Inorganica Chimica Acta 362 (2009) 1247–1252

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Copper(II) complexes of bidentate ligands containing nitrogen and sulfur donors: Synthesis, structures, electrochemistry and catalytic properties

Mitchell R. Malachowski [a,*], Mark E. Adams [a], Daniel Murray [a], Ryan White [a], Nadia Elia [a], Arnold L. Rheingold [b], Lev N. Zakharov [b], Richard S. Kelly [c]

[a] Department of Chemistry, University of San Diego, Alcala Park, San Diego, CA 92110, USA
[b] Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093, USA
[c] Department of Chemistry, East Stroudsburg University, East Stroudsburg, PA 18301, USA

ARTICLE INFO

Article history:
Received 5 January 2008
Received in revised form 10 June 2008
Accepted 10 June 2008
Available online 17 June 2008

Keywords:
Copper complexes
Biological models
Blue copper proteins
Imidazole
Pyridine

ABSTRACT

Two nitrogen and sulfur containing ligands, 1-methyl-4-((4-methylimidazol-5-yl)methylthio)benzene (NS-mim) (**1**) and 1-methyl-4-(2-pyridylmethylthio)benzene (NS-mpy) (**2**) were synthesized and a series of their Cu(II) complexes, **3–10**, prepared. The imidazole-containing complexes (**3–6**) have the form $[Cu(NS\text{-}mim)_2(solvent)_2](X)_2$ where X = ClO_4, $BF_4$and $[Cu(NS\text{-}mim)_2(Y)_2]$ where Y = Cl or Br and the pyridine-containing complexes (**7–10**) have the form $[Cu(NS\text{-}mpy)_2]X_2$ (where X = ClO_4, BF_4) and $[Cu_2(NS\text{-}mpy)_2Y_4]$ (where Y = Cl or Br). These complexes were characterized by a combination of elemental analysis, FAB-MS and electrochemistry. The X-ray structure of the imidazole-containing $[Cu(NS\text{-}mim)_2(DMF)_2](ClO_4)_2$ (**3**) was determined and it showed the copper(II) coordinated only by the nitrogen donors while the sulfurs remain uncoordinated. In comparison, the X-ray structure of the pyridine-containing $[Cu_2(NS\text{-}mpy)_2(Cl)_4]$ (**9**) shows a dinuclear copper(II) complex with the nitrogens and the sulfurs coordinated along with a terminal chloride and two μ-chloro atoms bridging the coppers. Cyclic voltammetry studies indicated that the complexes undergo quasi-reversible one-electron reductions in acetonitrile at potentials between 0.31 and 0.51 V versus SCE. The complexes were found to be active for the oxidation of di-*tert*-butyl catechol (DTBC) with the rate dependent on the ligand and the counter-ion present.

1. Introduction

The existence of metal complexes at the active site of numerous biological systems has fueled tremendous interest in preparing synthetic metal complexes. Among the ligand sets of interest are those that contain both sulfur and nitrogen atoms due to the presence of these donors in a number of metalloproteins [1]. Some of the most important of these are the blue copper proteins that are involved in electron transfer [2–4]. Blue copper proteins, such as plastocyanin and azurin, function as biological electron carriers.

Models for the blue copper proteins require the preparation of ligands that include sulfur and nitrogen donors [5–7]. In order to prevent disulfide formation or to reproduce the unusual distorted tetrahedral geometry, steric constraints often are built into the ligand sets or thioethers are used in place of the thiolate sulfur. Among the best synthetic models are those that include hindered pyrazolylborate compounds as they have been shown to recreate many of the properties of the naturally occurring compounds [8].

We are involved in a systematic study of multidentate ligands and their copper(II) and copper(I) complexes in order to better understand copper-containing biological systems [9–13]. In our earlier work, we showed that the presence of sulfur donors and a biphenyl moiety led to spontaneous reduction of Cu(II) to a Cu(I) complex but in the absence of the sulfur donors, no spontaneous reduction was found [10]. The premise of that work was that due to the dihedral twist angle in the biphenyl ring, it would impart a non-planar geometry around the copper resulting in more tetrahedral-like geometries. To further probe whether the biphenyl ring is essential for this spontaneous reduction process for these types of ligand sets, in this work we prepared the copper complexes from the corresponding bidentate NS ligands that are based on a benzene ring rather than the more sterically encumbering biphenyl moiety.

