that links the pyridinyl and imidazolyl moieties is the only way in which these rings can move relative to each other. We have also prepared SNS ligands with a greater degree of flexibility (**2a-c** and **3a-c**) by employing 2,6-(dibromomethyl)pyridine, thereby introducing a methylene linker into the ligand set. We were able to fine-tune further the electronic environment within the framework of these systems by using imidazolyl- (**2a-c**) and triazolyl- (**3a-c**) based precursors in the preparation of the pincer ligands.



**Figure 1.** SNS ligand precursors previously prepared by Miecznikowski *et al.*[1-2] and Jin *et al* [3]

The use of zinc(II) chloride to prepare zinc(II) compounds that contain these ligand precursors (Figure 1, **1a-c**, **2a-c**, and **3a-c**) has proven to be straightforward and demonstrates the influence that various modifications within the ligand set can have on the coordination of the metal center. By and large, these syntheses result in the formation of four-coordinate pseudo-tetrahedral zinc(II) complexes in which a chloride and the SNS tridentate ligand are bound to the metal center. The specific SNS ligands that gave rise to these systems were of two types: they either (1) possessed methylene linkers between the pyridinyl and the imidazolyl or triazolyl groups or (2) they did not have such a linker and contained only imidazolyl (not triazolyl) groups. The counterion for such systems was found to be a trichloro- or a tetrachlorozincate anion. In one instance, however, a five-coordinate pseudo-trigonal-bipyramidal zinc(II) complex resulted when the ligand contained thiotriazolyl functionalities and no methylene linkers between the triazolyl and pyridinyl groups. In this complex, the tridentate ligand bonded to the zinc(II) center via the pyridinyl N atom and the available triazolyl N atoms. This NNN binding of the ligand placed these three atoms in a meridional arrangement about the metal center with

the pyridinyl N atom occupying an equatorial position and the two triazolyl N atoms in axial positions.

Given that copper metalloproteins contain nitrogen (N-His) and sulfur (cysteine) donor atoms to the metal center, we have chosen to investigate the synthesis of copper-containing systems that contain our SNS ligand sets. The preparation of copper complexes that contain nitrogen and sulfur donor atoms is certainly of interest in bioinorganic chemistry. For example, in electron-transfer proteins, cysteine-thiolate copper ion interactions are important.[4-5] Sulfide-Cu interactions are found in the Cu<sub>4</sub>-S cluster in the enzyme nitrous oxide reductase.[6-8] In addition, thioether methionecopper ion interactions occur in type 1 “blue” electron transfer proteins and in the active site of certain monooxygenases.[9-10] Recently, Hor and co-workers reported a five-coordinate mononuclear Cu(II) complex that contained a tridentate ligand with SNS donor atoms.[11] Three-, [12-16] four-, [17-20] and five-coordinate [11,18, 19, 21-34] mononuclear copper(II) complexes have been reported previously. For the five-coordinate copper(II) complexes, both pseudo-trigonal bipyramidal and pseudo-square pyramidal coordination environments at the copper(II) center have been reported.

We have recently published a synthetic, spectroscopic, and computational study of several copper(I) systems that we have prepared using our SNS ligands **2a**, **3a**, and **3c**. [35] Of particular note is that when the ligand set possesses a methylene linker between the pyridinyl and the thioimidazolyl or thiotriazolyl groups, the resulting metal-bound systems exhibit pseudo-trigonal-planar binding of the tridentate ligand set in an SNS fashion. Also of interest was our finding that when copper(II) chloride is used as the source of the metal ion, a disproportionation reaction occurs in which copper(I) ions



are produced and bound by the SNS ligand to give a monocationic copper(I)-bound complex with the general formula [(SNS)Cu]<sup>+</sup>. Two of these cations are balanced by one copper(II)-containing CuCl<sub>4</sub><sup>2-</sup> anion.

For our current work, our focus is on the synthesis and characterization of novel copper-SNS complexes with the ligand precursors that were not used in our previous study. Reaction of copper(II) chloride with ligand sets **1a-c**, which have thioimidazolyl groups and no internal methylene linkers, gives rise to five-coordinate copper(II) complexes in which the SNS ligand set and two chlorides are bound to the metal center. Disproportionation of the metal was not observed during these syntheses.

Therefore, we present here the syntheses, X-ray crystallographic, spectroscopic and electrochemical characterizations of copper(II) complexes that contain ligand precursors **1a-c**. As with our previous work with zinc(II), we find that fine-tuning of the SNS ligand set allows for the preparation of copper complexes with various coordination environments about the metal center. The availability of the copper(I) and copper(II) oxidation states allows an extra area of study in which the charge on the metal center can be controlled through modification of the ligand set. Our computational study of these systems provides insight into the influence of the ligand sets on the oxidation state and the coordination environment of our Cu-SNS systems.

## **Experimental:**

### ***General Procedures:***

All reagents used are commercially available and were used as received. All of the reagents and solvents were purchased from Acros Organics except for diethyl ether,

and sodium acetate, which were purchased from Fisher. 2,6-bis {[N-butyl]imidazole-1-ylidene-2-thione} pyridine, and 2,6-bis {[N-isopropyl]imidazole-1-ylidene-2-thione}pyridine, 2,6-bis {[N-neopentyl]imidazole-1-ylidene-2-thione} pyridine were reported previously.[1,3]

Each sample was analyzed by direct flow injection (injection volume = 3 or 10  $\mu$ L) ElectroSpray Ionization (ESI) on a Waters Qtof API US instrument in the positive mode. The optimized conditions were found as follows: Capillary = 3000 kV, Cone = 10 or 35 V, Source Temperature = 120  $^{\circ}$ C and Desolvation Temperature = 120 or 350  $^{\circ}$ C.

Cyclic voltammetry experiments were performed using a Cypress Electroanalytical System with a silver wire reference electrode, a glassy carbon working electrode, and a platinum counter electrode. The supporting electrolyte for the cyclic voltammetry experiments was tetra-N-butylammonium tetrafluoroborate. The solvent for the cyclic voltammetry experiments was dimethyl sulfoxide. The ferrocenium/ferrocene couple was used as an internal reference; reduction potential values were corrected by assigning the ferrocenium/ferrocene couple to 0.40 V versus SCE.

IR spectra were collected using a Thermo Nicolet AVATAR 380-FT-IR with a SMART SPECULATR reflectance adaptor. C, H, N elemental analyses were performed by Atlantic Microlab Inc. (Norcross, GA).

Low temperature (10K) EPR measurements were made using a Bruker X-band ESEXSYS E 500 spectrometer equipped with an ESR900 continuous flow liquid helium cryostat. EPR spectra were collected at (9.24 GHz), (2mW) microwave power, and with a (1G) modulation amplitude. The EPR sample of a copper complex was prepared by

dissolving 3 mg of the copper complex in 0.8 mL of methanol. Spectra were collected of oxidized samples and required no reduction prior to data collection.

### **Density Functional Calculations:**

Gaussian 03 was used to perform single-point calculations and geometry optimizations using the B3LYP hybrid functional. The 6-311g(d) basis set as provided with the software was employed for H, C, N, and S and 6-311g(d,p) was used for Cu. Calculations were performed using N-methyl pendant groups and C<sub>2</sub> symmetry in all cases. Frequency analyses were performed on the optimized structures to determine whether or not they represented true minima. All structures presented no imaginary frequencies.

