2-24-2014

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Miecznikowski, John R.; Lynn, Matthew A.; Jasinski, Jerry P.; Reinheimer, Eric; Bak, Daniel; Pati, Mekhala; Butrick, Elizabeth E.; Drozdoski, Anne Elise R.; Archer, Kerry A.; Villa, Christine E.; Lemons, Elise G.; Powers, Erin; Siu, Margaret; Gomes, Camile D.; and Morio, Kaitlyn N., "Synthesis, Characterization, and Computational Study of Three-Coordinate SNS Copper(I) Complexes Based on Bis-Thione Ligand Precursors" (2014). *Chemistry & Biochemistry Faculty Publications*. 21.
http://digitalcommons.fairfield.edu/chemistry-facultypubs/21

Published Citation

Miecznikowski, John R.; Lynn, Matthew A; Jasinski, Jerry P.; Reinheimer, Eric; Bak, Daniel; Pati, Mekhala; Butrick, Elizabeth E.; Drozdoski, Anne Elise R.; Archer, Kerry A.; Villa, Christine E.; Lemons, Elise G.; Powers, Erin; Siu, Margaret; Gomes, Camile D.; Morio, Kaitlyn N. "Synthesis, Characterization, and Computational Study of Three-Coordinate SNS Copper(I) Complexes Based on Bis-Thione Ligand Precursors", Journal of Coordination Chemistry, 2014, 67(1), 29-44, Published online: 24 Feb 2014

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Synthesis, Characterization, and Computational Study of Three-Coordinate SNS-Copper(I) Complexes Based on Bis-Thione Ligand Precursors

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Abstract

A series of tridentate pincer ligands, each possessing two sulfur- and one nitrogen-donor functionalities (SNS), based on bis-imidazolyl or bis-triazolyl salts were metallated with $CuCl_2$ to give new tridentate SNS pincer copper(I) complexes $[(SNS)Cu]^+$. These orange complexes exhibit a three-coordinate pseudo-trigonal-planar geometry at the copper center. During the formation of these copper(I) complexes, disproportionation is observed to occur as the copper(II) salt precursor is converted into the Cu(I) $[(SNS)Cu]^+$ cation and the $[CuCl_4]^{2-}$ counteranion. The $[(SNS)Cu]^+$ 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 ($g_∥$) and g-values consistent with the presence of the tetrachlorocuprate counteranion. Various electronic transitions are apparent in the UV-Vis spectra of the complexes and originate in the copper-containing cations and anions. Density functional calculations, which investigate and support the nature of the SNS binding, allow us to assign a number of features present in the UV-Vis, and IR spectra and cyclic voltammograms of these complexes.

Keywords

1. Introduction

Recently, we have reported a series of tridentate pincer ligand precursors possessing SNS donor atoms [1-2]. In our previous studies, we have used these ligands to gauge the impact of ligand flexibility on the structure and catalytic reactivity of tridentate zinc(II) SNS pincer complexes. Through the fusion of variously substituted pyridine precursors with N-heterocycles, followed by reaction of the ligand precursor salt with sodium acetate and sulfur, SNS ligand systems with variable flexibility and electronic properties can be prepared (Figure 1).

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

Using 2,6-dibromopyridine as a starting material permits the thioimidazolyl groups to bind directly to the pyridine moiety (**1a-c**). Such a ligand system is relatively stiff; 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 by employing 2,6-(dibromomethyl)pyridine, thereby introducing a methylene linker between the fragments (**2a-c** and **3a-c**). 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. Use of these variously tuned tridentate ligand sets has allowed us to compare the effect of ligand flexibility on the reactivity of their zinc-bound complexes toward the catalytic reduction of electron-poor aldehydes [1-2]. Jin and co-

workers have prepared ligand precursor **1a** (Figure 1) as well and have used it to prepare half-sandwich iridium and rhodium complexes that contain this ligand [3].