We report a variation on the synthesis of the imidazole-containing ligand, 1-methyl-4-((4-methylimidazol-5-yl)methylthio)benzene (NS-mim) (**1**) [14], and a series of its copper(II) complexes of the form $[Cu(NS\text{-}mim)_2(solvent)_2](X)_2$ where X = ClO_4, $BF_4$and $[Cu(NS\text{-}mim)_2(Y)_2]$ where Y = Cl or Br. In order to assess the importance of the biologically relevant imidazole in these complexes, we also have made the new pyridine-containing complexes

* Corresponding author.
E-mail address: malachow@sandiego.edu (M.R. Malachowski).

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doi:10.1016/j.ica.2008.06.008

$[Cu(NS\text{-}mpy)_2]X_2$ (where X = ClO_4, BF_4) and $[Cu_2(NS\text{-}mpy)_2Y_4]$ (where Y = Cl or Br) from the previously prepared 1-methyl-4-(2-pyridylmethylthio)benzene (NS-mpy) ligand [10]. The molecular structures of $[Cu(NS\text{-}mim)_2DMF_2](ClO_4)_2$ (**3**) and $[Cu_2(NS\text{-}mpy)_2(Cl)_4]$ (**9**) have been determined. The electrochemistry of the complexes has been determined by cyclic voltammetry and the catalytic properties of the complexes towards the oxidation of 3,5-di-*tert*-butylcatechol studied.

2. Experimental

2.1. Materials and methods

All reagents and solvents were purchased from commercial sources and used as received unless noted otherwise. 1-methyl-4-(2-pyridylmethylthio)benzene was prepared by the literature method [10]. C, H, N and Cu chemical analyses were performed at Desert Analytical, Tucson, AZ. IR spectra were recorded on a Jasco 480 instrument. Mass spectra were run at the Nebraska Center for Mass Spectrometry in Lincoln, NE. ^1H and ^{13}C NMR were recorded on a Varian 400 MHz instrument.

Cyclic voltammetric data were collected using a Cypress Systems Model 1090 electrochemical analyzer (Cypress Systems, Lawrence, KS). All scans were done at 0.050 V/s with 3 mm glassy carbon electrodes (BAS, West Lafayette, IN) in acetonitrile (Aldrich, 99.5% spectrophotometric grade) that contained 0.10 M tetrabutylammonium hexafluorophosphate (Aldrich, 98%) as the supporting electrolyte. The glassy carbon electrodes were polished with 0.3 and 0.05 μm alumina on microcloth pads (all Buehler, Lake Bluff, IL), sonicated for 5 s in distilled water, and dried carefully before introduction into the electrochemical cell.

A three-electrode system was used in all the measurements, with potentials recorded versus a zero-leakage $Ag^+/AgCl$ reference electrode (SDR2, World Precision Instruments, Sarasota, FL). The potential of this reference was measured daily versus an aqueous saturated calomel electrode (SCE) and an appropriate correction made so that the $E^{\circ\prime}$ values for each complex could be reported versus SCE. A platinum wire served as the auxiliary electrode. The electrochemical cell consisted of a glass vial of ca. 10.0 mL volume with a fitted Teflon cap. All solutions were sparged with solvent-saturated nitrogen prior to data collection.

Caution: Although there were no incidents in our laboratory, transition metal perchlorates may explode violently. They should be prepared in small quantities and handled with care.

2.2. Synthesis of 1-methyl-4-((4-methylimidazol-5-yl)methylthio)benzene (NS-mim) (**1**)

To 17.80 g (0.143 mol) of *p*-thiocresol in 250 mL of acetic acid was added 21.30 g (0.143 mol) of 4-methyl-5-imidazole methanol hydrochloride. The solution was refluxed for 3 h. One hundred millilitres of hot EtOH were added followed by 200 mL of NH_4OH. The solution was cooled to −10 °C overnight. Crystals formed which were collected and recrystallized from EtOH to yield 24.4 g (78.3%) of colorless crystals, mp 133–134 °C. ^1H NMR δ_H ($CDCl_3$, 400 MHz) 2.06 (3H, s), 2.32 (3H, s), 4.01 (2H, s), 6.24 (1H, broad s). 7.07–7.42 (4H, m). ^{13}C NMR δ ($CDCl_3$,): 135.5, 135.2, 134.8, 133.4, 131.7, 129.4, 129.3, 126.8, 126.6, 28.6, 25.3, 12.5.