### **Syntheses:**

#### ***Synthesis of dichloro-[( $\eta^3$ -S,S,N)(2,6-bis){[N-isopropyl]imidazole-1-ylidene-2-thione}pyridine copper (II)] [4]***

In 25 mL round bottom flask, 0.0784 g (0.000218 mol) of 2,6-bis{[N-isopropyl]imidazole-1-ylidene-2-thione}pyridine was combined with 0.0591 g CuCl<sub>2</sub> (0.000440 mol) and dissolved in 10 mL of dichloromethane. The solution mixture was refluxed for 20 h. After this time, the solvent was removed under reduced pressure. Yield: 0.16 g (98 %). Single crystals for X-ray diffraction and elemental analysis were grown by a slow vapor diffusion of diethyl ether into a methanol solution containing the copper complex.

IR bands (reflectance, solid crystal),  $\nu_{\max}/\text{cm}^{-1}$  (intensity) 3078.85 (w), 2976.60 (w), 1597.46 (m), 1452.54 (s), 1430.57 (s), 1408.82 (m), 1368.07 (w), 1330.08 (w), 1296.16 (w), 1283.16 (w), 1219.62 (s), 1137.59 (w), 1075.82 (w), 1022.85 (w), 997.84 (w), 882.87 (w), 808.48 (m), 780.84 (m), 732.94 (s), 690.28 (m), 652.95 (m).

Mass Spec Electrospray MS (MeOH, 10V, positive ion mode (m/z): Expected: 422.05 (100 %)  $[\text{C}_{17}\text{H}_{21}\text{N}_5\text{S}_2\text{Cu}]^{2+}$ , Found: 422.0524 (100%)  $[\text{C}_{17}\text{H}_{21}\text{N}_5\text{S}_2\text{Cu}]^{2+}$ .

Anal. Calc for  $[\text{C}_{17}\text{H}_{21}\text{Cl}_2\text{CuN}_5\text{S}_2]$ : C, 41.34; H, 4.29; N, 14.18. Found: C, 40.90; H, 4.43; N, 14.00.

Electronic absorption,  $\lambda_{\max}$  (CH<sub>3</sub>OH)/nm ( $\epsilon/\text{M}^{-1}\text{cm}^{-1}$ ): 581 (107), 410 sh. (246), 305 sh. (4771), 270 (9090), 268 (9250), 261 (9580), 254 (9860), 249 (10100), 246 (9810), 244 (9850), 242 (10080), 238 (9750), 235 (9580), 231 (9310), 219 (7620).

***Synthesis of dichloro-[( $\eta^3$ -S,S,N)(2,6-bis){[N-neopentyl]imidazole-1-ylidene-2-thione}pyridine copper (II)] [5]***

In 25 mL round bottom flask, 0.1440 g (0.0003468 mol) of 2,6-bis{[N-neopentyl]imidazole-1-ylidene-2-thione}pyridine was combined with 0.0461 g CuCl<sub>2</sub> (0.000343 mol) and dissolved in 10 mL of dichloromethane. The solution mixture was refluxed for 20 h. After this time, the solvent was removed under reduced pressure. Yield: 0.18 g (96 %). Single crystals for X-ray diffraction and elemental analysis were grown by a slow vapor diffusion of diethyl ether into a methanol solution containing the copper complex.

IR bands (reflectance, solid crystal),  $\nu_{\max}/\text{cm}^{-1}$  (intensity) 3082.12 (br), 2954.85 (br), 2868.86 (br), 1596.28 (m), 1455.70 (s), 1418.14 (m), 1397.96 (s), 1365.68 (m), 1300.64 (w), 1280.50 (m), 1234.15 (s), 1184.01 (w), 1146.35 (w), 1119.85 (w), 1100.70 (w),

1061.83 (w), 997.49 (w), 957.30 (w), 936.96 (w), 903.23 (w), 807.42 (m), 784.56 (m),  
731.62 (s), 689.43 (m), 672.11 (m)

Mass Spec Electrospray MS (MeOH, 10V, positive ion mode (m/z): Expected: 478.12  
(100 %)  $[\text{C}_{21}\text{H}_{29}\text{N}_5\text{S}_2\text{Cu}]^{2+}$ , Found: 478.1156 (100%)  $[\text{C}_{21}\text{H}_{29}\text{N}_5\text{S}_2\text{Cu}]^{2+}$ .

Anal. Calc. for  $[\text{C}_{21}\text{H}_{29}\text{Cl}_2\text{CuN}_5\text{S}_2] \cdot \text{H}_2\text{O}$ : C, 44.40; H, 5.50; N, 12.33. Found: C, 44.70;  
H, 5.15; N, 12.33.

Electronic absorption,  $\lambda_{\text{max}}$  (CH<sub>3</sub>OH)/nm ( $\epsilon/\text{M}^{-1} \text{cm}^{-1}$ ): 571 (396), 403.16 sh. (647), 310  
(8100), 266.90 sh. (17900), 249.46 sh. (20700), 229.55 sh. (23100), 215 (25800).

***Synthesis of dichloro-[( $\eta^3$ -S,S,N)(2,6-bis){[N-butyl]imidazole-1-ylidene-2-thione}  
pyridine copper (II)] [6]***

In 25 mL round bottom flask, 0.1414 g (0.0003648 mol) of 2,6-bis {[N-  
butyl]imidazole-1-ylidene-2-thione}pyridine was combined with 0.0486 g CuCl<sub>2</sub>  
(0.000361 mol) and dissolved in 10 mL of dichloromethane. The solution mixture was  
refluxed for 20 h. After this time, the solvent was removed under reduced pressure.

Yield: 0.18 g (95 %). Single crystals for X-ray diffraction and elemental analysis were  
grown by a slow vapor diffusion of diethyl ether into a methanol solution containing the  
copper complex.

IR bands (reflectance, solid crystal),  $\nu_{\text{max}}/\text{cm}^{-1}$  (intensity) 3077.90 (br), 3029.02 (br),  
2957.19 (br), 2929.65 (br), 2869.98 (br), 1738.27 (s), 1596.14 (s), 1506.03 (w), 1453.23  
(s), 1424.06 (m), 1403.69 (m), 1371.03 (s), 1284.97 (m), 1231.56 (s), 1216.71 (s),  
1154.12 (w), 1116.70 (w), 1106.03 (w), 1072.38 (w), 997.02 (m), 955.19 (w), 904.67  
(w), 877.03 (w), 807.57 (s), 689.67 (m), 676.69 (m), 649.27 (m), 609.19 (w)

Mass Spec Electrospray MS (MeOH, 10V, positive ion mode (m/z): Expected: 450.08 (100 %)  $[\text{C}_{19}\text{H}_{25}\text{N}_5\text{S}_2\text{Cu}]^{2+}$ , Found: 450.0865 (100%)  $[\text{C}_{19}\text{H}_{25}\text{N}_5\text{S}_2\text{Cu}]^{2+}$ .

Anal. Calc. for  $[\text{C}_{19}\text{H}_{25}\text{Cl}_2\text{CuN}_5\text{S}_2]$ : C, 43.72; H, 4.83; N, 13.42. Found: C, 43.63; H, 4.90; N, 13.44.