The preparation of ligands that contain nitrogen and sulfur donor atoms as well as of copper complexes that contain these ligands is of considerable interest in bioinorganic chemistry. In electron-transfer proteins, interactions between copper and the thiolate functionality of cysteine are important [4-5]. Sulfide-copper interactions are also found in the Cu_4-S cluster in nitrous oxide reductase [6-8]. In addition, thioether-methionine-copper ion interactions occur in Type 1 "blue" electron-transfer proteins and in the active site of certain monooxygenases [9-10].

Using the ligand precursors shown in Figure 1, we focused attention in our current work on the preparation of novel SNS-bound copper complexes using ligand precursors **2a, 3a, and 3c** (Figure 1). Of course, numerous three-coordinate mononuclear copper(I) [11-22] and copper(II) [23-27] complexes are known with various kinds of coordination observed at the metal center. The Cu(I) complexes reported previously all exhibit pseudo-trigonal planar geometry about the copper center. The three-coordinate copper(II) complexes possess either a pseudo-trigonal planar [23, 26] or a T-shaped coordination environment [24, 25] about the copper center. To the best of our knowledge, a three coordinate copper complex with donor atoms of S, S, and N has not been reported. An iridium piano stool complex with a tridentate SSN ligand has been reported recently [28].

We present here the syntheses, X-ray crystallographic, spectroscopic and electrochemical characterizations, and computational analysis of our new three-coordinate copper(I) complexes containing a tridentate ligand with two sulfur and one

nitrogen donor atoms.

2. Experimental

2.1. 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. We have previously reported the syntheses of the ligand precursors 2,6-bis{[N-butyl]imidazol-1-ylidene-2-thione}pyridine, 2,6-bis{[N-isopropyl]imidazol-1-ylidene-2-thione}pyridine,2,6-bis{[N-neopentyl]imidazol-1-ylidene-2-thione}pyridine, 2,6-bis{[N-isopropyl-N′-methylene] imidazol-1-ylidene-2-thione}pyridine, 2,6-bis{[N-isopropyl-N′-methylene]triazole-2-thione}pyridine, and 2,6-bis{[N-butyl-N′-methylene]imidazol-1-ylidene-2-thione}pyridine used herein [1-3].

Each sample was analyzed by direct flow injection (injection volume = 3 or 10 μL) 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 °C and Desolvation Temperature = 120 or 350 °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, or a Bruker Tensor 27 FT-IR with an attenuated total reflectance adaptor. C, H, and 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 samples of the copper complexes were 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.

2.2. Syntheses

2.2.1. Bis-[(η^3-S,S,N)(2,6-bis){[N-isopropyl-N′-methylene]imidazole-1-ylidene-2-thione} pyridine copper(I) tetrachlorocuprate] [4]

In 25 mL round-bottom flask, 2,6-bis{[N-isopropyl-N′-methylene]imidazole-1-ylidene-2-thione}pyridine (0.0967 g, 0.000269 mol) was combined with $CuCl_2$ (0.0365 g, 0.000271 mol) and dissolved in dichloromethane (10 mL). The solution mixture was refluxed for 20 h. After this time, the solvent was removed under reduced pressure. Single crystals for elemental analyses were grown by a slow vapor diffusion of diethyl ether into a methanol

solution containing the copper complex. Yield: 0.12 g (69 %). FT-IR (reflectance, solid crystal, ν_{max}/ cm^{-1}, assignment): 3051 (br, C-H stretch), 2971 (br, C-H stretch). ESI MS (m/z): 450.0874 (450.08 calcd for $[C_{19}H_{25}N_5S_2Cu]^+$). Elemental Anal. calcd (found) for $[C_{19}H_{25}Cu_1N_5S_2]_2[CuCl_4]\bullet H_2O$: C, 40.55 (40.37); H, 4.66 (4.50); N, 12.44 (12.31). UV VIS λ_{max} (CH$_3$CN)/nm (ε/M^{-1} cm^{-1}): 462 (260), 265 (36 000), 204 (46 000).