2.3. Synthesis of $[Cu(NS\text{-}mim)_2(DMF)_2](ClO_4)_2$ (**3**)

To 0.20 g (0.92 mmol) of NS-mim in 15 mL of hot EtOH was added a solution of 0.17 g (0.46 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ in 20 mL of EtOH. The solution was filtered and cooled to room temperature. Green plates formed that were collected and washed with cold EtOH to yield **3** (0.12 g, 38.8%). X-ray quality crystals were grown by slow diffusion of ether into a solution of the complex in DMF. *Anal.* Calc. for $C_{24}H_{28}Cl_2CuN_4O_8S_2$: C, 41.23; H, 4.05; N, 8.01, Cu, 9.09. Found: C, 40.88; H, 4.02; N, 7.97, Cu, 9.20%. Mass spectrum (FAB MS): *m*/*z* (relative intensity) 598 (22), 499 (94), 375 (10), 281 (100), 220 (90).

2.4. Synthesis of $[Cu(NS\text{-}mim)_2](BF_4)_2$ (**4**)

To 0.20 g (0.92 mmol) of NS-mim in 15 mL of hot EtOH was added a solution of 0.16 g (0.46 mmol) of Cu $(BF_4)_2 \cdot 6H_2O$ in 20 mL of EtOH. The solution was filtered and cooled to room temperature. Dark green crystals of **4** (0.15 g, 47.3%) formed that were collected and washed with cold EtOH. *Anal.* Calc. for $C_{24}H_{28}B_2CuF_8N_4S_2$: C, 42.77; H, 4.20; N, 8.31, Cu, 9.43. Found: C, 42.42; H, 4.21; N, 8.55, Cu, 9.34%. Mass spectrum (FAB MS): *m*/*z* (relative intensity) 499 (65), 375 (22), 281 (100), 220 (78), 154 (18).

2.5. Synthesis of $[Cu(NS\text{-}mim)_2(Cl)_2]$ (**5**)

To 0.20 g (0.92 mmol) of NS-mim in 15 mL of hot EtOH was added a solution of 0.078 g (0.46 mmol) of $CuCl_2 \cdot 2H_2O$ in 10 mL of EtOH. The solution was filtered and cooled to room temperature. Dark green crystals of **5** (0.15 g, 58.3%) formed that were collected and washed with cold EtOH. *Anal.* Calc. for $C_{24}H_{28}Cl_2CuN_4S_2$: C, 50.47; H, 4.95; N, 9.81, Cu, 11.12. Found: C, 50.22; H, 5.03; N, 9.78, Cu, 11.01%. Mass spectrum (FAB MS): *m*/*z* (relative intensity) 536 (32), 534 (28), 499 (77), 375 (34), 281 (100), 220 (62), 151 (67).

2.6. Synthesis of $[Cu(NS\text{-}mim)_2(Br)_2] \cdot 2H_2O$ (**6**)

To 0.20 g (0.92 mmol) of NS-mim in 15 mL of hot EtOH was added a solution of 0.10 g (0.46 mmol) of $CuBr_2$ in 10 mL of EtOH. The solution was filtered and cooled to room temperature. Brown crystals of **6** (0.10 g, 34.2%) formed that were collected and washed with cold EtOH. *Anal.* Calc. for $C_{24}H_{32}Br_2CuN_4O_2S_2$: C, 41.41; H, 4.64; N, 8.04, Cu, 9.13. Found: C, 41.50; H, 4.58; N, 8.00, Cu, 9.27%. Mass spectrum (FAB MS): *m*/*z* (relative intensity) 499 (82), 375 (77), 281 (100), 220 (39), 151 (89).

2.7. Synthesis of $[Cu(NS\text{-}mpy)_2](ClO_4)_2$ (**7**)

A solution of 0.30 g (1.3 mmol) of NS-mpy in 10 mL of absolute ethanol was treated with 0.24 g (0.70 mmol) of $Cu(ClO_4)_2 \cdot 6H_2O$ in 10 mL of absolute ethanol. The resulting solution was heated to reflux, filtered and allowed to cool to room temperature. Large brown crystals of **7** (0.25 g, 51.3%) formed overnight that were filtered and washed with cold EtOH. *Anal.* Calc. for $C_{26}H_{26}Cl_2CuN_2O_8S_2$: C, 45.05; H, 3.79; N, 4.04, Cu, 9.17. Found: C, 45.40; H, 3.91; N, 4.13, Cu, 9.33%. Mass spectrum (FAB MS): *m*/*z* (relative intensity) 495 (30), 493 (23), 371 (8), 307 (31), 216 (32), 154 (100).