Electronic absorption,  $\lambda_{\text{max}}$  (CH<sub>3</sub>OH)/nm ( $\epsilon/\text{M}^{-1} \text{cm}^{-1}$ ): 578 (18), 310 (2550), 275 (4760), 268 (4980), 266 (4980), 263 (5020), 260 (5010), 256 (5280), 254 (5410), 250 (5330), 244 (5330), 241 (5190), 239 (5170), 237 (5100), 234 (5010).

### ***Crystallographic Analyses:***

A crystal of **4** (*vide infra*) was mounted on a CryoLoop (Hampton Research) and placed in a -100 °C compressed air stream on an Agilent Gemini-EOS Single Crystal Auto diffractometer at Keene State College (Keene, NH). Crystallographic data were collected using graphite monochromated 0.71073 Å Mo-K $\alpha$  radiation and integrated and corrected for absorption using the *CrysAlisRed* software package.[36] The structures were solved using direct methods and refined using least-square methods on F-squared.[37] All other pertinent crystallographic details such as h, k, l ranges, 2 $\theta$  ranges, and R-factors can be found in Table 1. CCDC file 955935 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

A crystal of **5** (*vide infra*) was mounted on a CryoLoop (Hampton Research) and placed in a -100 °C compressed air stream on an Agilent Gemini-EOS Single Crystal Autodiffractometer at Keene State College (Keene, NH). Crystallographic data were collected using graphite monochromated 0.71073 Å Mo-K $\alpha$  radiation and integrated and

corrected for absorption using the CrysAlisRed software package.[36] The structures were solved using direct methods and refined using least-square methods on F-squared.[37] Unresolved solvent electron density was voided and further refined using PLATON SQUEEZE.[38-40] All other pertinent crystallographic details such as h, k, l ranges,  $2\theta$  ranges, and R-factors can be found in Table 1. CCDC file 955937 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

A crystal of **6** was mounted on a glass loop and placed in an -80 °C nitrogen stream on a Bruker diffractometer equipped with a Smart CCD at Boston College (Chestnut Hill, MA). Crystallographic data were collected using graphite monochromated 0.71073 Å Mo-K $\alpha$  radiation and integrated and corrected for absorption using the Bruker SAINTPLUS software package.[41, 42] The structures were solved using direct methods and refined using least-square methods on F-squared.[37] All other pertinent crystallographic details such as h, k, l ranges,  $2\theta$  ranges, and R-factors can be found in Table 1. CCDC file 955936 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table 1.** Crystal and Structure Refinement Data for **4-6**

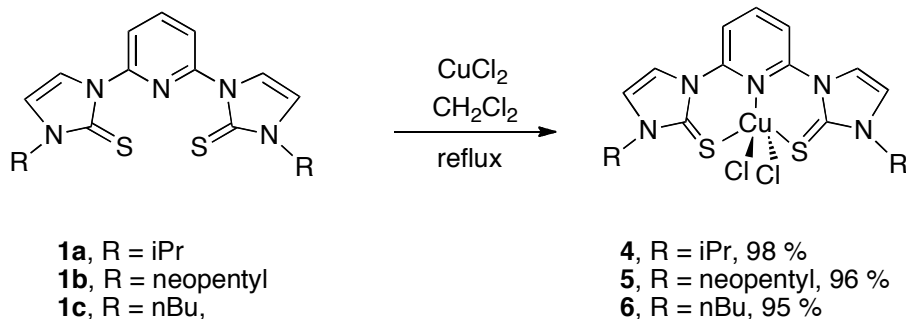
	R = <i>i</i> Pr [4]	R = <i>n</i> P [5]	R = <i>n</i> Bu [6]
Formula	C <sub>20</sub> H <sub>28</sub> Cl <sub>2</sub> CuN <sub>5</sub> S <sub>2</sub> •2H <sub>2</sub> O	C <sub>21</sub> H <sub>29</sub> Cl <sub>2</sub> CuN <sub>5</sub> S <sub>2</sub> •2(CH <sub>3</sub> OH)	C <sub>19</sub> H <sub>25</sub> Cl <sub>2</sub> CuN <sub>5</sub> S <sub>2</sub>
FW (g/mol)	499.94	614.17	522.00
Temperature (K)	173(2)	173(2)	193(2)
Wavelength (Å)	1.54184	1.54184	0.71073
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	P2(1)/n	P2(1)/c	P2(1)/n
a (Å)	9.2294(4)	16.1818(3)	9.6406(5)
b (Å)	15.8843(6)	15.5578(2)	16.4452(9)
c (Å)	14.7667(6)	26.9147(5)	14.8423(7)
α (°)	90	90	90
β (°)	95.762(4)	105.1594(18)	99.610(2)
γ (°)	90	90	90
Volume (Å) <sup>3</sup>	2153.91(15)	6540.10(19)	2320.1(2)
Z	4	8	4
r (calc) (g/cm <sup>3</sup> )	1.542	1.247	1.494
Abs (mm <sup>-1</sup> )	5.645	3.848	1.368
F(000)	1025	2568	1076
Crystal Size (mm <sup>3</sup> )	0.08 x 0.06 x 0.04	0.44 x 0.42 x 0.22	0.08 x 0.08 x 0.07
Theta Range (°)	4.10 to 70.69	3.31 to 72.60	1.86 to 26.33
Refl/Uniq	16138/4079	45624/12795	17923/4715
R(int)	0.0332	0.0413	0.0289
Abs Correction	None	None	None
Max./Min.	1.00000/0.616	0.42900/0.23000	0.9103/0.8985
Ref Method	Full Matrix least squares on F <sup>2</sup>	Full Matrix least squares on F <sup>2</sup>	Full Matrix least squares on F <sup>2</sup>
Data / restr / par	4079 / 15 / 285	12795 / 0 / 651	4715/0/264
GOF on F <sup>2</sup>	1.050	1.095	1.014
R1 indices (I>2s)	0.0390	0.0712	0.0322
wR2	0.1007	0.1868	0.0685
Peak/hole (e/Å <sup>-3</sup> )	0.744 and -0.407	1.065 and -1.173	0.541 and -0.297



## Results and Discussion:

### Syntheses

As shown in Scheme 1, ligand precursors **1a-c** react with one equivalent of  $\text{CuCl}_2$  in refluxing  $\text{CH}_2\text{Cl}_2$  to afford the five-coordinate copper complexes **4-6**. The driving force for the metallation is the formation of the the copper complex, which is sparingly soluble in  $\text{CH}_2\text{Cl}_2$ . All of the reactions (scheme 1) were performed in air and proceeded with yields at or above 95 %. Complexes **4-6** are soluble in dimethyl sulfoxide, acetonitrile and methanol and are sparingly soluble in dichloromethane and chloroform. Complexes **4-6** are dark purple. Crystals suitable for X-ray diffraction were grown by allowing diethyl ether vapor to slowly diffuse into a methanol solution containing the copper complex.