2.2.2. Bis[(η^3-S,S,N)(2,6-bis){[N-isopropyl-N′-methylene]triazole-2-thione} pyridine copper (I) tetrachlorocuprate] [5]

In a 25 mL round-bottom flask, 2,6-bis{[N-isopropyl-N′-methylene]triazole-2-thione}pyridine (0.1491 g, 0.0003831 mol) was combined with CuCl$_2$ (0.0514 g, 0.000390 mol) and dissolved in dichloromethane (10 mL). The solution mixture was refluxed for 20 h. After this time, the solvent was removed under reduced pressure. Single crystals for X-ray diffraction and elemental analyses were grown by a slow vapor diffusion of diethyl ether into a methanol solution containing the copper complex. Yield: 0.16 g (64 %). FT-IR (reflectance, solid crystal, ν_{max}/ cm^{-1}, assignment): 3035 (br, C-H stretch), 2984 (br, C-H stretch), 2971 (br, C-H stretch), 2941 (br, C-H stretch). ESI MS (m/z): 452.0748 (452.08 calcd for $[C_{17}H_{23}N_7S_2Cu]^+$). Elemental Anal. Calcd (found) for $[C_{19}H_{23}Cu_1N_7S_2]_2[CuCl_4]\bullet 3H_2O$: C, 35.04 (35.14); H, 4.50 (4.10); N, 16.82 (16.67). UV VIS λ_{max} (CH$_3$CN)/nm (ε/M^{-1} cm^{-1}): 461 (1 200), 299 (5 100), 258 (34 000).

2.2.3. Bis-[(η^3-S,S,N)(2,6-bis){[N-butyl-N′-methylene]triazole-2-thione} pyridinecopper (II) tetrachlorocuprate] [6]

In 25 mL round-bottom flask, 2,6-bis {[N-butyl-N′-methylene] triazole-2-thione} pyridine (0.1415 g, 0.0003389 mol) was combined with $CuCl_2$ (0.0942 g, 0.000701 mol) and dissolved in dichloromethane (11 mL). The solution mixture was refluxed for 20 h. After this time, the solvent was removed under reduced pressure. Single crystals for X-ray diffraction and elemental analyses were grown by a slow vapor diffusion of diethyl ether into a methanol solution containing the copper complex. Yield: 0.23 g (99 %).   FT-IR (reflectance, solid crystal, ν_{max}/ cm^{-1}, assignment): Select IR bands (reflectance, solid crystal), ν_{max}/ cm^{-1} (intensity, assignment) 3032(w, C-H stretch), 2955 (br, C-H stretch), 2870 (w, C-H stretch).   ESI MS (m/z): 480.1064 (480.11 calcd for $[C_{19}H_{27}N_5S_2Cu]^+$). Elemental Anal. Calc. for $[C_{19}H_{27}CuN_7S_2]_2[CuCl_4] \cdot 2H_2O$: C, 37.92; H, 4.86; N, 16.29. Found: C, 38.32; H, 4.65; N, 16.13.   UV VIS λ_{max} (CH$_3$CN)/nm (ε/M^{-1} cm^{-1}): 461 (1 300), 307 (5 400), 258 (37 000).

2.3. Crystallographic Analyses:

  A red-orange, plate-like crystal of **5,** which had dimensions of 0.35 x 0.27 x 0.15 mm^3, was secured to a cryoloop using Paratone Oil and placed into the liquid nitrogen stream of a Bruker SMART 1K diffractometer.   Data was collected using graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) at 203 K in four independent wedges of 606 frames each at phi angles of 0, 90, 180 and 270°. A final set of 50 frames at φ = 0° was collected to evaluate the single crystal for indications of decay. No appreciable decay was found to have occurred after comparison of measured intensities. All 2474 frames were collected at a width of 0.3°. Data collection and initial indexing were handled using SMART [28]. Frame integration, Lorentz-polarization corrections, and