2.8. Synthesis of $[Cu(NS\text{-}mpy)_2](BF_4)_2$ (**8**)

A solution of 0.30 g (1.3 mmol) of NS-mpy in 10 mL of absolute ethanol was treated with 0.24 g (0.70 mmol) of $Cu(BF_4)_2 \cdot 6H_2O$ in 10 mL of absolute ethanol. The resulting solution was heated to reflux, filtered and allowed to cool to room temperature. Small brown crystals of **8** (0.14 g, 29.3%) formed overnight that were filtered and washed with cold EtOH. *Anal.* Calc. for $C_{26}H_{26}B_2CuF_8N_2S_2$: C, 46.76; H, 3.93; N, 4.20, Cu, 9.51. Found: C, 46.33; H, 3.78; N, 3.93, Cu, 9.86%. Mass spectrum (FAB MS): *m*/*z* (relative intensity) 493 (54), 371 (20), 307 (31), 216 (63), 154 (100).

2.9. Synthesis of $[Cu_2(NS\text{-}mpy)_2(Cl)_4]$ (**9**)

A solution of 0.30 g (1.3 mmol) of NS-mpy in 10 mL of absolute ethanol was treated with 0.24 g (0.70 mmol) of $CuCl_2 \cdot 2H_2O$ in 10 mL of absolute ethanol. The resulting solution was heated to reflux, filtered and allowed to cool to room temperature. Lime green crystals of **9** (0.19 g, 46.9%) formed overnight that were filtered and washed with cold ethanol. X-ray quality crystals were grown by slow diffusion of pentane into a solution of the compound dissolved in MeOH. *Anal.* Calc. for $C_{26}H_{26}Cl_4Cu_2N_2S_2$: C, 44.63; H, 3.75; N, 4.00, Cu, 18.17. Found: C, 44.61; H, 3.98; N, 4.10, Cu, 18.28%. Mass spectrum (FAB MS): *m*/*z* (relative intensity) 593 (54), 530 (38), 528 (42), 509 (22), 495 (30), 493 (30), 307 (30), 216 (60), 154 (100).

2.10. Synthesis of $[Cu_2(NS\text{-}mpy)_2(Br)_4]$ (**10**)

A solution of 0.30 g (1.3 mmol) of NS-mpy in 10 mL of absolute ethanol was treated with 0.20 g (0.70 mmol) of $CuBr_2$ in 10 mL of absolute ethanol. The resulting solution was heated to reflux, filtered and allowed to cool to room temperature. Brown crystals of **10** (0.19 g, 41.2%) formed overnight that were filtered and washed with cold EtOH. *Anal.* Calc. for $C_{26}H_{26}Br_4Cu_2N_2S_2$: C, 35.59; H, 2.99; N, 3.19, Cu, 14.49. Found: C, 35.44; H, 3.12; N, 3.26, Cu, 14.67%. Mass spectrum (FAB MS): *m*/*z* (relative intensity) 593 (32), 530 (77), 528 (54), 509 (20), 495 (12), 493 (45), 307 (55), 216 (23), 154 (100).

2.11. Kinetic measurements

Kinetic experiments were carried out at 25 °C by mixing methanolic solutions of 1 mM of the metal complex (0.3 mL) and 2.0 mL of DTBC (0.1 M). The appearance of the product, 3,5-di-*tert*-butylquinone, was detected at 400 nm ($\varepsilon = 1900\ M^{-1}\ cm^{-1}$) and initial rates were calculated from the linear slope.

2.12. X-ray crystallographic analysis

Single crystals of compounds **3** and **9** were mounted on quartz capillaries by using Paratone oil and were cooled in a nitrogen stream on the diffractometer. Data were collected on a Bruker P4 diffractometer with an APEX area detector. Peak integrations were performed with the Bruker SAINT software package. Absorption corrections were applied using the program SADABS. Space group determinations were performed by the program XPREP. The structures were solved by direct methods and refined with the SHELXTL software package [15]. Hydrogen atoms were both fixed at calculated positions or located from difference maps and refined with isotropic thermal parameters, and all non-hydrogen atoms were refined anisotropically unless otherwise noted.

3. Results and discussion

3.1. Synthesis and spectroscopic studies

Pyridine and imidazole donors have found extensive use in a variety of multidentate ligands complexed to metal ions. The NS-mim ligand was prepared in one step by treating 4-methylthiocresol with 4-hydroxymethylimidazole resulting in isolation of **1** [14]. Imidazolylmethylation of thiols has been shown to occur for a variety of thiols, and the procedure smoothly led to the product here. Compound **2** was prepared as previously reported [10].