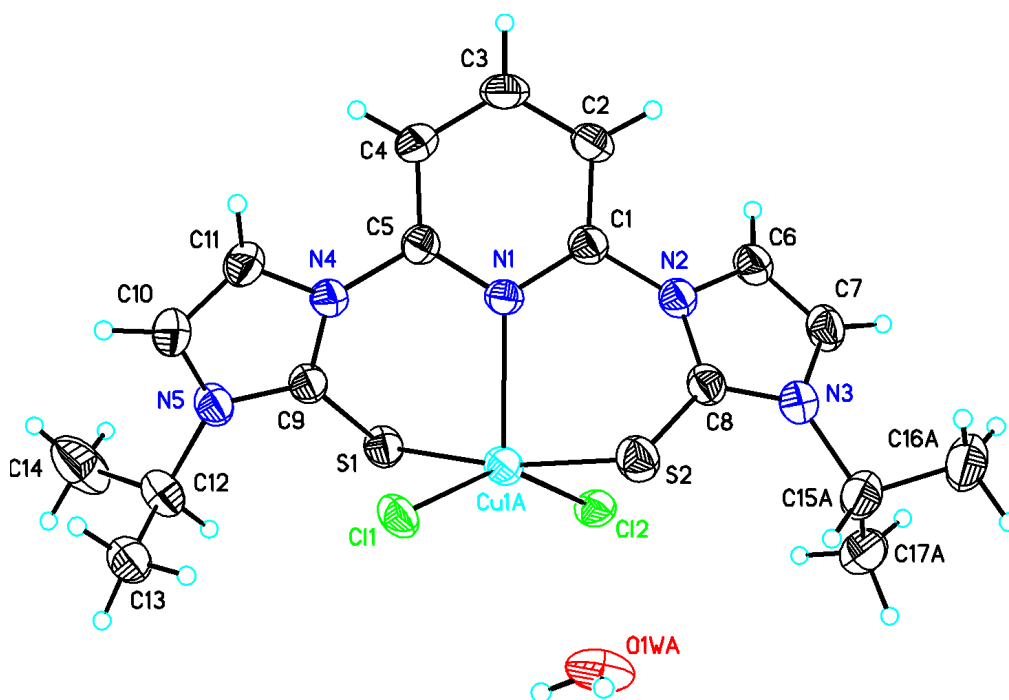
**Scheme 1:** Preparation of five-coordinate copper complexes that contain a tridentate SNS ligand.

All of these copper complexes were characterized using UV-visible spectroscopy, electrospray mass spectrometry, attenuated total reflectance infrared spectroscopy, electron paramagnetic resonance spectroscopy, cyclic voltammetry, and elemental

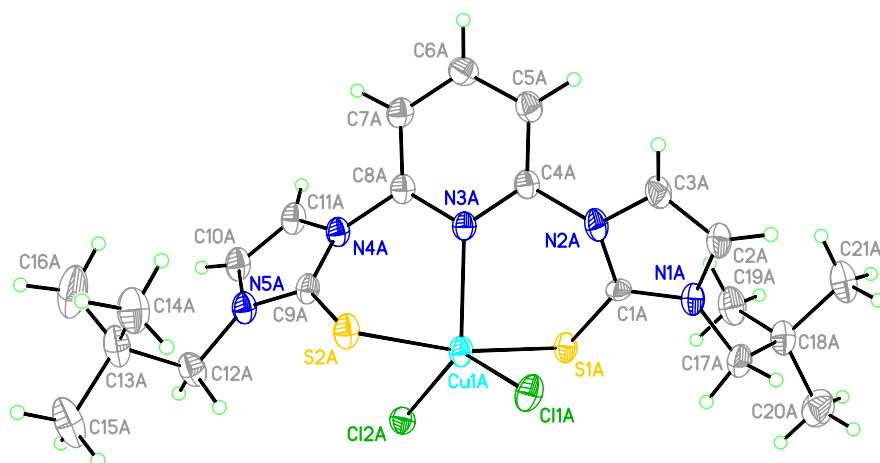
analysis. The following sections describe the characterization of these novel copper complexes.

### *Single Crystal X-ray structures*

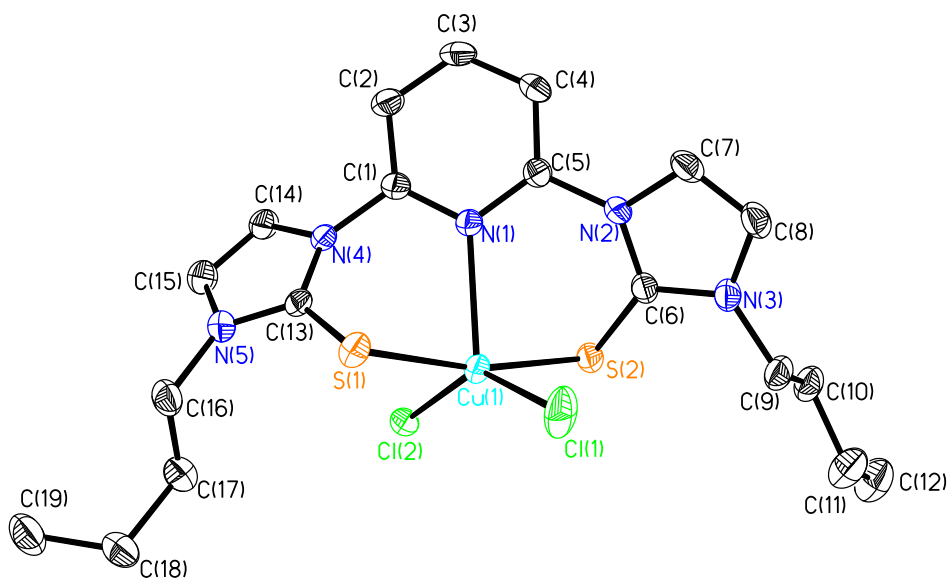
The solid-state structures of **4-6** are shown in Figures 1-3. These complexes, with a tridentate SNS donor ligand and two bound chlorides, possess pseudo-square-pyramidal geometry about the copper(II) center.



**Figure 1.** Molecular structure of **4** showing the atom labeling scheme and 50% probability ellipsoids.



**Figure 2.** Molecular structure of **5** showing the atom labeling scheme and 50% probability ellipsoids.



**Figure 3.** Molecular structure of **6** showing the atom labeling scheme and 50% probability ellipsoids. The hydrogen atoms on carbon atoms have been omitted for clarity.

Various bond lengths and angles for **4-6** are given in Tables 2-4, respectively.

**Table 2:** Selected bond lengths and angles (esd) for **4**.

[4]	
Cu(1A)-N(1) (Å)	2.289(2)
Cu(1A)-Cl(1) (Å)	2.3352(7)
Cu(1A)-Cl(2) (Å)	2.3113(7)
Cu(1A)-S(2) (Å)	2.3094(8)
Cu(1A)-S(1) (Å)	2.3274(8)
S(1)-C(9) (Å)	1.701(3)
S(2)-C(8) (Å)	1.708(3)
N(1)-Cu(1A)-Cl(1)	104.39(6)
N(1)-Cu(1A)-S(1)	84.95(6)
Cl(1)-Cu(1A)-S(2)	95.38(3)
S(1)-Cu(1A)-S(2)	170.97(3)
Cl(1)-Cu(1A)-Cl(2)	148.79(3)
S(1)-Cu(1A)-Cl(1)	96.96(3)

**Table 3:** Selected bond lengths and angles (esd) for **5**.

[5]	
Cu(1A)-N(3A) (Å)	2.223(4)
Cu(1A)-Cl(1A) (Å)	2.3609(11)
Cu(1A)-Cl(2A) (Å)	2.3129(12)
Cu(1A)-S(2A) (Å)	2.3235(13)
Cu(1A)-S(1A) (Å)	2.3218(12)Å
S(1A)-C(1A) (Å)	1.709(4)
S(2A)-C(9A) (Å)	1.704(4)
N(3A)-Cu(1A)-Cl(2A)	119.77(9)
N(3A)-Cu(1A)-S(1A)	84.29(10)
Cl(2A)-Cu(1A)-S(1A)	89.83(4)
S(1A)-Cu(1A)-S(2A)	169.62(5)
Cl(1A)-Cu(1A)-Cl(2A)	129.77(5)
S(1A)-Cu(1A)-Cl(1A)	95.15(4)