final cell parameter calculations were carried out using SAINT [29]. Multi-scan absorption corrections were performed using SADABS [30]. Space groups were unambiguously assigned by analysis of symmetry and systematic absences determined by XPREP and further verified by PLATON [31-32]. The structure was solved using direct methods and difference Fourier techniques. Hydrogen atoms bound to the isopropyl carbon atoms C2, C16, C19 and C33 and to the carbon atoms C5, C13, C22 and C30 within the triazole rings were identified using direct methods. All other hydrogen atoms were attached via the riding model at calculated positions. The final structural refinement included anisotropic temperature factors on all non-hydrogen atoms. Structure solution, refinement, graphics, and creation of publication material were performed using SHELXS, SHELXL and XSEED [33-34]. All other pertinent crystallographic details such as h, k, l ranges, 2θ ranges, and R-factors can be found in Table 1. CCDC file - 835944 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.

Table 1. Crystal and Structure Refinement Data for **5** and **6**

A crystal of **6** (*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-Kα radiation and integrated and corrected for absorption using the *CrysAlisRed* (Oxford Diffraction, 2010 software

package) [35]. The structures were solved using direct methods and refined using least-square methods on F-squared [36-37]. All other pertinent crystallographic details such as h, k, l ranges, 2θ ranges, and R-factors can be found in Table 2 or 3. CCDC file 955913 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.

2.4. Density Functional Calculations:

Gaussian 03 [38] was used to perform single-point calculations and geometry optimizations using the B3LYP hybrid functional with basis sets as provided with the software. Calculations were performed using N-methyl pendant groups and C_2 symmetry in all cases. Structures of the singly cationic imidazolyl- and triazolyl-containing $[(SNS)Cu]^+$ complexes were first optimized in the gas phase for the purpose of determining a basis set that resulted in molecular structures that matched well the experimentally determined crystal structures. Structures of the doubly cationic $[(SNS)Cu]^{2+}$ systems were then obtained as part of our electrochemical analysis. Solvent was later added via single-point calculations in the determination of the computed absorption spectra and oxidation potentials. Frequency analyses were performed on the optimized structures to determine whether or not they represented true minima. All structures presented no imaginary frequencies. The calculated IR spectra for the model systems are provided in the supporting information.

To model the electrochemical experiments, single-point SCRF calculations using DMSO via the CPCM solvent model were performed on the gas-phase optimized

structures using the ''radii = uff'' and ''nosymmcav'' directives. Oxidation potentials were computed by finding the difference in the total free energies in solution for the neutral and cationic species. These ΔG values were then referenced to the absolute SCE potential in DMSO by subtracting 3.83 V (the established correction to SHE in DMSO) and 0.241 V (the difference between SHE and SCE) [39-40].

In order to calculate electronic transitions in the UV-Vis region, time-dependent DFT calculations were performed using the B3LYP functional. A solvent model with all of the same parameters used to compute the oxidation potentials was employed except that acetonitrile was used instead of DMSO.

3. Results and Discussion

3.1. Syntheses

As shown in Scheme 1, ligand precursors **2a, 3a, and 3c** react with $CuCl_2$ in refluxing CH_2Cl_2 to afford copper complexes **4-6.** The driving force for the metallation is the formation of the the copper complex, which is sparingly soluble in CH_2Cl_2. Two equivalents of $CuCl_2$ were used to drive the reaction to completion in all cases. All reactions were performed in air and proceeded with yields at or above 64 %. Complexes **4-6** are orange**,** are soluble in dimethyl sulfoxide, acetonitrile, and methanol, and are sparingly soluble in dichloromethane and chloroform. Crystals of **5** and **6** suitable for X-ray diffraction were grown by allowing diethyl ether vapor to slowly diffuse into an methanol solution containing the copper complex.

Scheme 1. Preparation of three-coordinate [(SNS)Cu]$^+$ complexes.