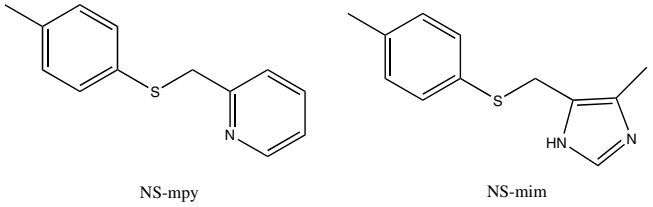
The Cu(II) complexes **3–10** were prepared in straightforward fashion from the appropriate ligand. We made a large number of different copper complexes from various anions as we were interested in seeing if any of them would lead to spontaneous reduction of the copper(II) upon complexation. Treatment of NS-mim, **1**, with copper(II) salts led to isolation of mononuclear copper(II) complexes with the formula $[Cu(NS\text{-}mim)_2](X)_2$where X = ClO_4, BF_4, or $[Cu(NS\text{-}mim)_2(X)_2]$ where X = Cl or Br. For **3**, two molecules of DMF were also found complexed to the copper(II) ion. On the other hand, treatment of NS-mpy, **2**, with the same copper salts led to isolation of either mononuclear or dinuclear complexes depending on the ability of the counterion to complex. Reaction with $Cu(ClO_4)_2 \cdot 6H_2O$ or $Cu(BF_4)_2 \cdot 6H_2O$ led to mononuclear complexes with the formula $[Cu(NS\text{-}mpy)_2](X)_2$while reaction with $CuCl_2$ or $CuBr_2$ led to dinuclear complexes with the formula $[Cu_2(NS\text{-}mpy)_2(X)_4]$ where X = Cl or Br. The stoichiometry of the compounds has been established from the elemental analysis. The infrared spectra of all the compounds show the presence of the ligand bands, and for complexes **3–4** and **7–8**, the presence of the BF_4 (1050 cm^{-1}) and ClO_4 (1100 cm^{-1}) anions, respectively. Regardless of the particular structure formed, what is most important is that in all cases copper(II) complexes were isolated rather than the copper(I) form so it is clear that the biphenyl ring was essential in leading to the spontaneous reduction of our previously prepared copper(I) complexes [10].

3.2. Mass spectrometry

Fast atom bombardment mass spectrometry (FAB-MS) has been shown to be a useful technique for analysis of metal complexes [16]. This technique has been used here to help characterize complexes **3–10** by using both the molecular ion present and the fragmentation patterns obtained. The presence of two NS-mim ligands per copper can be seen clearly in the mass spectrum of **3–6** with the $[Cu(NS\text{-}mim)_2]^+$ found at 499 *m*/*z*. In the case of complex **3**, a small peak corresponding to $[Cu(NS\text{-}mim)_2](ClO_4)^+$ was observed at *m*/*z* 598. For the NS-mpy complexes, **7–10**, two NS-mpy ligands per copper can be seen in the mass spectrum with $[Cu(NS\text{-}mpy)_2]^+$ found at 493 *m*/*z* for the Cl and ClO_4 complexes. No evidence of any exogenous donors is found in any of the NS-mpy complexes. The fragmentation patterns found for complexes **3–10** are also consistent with the presence of their respective ligands (Fig. 1).

3.3. Crystallographic analysis

Single crystals of $[Cu(NS\text{-}mim)_2(DMF)_2](ClO_4)_2$ (**3**) suitable for X-ray diffraction structural determination were grown by vapor diffusion of ether into a solution of the complex in DMF while $[Cu_2(NS\text{-}mpy)_2(Cl)_4]$ (**9**) was crystallized by vapor diffusion of pentane into CH_3OH. The molecular structure of complex **3** is shown in Fig. 2. It crystallizes in a monoclinic crystal system with space group $P2(1)/n$ while **9** (shown in Fig. 3) is triclinic with space group $P\bar{1}$. The relevant details of the crystals, data collection and structure refinement are found in Table 1. Selected bond distances and bond angles are presented in Tables 2 and 3. The complete list of bond distances, bond angles, atomic coordinates and anisotropic thermal parameters are presented in Supplementary material.



NS-mpy NS-mim

Fig. 1. NS-mpy and NS-mim ligands.