**Table 4:** Selected bond-lengths and angles (esd) for **6**.

[ <b>6</b> ]	
Cu(1)-N(1) (Å)	2.3385(18)
Cu(1)-Cl(1) (Å)	2.2797(6)
Cu(1)-Cl(2) (Å)	2.3032(6)
Cu(1)-S(2) (Å)	2.3292(7)
Cu(1)-S(1) (Å)	2.3163(7)
S(1)-C(6) (Å)	1.708(2)
S(2)-C(13) (Å)	1.703(2)
N(1)-Cu(1)-Cl(1)	113.65(5)
N(1)-Cu(1)-S(1)	84.65(5)
Cl(1)-Cu(1)-S(2)	94.11(2)
S(1)-Cu(1)-S(2)	168.53(2)
Cl(1)-Cu(1)-Cl(2)	141.15(3)
S(1)-Cu(1)-Cl(2)	95.16(2)

As can be seen in Tables 2-4, the Cu-N bond length is shorter in **5** (2.22 Å) than in **4** and **6** (2.29 Å and 2.33 Å, respectively). The Cu-S bond lengths are nearly identical for all of the complexes (ca. 2.31-2.32 Å). The Cu-Cl bond lengths are longest in **5** (2.36 and 2.31 Å) and shortest in **6** (2.27 and 2.30 Å). The Cu-Cl bond lengths in **4** (2.33 and 2.31 Å) are between those found in **5** and **6**.

The carbon-sulfur bond lengths in **4-6** are between what is normally associated with a C-S single bond (1.83 Å) and a C=S double bond (1.61 Å).[43] In these

complexes, the carbon-sulfur bond lengths range between 1.695 Å and 1.714 Å are closer to that of a C=S double bond than a C-S bond. The Cu-Cl bond lengths are about 0.2 Å shorter than previously reported for a Cu(II) complex with pseudo-square pyramidal geometry.[26] The Cu-N bond length is between 0.2 to 0.3 Å longer than that for a previously reported Cu-N(pyridine) bond length for a Cu(II) complex with pseudo-square pyramidal geometry.[26] The copper-sulfur bond lengths are consistent with those of single bonds in five-coordinate copper-complexes with pseudo-square pyramidal geometry.[11]

### *Electrospray Mass Spectroscopy*

ESI-MS data for complexes **4-6** were collected with cone voltages of 10V and 35 V. The predominant features in the spectra of **4-6** are that of the [(SNS)Cu]<sup>2+</sup> ion. For complexes **4-6**, these findings suggest that two chloride ligands are displaced in the mass spectrometer and that the tridentate ligand remains coordinated to the copper(II) ion. The isotopic pattern in the mass spectrometry data fits the assigned structure.

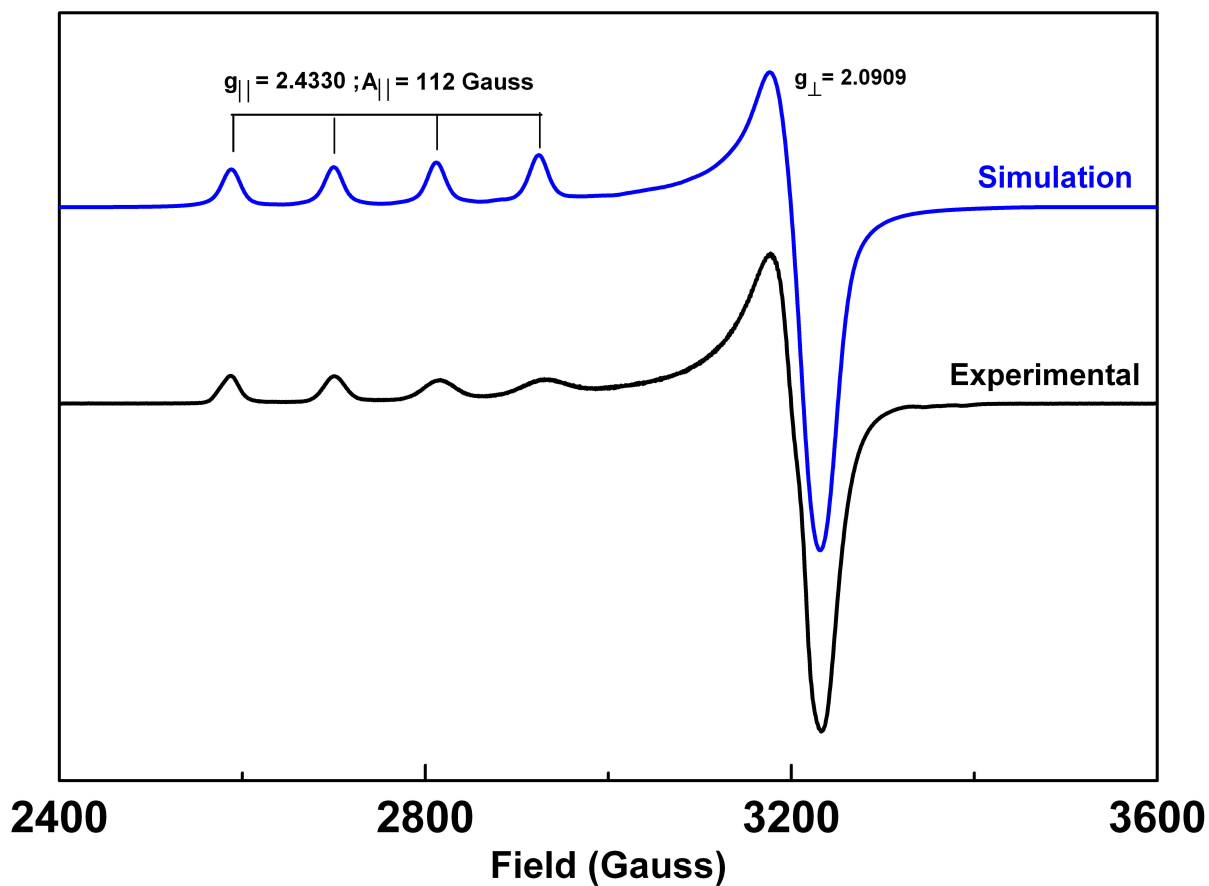
### *EPR Spectroscopy*



The EPR samples of the copper complexes were prepared by dissolving 3 mg of the copper complex in 1 mL of dry methanol. The complexes were stored at room temperature prior to analysis. The spectra were collected as frozen glass after flash freezing the samples in liquid N<sub>2</sub>. All three spectra are typical anisotropic Cu(II) signals with four hyperfine splittings in the lower-field region ( $g_{\parallel}$ ) and  $g$ -values consistent with previously reported copper complexes from the literature.[44-46]

Figure 4 shows experimental (black graph) and simulated (blue graph) frozen glass EPR spectrum of **6** at 10 K using a Bruker X-band ELEXSYS E500 spectrometer equipped with an ESR900 continuous flow liquid helium cryostat. EPR spectra were collected at X-band, 2 mW microwave power, and 1 gauss modulation amplitude.