The copper complexes were characterized using single crystal X-ray diffraction (complexes **5** and **6**), UV-visible spectroscopy (**4-6**), electrospray mass spectrometry (**4-6**), attenuated total reflectance infrared spectroscopy (**4-6**), electron paramagnetic resonance spectroscopy (**4** and **5**), cyclic voltammetry (**4** and **5**), and elemental analysis. (**4-6**) The characterizations of these novel copper complexes are described below.

3.2. Single Crystal X-ray Structures

The solid-state structure of **5** is presented in Figure 2. Bond lengths and angles for this compound are summarized in Table 2.   For this system, as well as for complexes **4** and **6**, disproportionation [41] was observed in the solid state. Two [(SNS)Cu]$^+$ cations and one [CuCl$_4$]$^{2-}$ anion are present in each unit cell.   The elemental analyses for **4**, **5**, and **6** are consistent with this determination. To probe further this finding, an EPR spectrum of complex **5** dissolved in frozen methanol solution was acquired at 4K and will be discussed in a subsequent section.

Figure 2. Molecular structure of **5** showing the atom labeling scheme and 50% probability ellipsoids.   The hydrogen atoms have been omitted for clarity.

Table 2: Selected bond-lengths (Å) and angles (deg) for **5**.

The solid-state structure of **6** is shown in Figure 3 and associated bond lengths and angles are given in Table 3. As was observed in the crystal structure for **5**, disproportionation gives rise to two $[(SNS)Cu]^+$ cations and one $[CuCl_4]^{2-}$ anion in the unit cell for **6**.

Figure 3. Molecular structure of **6** showing the atom labeling scheme and 50% probability ellipsoids.

Table 3: Selected bond-lengths (Å) and angles (deg) for **6**.

Figures 2 and 3 and Tables 1 and 2 demonstrate a number of important structural features that **5** and **6** possess. Both molecules exhibit pseudo-trigonal-planar geometry about the copper center as has been reported for other three-coordinate copper (I) complexes [11-23]. The Cu-N bond lengths in each system are approximately 2.0 Å and the Cu-S bonds are on the order of 2.2 Å. For **5** and **6**, the Cu-N bond lengths are similar to those reported previously for three-coordinate copper(I) complexes with trigonal planar geometry [18-19]. The carbon-sulfur bond lengths in **5** and **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) [42]. In our complexes, the carbon-sulfur bond lengths range from 1.695 Å to 1.714 Å, meaning that they are closer to that of a C=S double bond than to a C-S single bond. Furthermore, these Cu-S bond distances are 0.02-0.04 Å shorter than reported by Lobana and co-workers for a thiophosphenyl-bound Cu(I) complex [43].

Also present in the solid-state structures of **5** and **6** is the Cu(II)-containing $[CuCl_4]^{2-}$

counter-anion. Inspection of Tables 2 and 3 shows that the Cu-Cl bond lengths are not all equivalent in this Jahn-Teller distorted d^9 anion. The tetrachlorocuprate anion in each structure has a flattened tetrahedral structure as has been reported previously [44].

Our calculations using the B3LYP functional in Gaussian 03 demonstrate that it is the less expensive basis sets that not only allow for geometry optimizations that provide molecular structures that most closely resemble the experimentally determined X-ray crystal structures, but also provide electronic structure data that fit well with the UV-Vis spectra and the electrochemical data to be presented shortly. The calculations in which the 6-31G(d) basis set was used for the H, C, N, and S atoms and the 6-311G(d,p) basis set was employed for the Cu atom result in structures that have Cu-N and Cu-S bond lengths and N-Cu-S and S-Cu-S bond angles that are quite close to those found in the crystal structures. The Cartesian coordinates of the optimized structures determined here and employed in our study are provided in the Supplementary Information.

3.3. Electrospray Mass Spectroscopy

ESI-MS data for complexes **4-6** were collected with cone voltages of 10 V and 35 V. The predominant feature in the spectra of **4-6** corresponds to the $[(SNS)Cu]^+$ parent ion, indicating that the tridentate ligand remains coordinated to the copper ion during the analysis. For all of these spectra, the isotopic pattern in the mass spectrometry data fits the assigned structure.