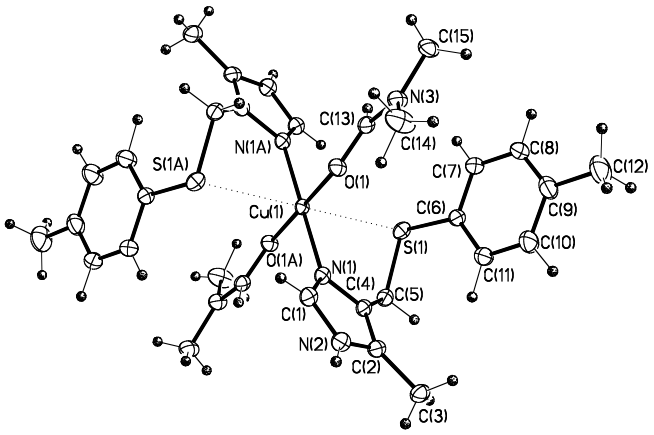


Fig. 2. Structural diagram of $[Cu(NS\text{-}mim)_2(DMF)_2](ClO_4)_2$ (**3**) with partial atom. numbering schemes (ORTEP, 50% probability ellipsoids).

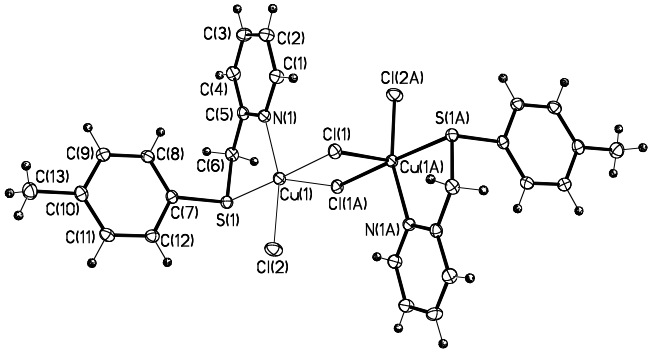


Fig. 3. Structural diagram of $[Cu_2(NS\text{-}mpy)_2(Cl)_4]$ (**9**) with partial atom numbering schemes (ORTEP, 50% probability ellipsoids).

Table 1
Crystal data and structure refinement for $[Cu(NS\text{-}mim)_2(DMF)_2](ClO_4)_2$ (**3**) and $[Cu_2(NS\text{-}mpy)_2(Cl)_4]$ (**9**)

	3	**9**
Empirical formula	$C_{30}H_{42}Cl_2CuN_6O_{10}S_2$	$C_{26}H_{26}Cl_4Cu_2N_2S_2$
Formula weight	845.26	699.49
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	triclinic
Space group	$P2(1)/n$	$P\bar{1}$
a (Å)	10.3776(8)	7.8055(5)
b (Å)	7.6819(6)	8.7399(5)
c (Å)	23.3602(18)	11.4430(7)
α (°)	110.350(2)	107.6010(10)
β (°)	95.181(2)	98.8160(10)
γ (°)	102.478(2)	109.7810(10)
Volume (Å^3)	1858.6(2)	671.15(7)
Z	4	1
D_{calc} (Mg/m^3)	1.510	1.731
Absorption coefficient (mm^{-1})	0.905	2.159
$F(000)$	878	354
Crystal size (mm)	0.25 × 0.20 × 0.16	0.30 × 0.22 × 0.08
Reflections collected	15494	4886
Independent reflections (R_{int})	4227 (0.0268)	3039 (0.0177)
Data/restraints/parameters	4227/0/316	3039/0/215
Goodness-of-fit on F^2	1.115	1.043
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0520$, $wR_2 = 0.1323$	$R_1 = 0.0309$, $wR_2 = 0.0834$
R indices (all data)	$R_1 = 0.0571$, $wR_2 = 0.1357$	$R_1 = 0.0328$, $wR_2 = 0.0854$
Largest difference in peak and hole (e Å^{-3})	0.740 and −0.352	0.633 and −0.568

Table 2
Select bond lengths (Å) and angles (°) for $[Cu(NS\text{-}mim)_2(DMF)_2](ClO_4)_2$ (**3**)

Cu(1)–N(1A)	1.958(2)
Cu(1)–N(1)	1.958(2)
Cu(1)–O(1)	1.9897(17)
Cu(1)–O(1A)	1.9897(17)
N(1A)–Cu(1)–N(1)	180.00(13)
N(1A)–Cu(1)–O(1)	92.13(8)
N(1)–Cu(1)–O(1)	87.87(8)
N(1A)–Cu(1)–O(1A)	87.87(8)
N(1)–Cu(1)–O(1A)	92.13(8)
O(1)–Cu(1)–O(1A)	180.00(11)

Table 3
Select bond lengths (Å) and angles (°) for $[Cu_2(NS\text{-}mpy)_2(Cl)_4]$ (**9**)