A locally developed program known as *doublet*,[47] was used to simulate the frozen-glass EPR spectrum at 10 K based on the standard spin Hamiltonian of an  $S=1/2$  system. Resonance fields are calculated by diagonalization of the energy matrix. Temperature does not affect the  $S=1/2$  spectra in a way it affects the high-spin spectra, thus temperature was not used as a varying parameter in the simulation. The simulation was carried out with different values of  $g$  and  $A$  until a match was found. The final simulation yielded the parameters  $g$  along with the hyperfine structure  $A$  where  $g_{\parallel} = g_z$  and  $g_{\perp} = (g_x + g_y)/2$ . Simulated line widths are 12 gauss for both the  $y$  and  $z$  component and 15 gauss for the  $x$  component in compound **6**.



**Figure 4.** Simulated (blue) and experimental (black) frozen glass EPR spectra of **6** at 9.4 GHz and 10 K.

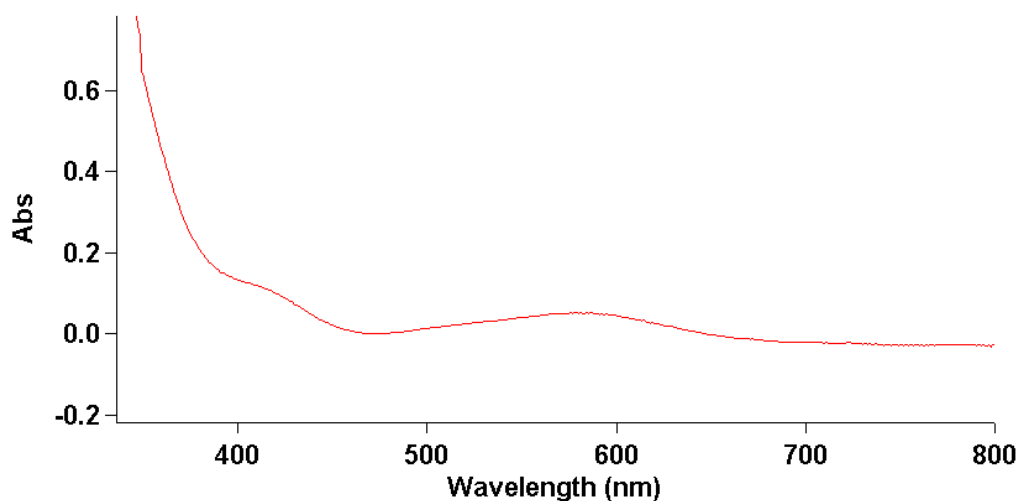
The simulated parameters for **6**, ( $I = 3/2$  signal) are  $g_x = 2.0822$ ;  $g_y = 2.0997$ ;  $g_z = 2.4330$ ; and  $A_z = 112$  Gauss.

#### *ATR-IR Spectroscopy*

Attenuated total reflectance IR spectra were collected for **4-6**. All compounds present unique IR spectra. Previously, we reported the C=S stretching frequencies for the ligand precursors **1a-c** at  $1126\text{ cm}^{-1}$  [1] and for **3b** to be  $1149\text{ cm}^{-1}$ . [2] This stretch was absent in the corresponding copper complexes.

### *UV-Vis Spectroscopy*

Complexes **4-6** were characterized with UV-Visible spectroscopy. A representative UV-Vis spectrum for complexes **4** is included below in figure 5. Given the  $d^9$  electron configuration of Cu(II) complexes, d-to-d transitions are possible. The spectroscopic features for complexes **4-6** are summarized in table 5.



**Figure 5.** UV-Vis absorption spectrum of **4** (0.49 mM) in methanol.

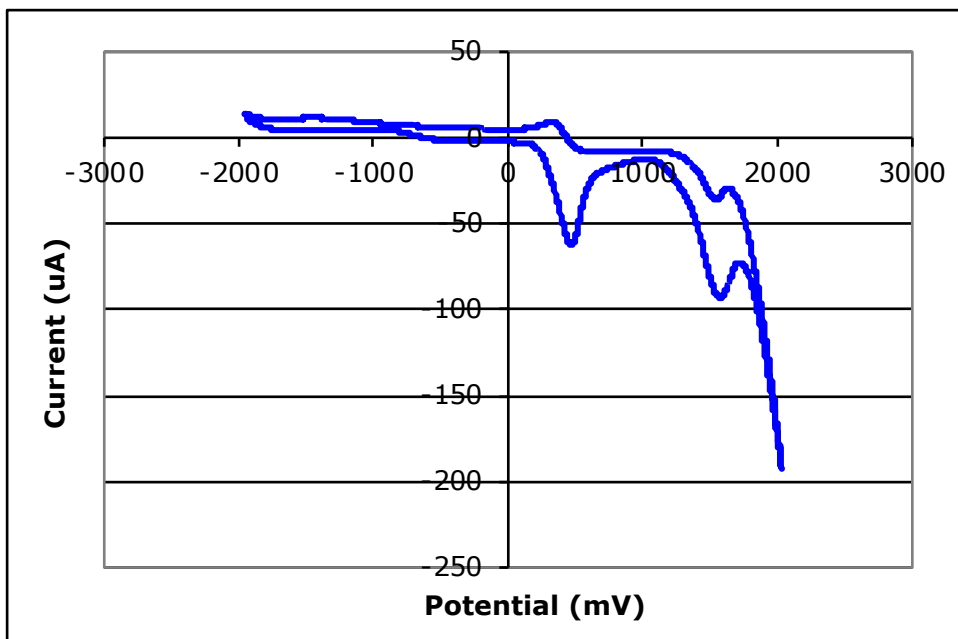
**Table 5.** Spectroscopic features of Complexes **4-6**

Complex	$\lambda_1$	$\Delta$ (cm <sup>-1</sup> )	$\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> )
<b>4</b>	581	1.72•10 <sup>4</sup>	110
<b>5</b>	571	1.75•10 <sup>4</sup>	4.0 x 10 <sup>2</sup>
<b>6</b>	578	1.73•10 <sup>4</sup>	18

The UV-vis spectra of **4-6** clearly show d-to-d transitions. Complexes **4-6** have a d-to-d transition between 581nm-571nm. Complexes **4-6** all exhibit ligand-to-metal charge-transfer (Cl<sup>-</sup> → Cu<sup>II</sup> or S → Cu<sup>II</sup> LMCT) transitions between 310nm-200nm. Extinction coefficients for complexes **4-6** ligand-to-metal charge-transfer transitions range from 2500-25,800 M<sup>-1</sup>cm<sup>-1</sup>.

### Cyclic Voltammetry

Compound **6** was studied by cyclic voltammetry in DMSO as part of its characterization. The cyclic voltammogram for **6** (Figure 6) shows oxidation features at 1576, and 1709 mV, and reduction waves at 1526 and -509 mV. The oxidation and reduction waves are broad and located at the same potential across consecutive scans. This cyclic voltammogram is representative of an irreversible process. We reported previously that ligand precursor **1** shows oxidation feature at 1289 mV and a reduction wave at -2376 mV.[1] This profile shows that the complex is stable across the oxidation and reduction cycle.