3.4. EPR Spectroscopy

X-band EPR (9.24 GHz) spectroscopy was carried out in order to complement the

single-crystal X-ray diffraction and UV-Vis data presented herein. In Figure 4, the low-temperature (10 K) spectra for **4** and **5** are presented. 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 through the use of a frozen glass after flash-freezing the samples in liquid N_2. Both spectra display 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 [45-48]. For the complexes prepared here, the Cu(II) signal results from the presence of the tetrachlorocuprate counteranion.

Figure 4. Low temperature (10 K) X-band EPR spectra of oxidized **4** and **5**, measured at 9.24 GHz.

Figure 5. Simulated (blue) and experimental (black) frozen glass EPR spectra of **5** at 9.4 GHz and 10 K.

A locally developed program known as *doublet* [49], was used to simulate the frozen-glass EPR spectrum at 10 K based on the standard spin Hamiltonian of an S=½ 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 $g_\perp = (g_X + g_Y)/2$. The simulated line widths of the x, y and z components are 15, 8 and 35 gauss for **5**, respectively. Simulated parameters are given in Table 4.

Table 4. Simulated EPR parameters for **5**.

Complexes **4** and **5** have $g_\perp$ and $g_\parallel$ values of 2.09 and 2.43 respectively. The $A_\parallel$ values for **4** is 11.5 mT and for **5** is 11.0 mT. These values are representative of the tetrachlorcuprate anion. An EPR spectrum of a $[CuCl_4]^{2-}$ anion has been reported previously [50]. The DFT calculations for this anion [50] are consistent with a distorted tetrahedral structure about the copper(II) metal center. In addition, DFT calculations for the EPR spectrum of a $[CuCl_4]^{2-}$ anion have been reported previously [51]. Rahemi and co-workers [51] calculated $g_\perp$ and $g_\parallel$ values of 2.085 and 2.243, respectively, for a $[CuCl_4]^{2-}$ anion with D_2d symmetry with a molecular charge of -2.6.

3.5. ATR-IR Spectroscopy

Attenuated total reflectance (ATR) 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 **1-3**, at 1126 cm^{-1} for **1**, 1128 cm^{-1} for **2**, and 1149 cm^{-1} for **3** [1-2]. These stretches are absent in the corresponding copper complexes. Based on previous reports, the Cu-S and Cu-N stretches should largely be found at energies less than 470

cm^{-1}, which is below the limit of detection of the IR spectrometer with an ATR cell [52-53]. Our Gaussian 03 calculations support the assignment of spectral features in this range for the metal-ligand stretches and other motions. For the N-methyl-substituted model for **4**, although a vibrational mode includes Cu-N stretching occurs at 634 cm^{-1} and other stretches in this region include S-Cu-S scissoring and rocking, these motions and Cu-S vibrations dominate the features between 200 and 500 cm^{-1}. Similarly, Cu-N stretching is observed at 632 cm^{-1} for the N-methyl-substituted triazolyl systems (model for **5** and **6**) and the various metal-ligand scissoring, rocking, and stretching motions are found between 200 and 560 cm^{-1}. A listing of all calculated molecular motions between 200 and 3400 cm^{-1},for the N-methyl-substituted model systems of **4**, **5**, and **6**, including the relative intensities of the spectral features and descriptions of the motions, is presented in the supporting information.

3.6. UV-Vis Spectroscopy

Complexes **4-6** were also characterized with UV-Vis spectroscopy. Representative UV-Vis spectra for complexes **4** and **5**, are shown in Figures 6 and 7. The spectroscopic features for complexes **4-6** are summarized in Table 5.

Figure 6. UV-Vis absorption spectrum of **4** (0.060 mM) in acetonitrile.

Figure 7. UV-Vis absorption spectrum of **5** (0.053 mM) in acetonitrile.