Cu(1)–N(1)	2.0355(16)
Cu(1)–Cl(2)	2.2373(6)
Cu(1)–Cl(1)	2.2881(5)
Cu(1)–S(1)	2.3603(5)
Cu(1)–Cl(1A)	2.6965(6)
Cu(1A)–Cl(1)	2.6965(6)
N(1)–Cu(1)–Cl(2)	162.57(5)
N(1)–Cu(1)–Cl(1)	94.23(5)
Cl(2)–Cu(1)–Cl(1)	93.85(2)
N(1)–Cu(1)–S(1)	83.82(5)
Cl(2)–Cu(1)–S(1)	88.27(2)
Cl(1)–Cu(1)–S(1)	177.849(18)
N(1)–Cu(1)–Cl(1A)	87.86(5)
Cl(2)–Cu(1)–Cl(1A)	106.89(2)
Cl(1)–Cu(1)–Cl(1A)	94.402(17)
S(1)–Cu(1)–Cl(1A)	84.621(17)
Cu(1)–Cl(1)–Cu(1A)	85.598(17)

As can be seen in Figs. 2 and 3, the structures of complexes **3** and **9**markedly differ. We did not anticipate the dramatic differences in their structures as we did not see the same variability in the previously prepared biphenyl analogs. In the mononuclear complex **3**, the structure shows the copper to be four-coordinate with the two imidazole nitrogens coordinated along with two molecules of DMF coordinating via the oxygens. Although the ligand is potentially tetradentate, the Cu–S distance of 2.955 Å indicates that the sulfurs are non-bonding [17,18]. The copper(II) is found in a nearly ideal square planar environment as evidenced by the bond angles. The Cu–N_{im} bond distances (1.958 Å) and Cu–O bond distances (1.9897 Å) are in the expected range for these bonds [19].

In contrast, complex **9** is a five-coordinate dimer with each copper coordinated by $NSCl_3$ donors. This is a result of the copper coordinating to only one NS-mpy ligand, a terminal Cl and two bridging μ-chloro donors. In this case, the Cu–S distance is 2.36 Å, a value clearly within bonding distance [20]. The coordination geometry around the $CuNSCl_3$ is best described as trigonal bipyramidal distorted square based pyramidal (TBDSBP) as revealed by the magnitude of the trigonality index τ of 0.25. For perfect square pyramidal and trigonal bipyramidal geometries, the τ values are zero and unity, respectively [21]. The corners of the square plane are occupied by the pyridine nitrogen, the sulfur, the terminal chlorine and Cl(1) with Cl(1A) in the axial position. As expected, the bond distance of the axially coordinated Cl(1A) is considerably longer (2.6965 Å) than the other μ-chloro donor, Cl(1) found at 2.2881 Å. The Cu–N_{py} distances fall within the ranges expected (2.00–2.11 Å) [20].

What is most important about the structures is that they show that spontaneous reduction of the copper(II) salt to a copper(I) complex does not take place for these complexes. This is in comparison to the corresponding biphenyl-based N_2S_2-mim and N_2S_2-mpy complexes where copper(I) complexes were isolated

Table 4
Cyclic voltammetry data for the reduction of copper(II) complexes and catalytic activities for complexes **3–10**

	$E^{\circ'}$ (V vs. SCE)	Activity (mmol substrate per mg catalyst per min)
$[Cu(NS\text{-}mim)_2(DMF)_2](ClO_4)_2$ (**3**)	0.47	.0305
$[Cu(NS\text{-}mim)_2](BF_4)_2$ (**4**)	0.46	.0438
$[Cu(NS\text{-}mim)_2(Cl)_2]$ (**5**)	0.31	.0502
$[Cu(NS\text{-}mim)_2(Br)_2]$ (**6**)	0.38	.0523
$[Cu(NS\text{-}mpy)_2](ClO_4)_2$ (**7**)	0.48	.0506
$[Cu(NS\text{-}mpy)_2](BF_4)_2$ (**8**)	0.48	.0545
$[Cu_2(NS\text{-}mpy)_2(Cl)_4]$ (**9**)	0.47	.0435
$[Cu(NS\text{-}mpy)_2(Br)_2]$ (**10**)	0.51	.0768

from copper(II) precursors [10]. It is clear that the presence of the nitrogen and sulfur donors and a biphenyl moiety is necessary for the spontaneous reduction process to occur for these ligand sets.