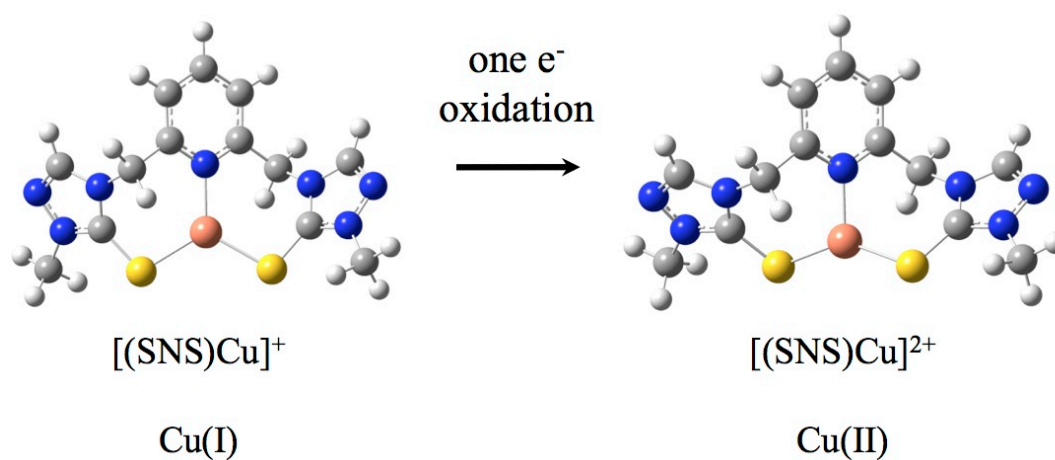
**Figure 6.** Cyclic Voltammogram of **6** in DMSO (5.6 mM) with 0.2 M TBAF. The scan rate was 100 mV/s with ferrocene ( $E_{1/2} = 400$  mV) used as an internal standard.

### **Electronic Structure Analysis: Influence of SNS Ligand Set in Determining Coordination Environment and Copper Oxidation State**

Given our recently reported three-coordinate Cu(I)-SNS systems and the five-coordinate Cu(II)-SNS complexes in our current study, it is evident that fine-tuning of the SNS ligand set affects the oxidation state and the coordination environment of the metal ion. We therefore are interested in understanding the factors that give rise to these differently constituted systems and have used Gaussian 03 to examine the effects that the constraints inherent to our ligand sets have on the electronic structures of these systems.

As part of our analysis of the three-coordinate Cu(I)-SNS complexes, we obtained the cyclic voltammograms on these systems and desired to investigate computationally

their observed one-electron oxidations.[35] Doing so required that geometry optimizations be performed on each cationic Cu(I) system and also on the corresponding one-electron oxidized dicationic Cu(II) counterpart in order to calculate the energy difference between these two states. Shown in Figure 7 are the computed structures for the  $C_2$ -symmetric N-methyl-substituted thiotriazolyl-based three-coordinate Cu(I) and Cu(II) systems that were obtained as part of that work. In Table 6 are presented the various bond lengths and angles in these two structures.



**Figure 7.** Ground-state optimized structures for the cationic N-methyl-substituted, thiotriazolyl-based Cu(I)  $[(\text{SNS})\text{Cu}]^+$  system and its one-electron oxidized Cu(II) counterpart.

**Table 6.** Optimized structural parameters for the cationic N-methyl-substituted, thiotriazolyl-based Cu(I)  $[(\text{SNS})\text{Cu}]^+$  system and its one-electron oxidized Cu(II) counterpart.

	[(SNS)Cu] <sup>+</sup> (crystal structures)	[(SNS)Cu] <sup>+</sup> (Gaussian 03)	[(SNS)Cu] <sup>2+</sup> (Gaussian 03)	Calculated change upon oxidation
Cu-N	2.005-2.012 Å	1.990 Å	1.969 Å	-0.021 Å
Cu-S	2.198-2.225 Å	2.242 Å	2.210 Å	-0.032 Å
N-Cu-S	117.5-120.5°	119.9°	108.0°	-11.9°
S-Cu-S	119.9-123.6°	120.1°	144.1°	24.0°

The calculated changes in metal-ligand bond lengths and angles resulting from the one-electron oxidation present an interesting story regarding the expected structural changes that occur with this electrochemically induced change in Cu oxidation state. As can be seen from the bond angles determined from the crystal structures and from the geometry optimization of the Cu(I) system, the coordination environment about the Cu center is quite close to that of a regular trigonal planar system. The methylene linkers in the SNS ligand set allow the S atoms to be oriented such that the N-Cu-S and S-Cu-S angles are quite close to 120°. Not surprisingly, the Cu-N and Cu-S bond lengths are calculated to become shorter with an increase in the Cu oxidation state. These changes are on the order of several hundredths of an Ångstrom whereas the changes in the N-Cu-S and S-Cu-S angles are more substantial. The S-Cu-S angle increases by 24.0° with a concomitant decrease in the N-Cu-S angle by 11.9°. The calculated S-Cu-S angle of 144.1° is intermediate what would be expected for trigonal planar (120°) and T-shaped (180°) configurations. Shown in Table 7 is similar computed data for the thioimidazolyl-based Cu-SNS system. The expected changes in bond lengths and angles are quite similar to what was calculated for the thiotriazolyl-containing complex.

**Table 7.** Optimized structural parameters for the cationic N-methyl-substituted, thioimidazolyl-based Cu(I) [(SNS)Cu]<sup>+</sup> system and its one-electron oxidized Cu(II) counterpart.

	[(SNS)Cu] <sup>+</sup> (Gaussian 03)	[(SNS)Cu] <sup>2+</sup> (Gaussian 03)	Calculated change upon oxidation
Cu-N	1.991Å	1.978Å	-0.013Å
Cu-S	2.239Å	2.203Å	-0.036Å
N-Cu-S	119.6°	109.2°	-10.4°
S-Cu-S	120.8°	141.7°	20.9°

Removing the methylene linker from the ligand set and performing a geometry optimization on such a structure provides a clue as to why we have had no success in preparing a three-coordinate Cu(I) complex with an SNS ligand that does not contain such a CH<sub>2</sub> unit. In Table 8 are summarized the optimized metal-ligand bond lengths and angles for three three-coordinate, N-methyl-substituted, and (for continuity with the immediately preceding discussion with and our work in [35]) thiotriazolyl-containing systems: a Cu(I) complex with the CH<sub>2</sub> linker, a Cu(I) structure without the linker, and a Cu(II) system without the linker; the optimized structure for the hypothetical three-coordinate Cu(I) complex without methylene linkers is shown in Figure 8. Although the calculated Cu-S bond length varies relatively little throughout these permutations, the Cu-N length changes quite dramatically between the Cu(I) systems. With the methylene linker included, the calculated Cu-N bond length is 1.990Å; without it, the distance is 2.308Å, an increase of 0.318Å caused merely by the removal of two methylene units from between the pyridinyl and thiotriazolyl moieties. The S-Cu-S bond angle also increases significantly to nearly 170°. Removal of an electron to generate a Cu(II) complex allows the Cu-N and Cu-S bond lengths to shorten relative to the analogous

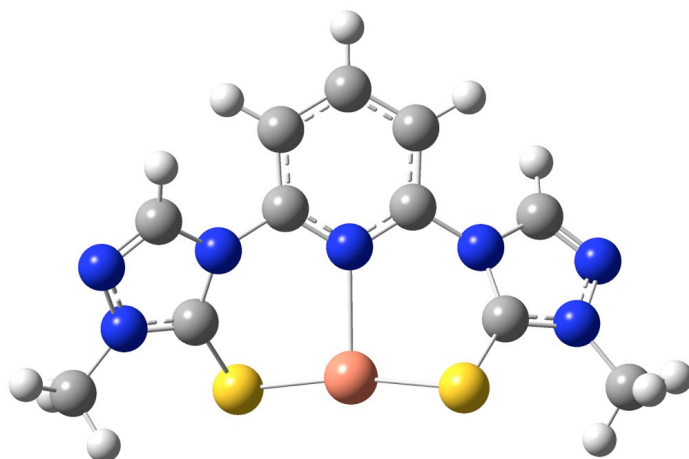


bond lengths found for the Cu(I) system with the linker, as would be expected on increasing the oxidation state from Cu(I) to Cu(II), while simultaneously maintaining the relatively large S-Cu-S bond length of 160.6°.