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

Several electronic transitions are apparent in the UV-Vis spectra of **4-6**. All systems exhibit a transition around 460 nm with an extinction coefficient between 200 and 1300 $M^{-1}cm^{-1}$. Other electronic transitions are present at wavelengths less than approximately 375 nm. Given that each system contains a cationic Cu(I) center as well as Cu(II) in the anion, the UV-Vis spectra of these compounds should represent admixtures of the absorption spectra of two UV-Vis-active species.

Shown in Figure 8 is the UV-VIS spectrum of K_2CuCl_4 collected as part of this work. At 461 nm is an absorption feature that is also readily apparent in the spectra of **4** and **5**. This absorption is therefore caused by the presence of the d^9 tetrachlorocuprate anion. Several other transitions with maximum absorptions at 355, 310, and 258 nm can also be seen. Taubert and co-workers [50] reported maximum absorptions at 200, 258, 311, and 458 nm for $[nBuPy]_2[CuCl_4]_2$.

Figure 8. UV-VIS Spectrum of K_2CuCl_4 (0.018 mM) in acetonitrile.

Because Gaussian 03 can be used to calculate absorption spectra, we have chosen to use this tool to understand the complex spectra collected here for the $[(SNS)Cu]^+$ complexes. Focusing first on the tetrachlorocuprate anion and using a Jahn-Teller distorted structure for this system with the 6-31G(d) basis set for all atoms, electronic transitions with the strongest computed oscillator strengths (f) are calculated to occur at

454 nm (f = 0.0126), 314 nm (0.0423), and 249 nm (0.0539) are computed; the shoulder at 355 nm is not found as a distinct feature in the calculated spectrum. Interestingly, using the 6-311G(d,p) basis set for the Cu atom (as was employed in the geometry optimizations), places the lowest energy absorption at 612 nm. We therefore have chosen to use the 6-31G(d) basis set for all atoms in our calculation of the absorption spectra of the imidazolyl- and triazolyl-containing Cu(I)-SNS systems because this basis set gives excellent agreement with the experimentally determined spectrum for $CuCl_4^{2-}$.

 Overall, our density functional calculations suggest that the absorptions in the UV-Vis region of the $[(SNS)Cu]^+$ systems are obscured by those of the tetrachlorocuprate ion. For the imidazolyl-containing complex, absorptions of strengths similar to those determined for $CuCl_4^{2-}$ are calculated to occur at 446 nm (f = 0.015), 382 nm (f = 0.0408), 361 nm (f = 0.0108), and 347 nm (0.0107) as well as at numerous higher energy wavelengths. In the UV-Visible spectrum of **4**, maximum absorptions are seen at 462 nm, 265 nm, and 204 nm. Contour plots for the molecular orbitals (MOs) involved in the two lowest energy metal-to-ligand charge transfers are shown in Figure 9. In both of these transitions, an electron is promoted from an MO with significant Cu and S character to one that is largely based on the two-node π system of the pyridinyl unit. The lower energy transition is from the second highest occupied MO (SHOMO) to the LUMO while the higher energy transition is from the fourth highest occupied MO to the LUMO. Other absorptions in this region, including the HOMO-to-LUMO transition are calculated as having much weaker oscillator strengths. For the triazolyl-based system, the analogous transitions are calculated to occur at 435 nm (f = 0.0142), 375 nm (f = 0.0117), and lower wavelengths. In the UV-Visible spectrum of **5**, maximum absorptions are seen at 461 nm,

299 nm, and 258 nm. Given that these wavelengths are in the region where $[CuCl_4]^{2-}$ absorbs, substituting this anion with one that does not absorb in this area of the spectrum will be necessary to locate experimentally the absorptions of the $[(SNS)Cu]^+$ systems. Current efforts are focusing on exchanging the counter-anions in the copper complexes.

Figure 9. Contour plots of molecular orbitals responsible for the absorptions calculated to occur at 446 nm and 382 nm for the N-methyl-substituted, imidazolyl-containing $[(SNS)Cu]^+$ system.