3.4. Electrochemistry

The reduction potentials for complexes **3–10** were measured by cyclic voltammetry at a glassy carbon electrode in acetonitrile. The cyclic voltammetry data are shown in Table 4. The average of the peak potentials is taken as an approximation of the formal potential, $E_\circ$. For all the complexes, a one-electron reduction is observed with the reduced form of the complexes displaying high chemical stability on the time scale of the cyclic voltammetry experiment. Ratios of reverse to forward currents (i_{pa}/i_{pc}) are close to 1.0 for the complexes at a scan rate of 0.050 V/s.

Surprisingly, the $E_\circ$, values for the NS-mpy complexes, **7–10**, are almost identical in all cases and only show a range of 0.03 V. In other Cu(II) complexes we have studied, notable differences occur as the nature of any exogenous donors or even counterions is changed [9–11,13]. For the NS-mim complexes, **3–6**, the spread of values is greater (0.16 V) but still quite modest. The presence of sulfur in the ligands raises the potential compared to other complexes. The electrochemical data show that the reduction potentials of the bound copper(II) species depend more on the nature of the ligand than on the counterion or exogenous donor.

In general, the reduction potential of the NS-mpy complexes are slightly more positive than the NS-mim complexes. This probably results from the fact that pyridine has a $pK_b = 8.7$ while imidazole has a $pK_b = 7.0$. Analogous to results found for comparisons of other nitrogenous donors [11,22], replacing imidazole by pyridine in the ligands should result in a more stable Cu(I) form for the pyridine complexes because of its higher pK_b. This feature will affect the reduction potentials of the complexes by shifting the $E_{1/2}$ values of the pyridine complex more positive compared to their imidazole-containing counterparts, a result that is borne out by the data.

Direct comparisons of the electrochemical properties of complex **7** ($E^{\circ'} = 0.48$ V) with the previously prepared biphenyl N_2S_2-mpy complex [10] that had a $E^{\circ'}$ of 0.77 V shows the large effect of the biphenyl ring in shifting the potential to a more positive value and that is most certainly the reason for the spontaneous reduction of the biphenyl complex in preference to isolation of the copper(II) form for the benzene-derived complex **7**.

3.5. Reactivity with 3,5-di-tert-butylcatechol

Although some of the copper-containing proteins act as catalysts, the blue copper proteins are not involved in catalyzing the oxidation of organic substrates. However, the preparation of a large series of complexes (**3–10**) from two similar ligands allows us to utilize these complexes to test the results we have obtained from previous oxidation studies [11–13]. We and others have shown that there is a complex interplay between the structural and electronic properties of the copper(II) complexes and their ability to serve as effective catalysts for the conversion of 3,5-di-*tert*-butylcatechol to 3,5-di-*tert*-butylquinone [23–29].

The reactivity of the Cu(II) complexes **3–10** towards 3,5-di-*tert*-butylcatechol under catalytic conditions (0.3 mL of a 1.0×10^{-3} M methanol solution of catalyst and 2.0 mL of a 0.1 M methanolic solution of 3,5-di-*tert*-butylcatechol) in the presence of atmospheric O_2 was studied using electronic spectroscopy by following the appearance of the absorption maximum of the 3,5-di-*tert*-butylquinone at 390 nm over time. The results of the oxidations are presented in Table 4.

As can be seen, all of the complexes catalyze the oxidation process with the rate varying from a high of 0.0768 for **10** to a low of 0.0305 for **3**. In some respects, we are surprised that these complexes catalyze the oxidation at all as their reduction potentials are much more positive than other complexes we have studied [11].

Although in the past we have made comparisons between pyrazole, imidazole and pyridine donors, we hesitate to make any here as the structures of the complexes are so vastly different. However, it is routinely assumed that a vacant coordination site needs to be present on the metal prior to the initiation of the reaction as electron transfer from catechol to copper can happen only after a copper catecholate intermediate is formed. The results for these complexes suggest that a vacant site is available for binding as the complexes have at least modest catalytic properties.

4. Conclusions

We have synthesized and characterized two series of copper(II) complexes formed from NS ligands that were inspired by the blue copper proteins although we have drifted far from modeling biological systems. One ligand contains thioether and imidazole donors and the second ligand has a thioether and a pyridine donor. In neither case does the complexation of the ligand with copper(II) lead to spontaneous reduction of the copper(II) as was found for the related ligands containing the biphenyl moiety [10]. It is clear from these results that the biphenyl ring is essential in enforcing particular geometrical results on the metal that led to the spontaneous reduction.

Acknowledgements

We are grateful to the Research Corporation and the University of San Diego Faculty Research Grants for financial support of this work.

Appendix A Supplementary material

CCDC 690102 and 690103 contain the supplementary crystallographic data for **3** and **9**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.06.008.

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