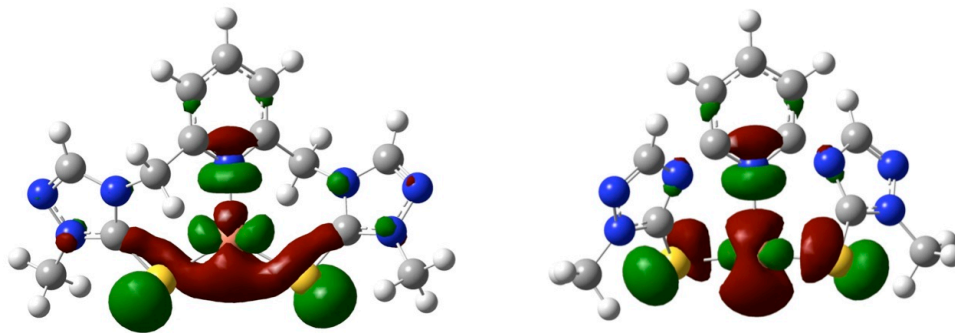
These changes in metal-ligand bond lengths and angles can be directly attributed to the change in orbital character in the highest occupied molecular orbitals (HOMOs) of these systems upon removal of the linkers. These molecular orbitals are presented in Figure 9 for the hypothetical Cu(I) systems with and without the methylene linkers. For the  $d^{10}$  Cu(I) metal centers, these HOMOs are electronically doubly occupied, contain what could be termed as Cu  $d_{x^2-y^2}$  character, and are both strongly Cu-N  $\sigma^*$  antibonding. The presence of the methylene linker allows the N-Cu-S angle to be close to 120°, thereby allowing the Cu-S orbital interaction to be simultaneously weakly Cu-S  $\sigma$  bonding and Cu-S  $\sigma^*$  antibonding as can be observed in the contour plot. Removal of the methylene linker forces the N-Cu-S bond angle to near 90° as a result of bonding constraints within the SNS ligand set. As a result, the HOMO becomes strongly Cu-N and Cu-S  $\sigma^*$  antibonding, an effect that is manifested in a considerably elongated Cu-N bond (2.308Å). Removal of an electron from this molecular orbital for the system without the linker eases this occupied antibonding interaction somewhat.

**Table 8.** Gaussian 03-optimized structural parameters for three three-coordinate, N-methyl-substituted, and thiotriazolyl-containing Cu-SNS systems.

	Cu(I) and with CH <sub>2</sub> linker	Cu(I) and without CH <sub>2</sub> linker	Cu(II) and without CH <sub>2</sub> linker
Cu-N	1.990Å	2.308Å	1.973Å
Cu-S	2.242Å	2.179Å	2.207Å
N-Cu-S	119.9°	95.1°	99.7°
S-Cu-S	120.1°	169.8°	160.6°



**Figure 8.** Optimized structure of a hypothetical three-coordinate Cu(I) [(SNS)Cu]<sup>+</sup> system in which there are no methylene linkers within the ligand set.



**Figure 9.** HOMOs of the model three-coordinate, N-methyl-substituted, thiotriazolyl-containing Cu(I)  $[(\text{SNS})\text{Cu}]^+$  systems with (left) and without (right) methylene linkers connecting the pyridinyl and thiotriazolyl moieties of the tridentate ligand.

The conclusion that we draw from these computations is that a  $d^9$  Cu(II) metal center is better situated than a  $d^{10}$  Cu(I) center to bind one of our tridentate SNS ligand sets when it does not contain an internal  $\text{CH}_2$  group. Without the methylene linker, the SNS ligand forces the N and S atoms into a T-shaped arrangement around the metal center. The Cu(II) systems prepared in the current study exemplify this finding. Complexes **4**, **5**, and **6** possess five-coordinate, not three-coordinate Cu(II) ions, but the SNS ligand is arranged as in the hypothetical T-shaped Cu(II) system: the S atoms are located in the axial positions and the pyridinyl N atom occupies one of the three equatorial sites to give S-Cu-S and N-Cu-S bond angles of approximately  $170^\circ$  and  $85^\circ$ , respectively. Coordination of two chlorides ensures that the metal center is Cu(II), not Cu(I). The relationship between these two coordination environments can be further emphasized by noting the similarity of the SNS ligand orientations in the five-coordinate structures in Figures 1, 2, and 3 and of the hypothetical three-coordinate structure shown in Figure 8.

## Conclusions

A series of novel SNS-coordinated copper(II) compounds has been prepared and characterized through the use of our own imidazolyl-based tridentate ligand systems. Based on X-ray crystal structures, the five-coordinate copper(II) complexes possess pseudo-square pyramidal geometry at the metal center. The EPR spectra of these systems are consistent with typical anisotropic copper(II) signals with four hyperfine splittings in the lower-field region ( $g_{\parallel}$ ) and  $g$ -values consistent with previously reported copper complexes from the literature. In the electronic spectra, d-to-d transitions and various charge-transfer transitions are apparent. We performed computational studies to understand the influence that structural constraints internal to our tridentate SNS ligand precursors have on the oxidation state of the resulting bound copper complex. We learned that a  $d^9$  copper(II) metal center is better situated than a  $d^{10}$  copper(I) center to bind one of our tridentate SNS ligand sets when it does not contain an internal  $\text{CH}_2$  group. Without the methylene linker, the SNS ligand forces the N and S atoms into where they would be found in a T-shaped system.

### Appendix 1. Supplementary data

CCDC 955935 contains the supplementary crystallographic data for 4.

CCDC 955937 contains the supplementary crystallographic data for 5.

CCDC 955936 contains the supplementary crystallographic data for 6.

These data can be obtained free of charge via

<http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

## **Acknowledgements**

This work was supported by generous funding from The Fairfield University Science Institute (JRM, EEB, KAA, CEV), Fairfield University Start-up Funding (JRM), Fairfield University Research Grants (JRM), Fairfield University Summer Research Kuck Fund (EEB, CEV, and EP) and an NTID Faculty Evaluation and Development Grant (MAL). JPJ acknowledges the NSF--MRI program (grant No.CHE1039027) for funds to purchase the X-ray diffractometer. JRM and DB also acknowledge the MRI grant program (grant No. CHE08539) for the purchase of an EPR spectrometer. JRM would like to thank Prof. L. Kraig Steffen for helpful suggestions.

## **Supporting Information**

The ESI-MS, UV-Vis, ATR-IR, of **4-6** are provided. Crystallographic details of **4-6** are also given. The Cartesian coordinates of all the optimized structures provided by density functional theory are also provided.

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