3.7. Cyclic Voltammetry

Complexes **4** and **5** were studied by cyclic voltammetry in DMSO as part of their characterizations. The cyclic voltammogram for **4** (Figure 10) shows oxidation features at 368, and 904 mV, and reduction waves at -43 and -1974 mV. The cyclic voltammogram for **5** (Figure 11) shows oxidation features at 452 and 1111 mV, and a reduction wave at -1799 mV. For both systems, the oxidation and reduction waves are broad. Previously, we reported that ligand precursor **2** shows oxidation features at 976 and 1339 mV and that ligand precursor **3** shows a single oxidation feature at 1178 mV [2]. As such, the electrochemical profiles presented here are more complex than what we have observed previously [2].

Figure 10. Cyclic voltammogram of **4** 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.

Figure 11. Cyclic Voltammogram of **5** 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.

The oxidation process can be modelled computationally by comparing the energies of

the optimized structures of the related $[(SNS)Cu]^+$ and $[(SNS)Cu]^{2+}$ species to obtain

calculated oxidation potentials. As was the case for the calculations of the absorption

spectra, using the 6-31G(d) basis set for all atoms gave results that were close to those

found experimentally. For the imidazolyl- and triazolyl-based $[(SNS)Cu]^+$ complexes,

oxidations are computed to occur at 830 mV and at 1076 mV, respectively. We believe

that these oxidations represent those found experimentally for **4** and **5** at 904 mV and

1111 mV, respectively, which would indicate removal of an electron from a

predominantly Cu-, N-, and S-based HOMO such as that depicted in Figure 12 for the

imidazolyl-based $[(SNS)Cu]^+$ complex. We also note that the difference in potentials

between the computed oxidations is 246 mV while that between the experimentally

observed oxidations is similar (207 mV) and that the potentials are calculated properly

relative to each other. As for the other features present in the experimentally determined

cyclic voltammograms, their origin is likely more complex what with the presence of the

paramagnetic tetrachlorocuprate anion that could be interacting with the $[(SNS)Cu]^{2+}$

cation that is generated via this experiment. We have noted previously [54] the

likelihood of intermolecular disulfide bond formation upon oxidation especially for the

triazolyl-containing ligand and therefore postulate that similar reactions could be

occurring here. For example, owing to the Cu-S σ-bonding character of this MO,

removal of an electron from this orbital would be expected to weaken the Cu-S bond,

thereby allowing the S atom to detach and react with any active species present.

Figure 12. Contour plot of the Cu-, N-, and S-based HOMO of the imidazolyl-based

$[(SNS)Cu]^+$ complex.

4. Conclusions

A series of novel SNS-coordinated Cu(I) compounds has been prepared and characterized through the use of our own imidazolyl- and triazolyl-based tridentate ligand systems. The three-coordinate copper complexes possess pseudo-trigonal planar geometry at the metal center. Our X-ray crystal structures, supported by elemental analysis, clearly indicate that disproportionation occurs during the formation of these systems resulting in the formation of tetrachlorocuprate counteranions. The EPR spectra of these systems are consistent with 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. In the electronic spectra, various charge-transfer transitions are apparent and we believe that the absorptions of the $[(SNS)Cu]^+$ complexes are coincident with those of $[CuCl_4]^{2-}$. The cyclic voltammograms do indicate a feature related to the oxidation of $[(SNS)Cu]^+$, but also indicate other redox activity occurring likely as a result of the presence of the tetrachlorocuprate anion as well as the functional groups of the tridentate ligand systems and related decomposition.

Supporting Information

The ESI-MS, UV-Vis, ATR-IR, and EPR spectra of **4-6** are provided. Crystallographic details of **5 and 6** are also given.   The Cartesian coordinates of all the optimized structures provided by density functional theory are also provided. In addition, the calculated IR spectra for the model systems are provided in the supporting information.

6. References

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