DALTON
FULL PAPER

Enforcing geometrical constraints on metal complexes using biphenyl-based ligands: spontaneous reduction of copper(II) by sulfur-containing ligands

Mitchell R. Malachowski,*[a] Mark Adams,[a] Nadia Elia,[a] Arnold L. Rheingold[b] and Richard S. Kelly[c]

[a] *Department of Chemistry, University of San Diego, San Diego, CA 92110, USA*
[b] *Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, USA*
[c] *Department of Chemistry, Merrimack College, North Andover, MA 01845, USA*

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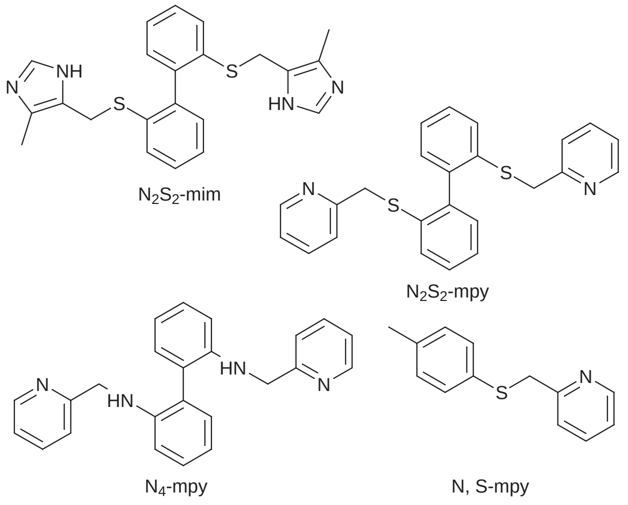
Two biphenyl-based N_2S_2 ligands, 2,2′-bis-(4-methylimidazol-5-yl)methylsulfanyl)biphenyl (N_2S_2-mim) and 2,2′-bis(2-pyridylmethylsulfanyl)biphenyl (N_2S_2-mpy), have been synthesized and their complexation with copper(II) precursors studied. In order to assess whether the biphenyl ring is influencing the geometry around the copper atom, the NS ligand 1-methyl-4-(2-pyridylmethylsulfanyl)benzene (NS-mpy) and its copper complexes were prepared. The N_4 ligand 2,2′-bis-(2-pyridylmethylamino)biphenyl (N_4-mpy) in which the sulfurs have been replaced by nitrogens also was prepared. Treatment of N_4-mpy with copper(II) salts led to isolation of copper(II) complexes with the formula $[Cu(N_4\text{-mpy})]X_2$ where X = ClO_4 or BF_4. These complexes were analysed by a combination of elemental analysis, IR spectroscopy, FAB MS and electrochemistry. Likewise, treatment of NS-mpy with copper(II) salts led to isolation of the copper(II) complexes $[Cu(NS\text{-mpy})_2][ClO_4]_2$ or $[Cu(NS\text{-mpy})_2][BF_4]_2$. In comparison to the results found for ligands N_4-mpy and NS-mpy, treatment of N_2S_2-mim or N_2S_2-mpy with $[Cu(H_2O)_6][ClO_4]_2$ or $[Cu(H_2O)_6][BF_4]_2$ in MeOH led to spontaneous reduction to form the copper(I) complexes $[Cu(N_2S_2\text{-mim})]ClO_4$ $[Cu(N_2S_2\text{-mim})]BF_4$, $[Cu(N_2S_2\text{-mpy})]ClO_4$ and $[Cu(N_2S_2\text{-mpy})]BF_4$. The formulation of these complexes as copper(I) species was confirmed by analytical methods, and for $[Cu(N_2S_2\text{-mpy})]ClO_4{\cdot}MeCN$ by X-ray crystallography. The copper(I) ion is in a distorted tetrahedral environment ligated by two nitrogens and two thioethers from the ligand. Cyclic voltammetry shows $[Cu(N_2S_2\text{-mpy})]ClO_4$, $[Cu(N_4\text{-mpy})][ClO_4]_2$ and $[Cu(NS\text{-mpy})_2][ClO_4]_2$ undergo quasi-reversible one-electron processes with $E^{\circ\prime}$ is +0.77, +0.21 and +0.53 V *vs.* SCE.

Controlling the geometry at a metal ion site is of fundamental importance in many areas of chemistry. The judicious choice of ligands which force metal ions into unusual geometries or which stabilize specific oxidation states are of interest in designing catalytic systems or in bioinorganic chemistry.[1] Our current interest in synthesizing ligands of this type revolves around exploiting what is known about biological systems and utilizing this information to obtain synthetic systems with similar properties. As an example, blue copper proteins, such as plastocyanin and azurin, function as biological electron carriers.[2] Crystallographic studies have shown that the active sites consist of a mononuclear copper(II) ion co-ordinated by two imidazoles, one thioether, and one thiolate. The geometry can be viewed as a distorted, flattened tetrahedron or as a trigonal-planar $Cu(histidine)_2(cysteine)$ unit with an additional methionine thioether apically bound.[3] The blue copper proteins also have very positive reduction potentials showing their ability to stabilize the copper(I) form.

Synthetic systems which incorporate the properties of the blue copper proteins require the preparation of tetradentate ligands which include both sulfur and nitrogen donors.[4–7] 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. As an example of a system which enforces tetrahedral geometry around copper, ligands with hindered pyrazolylborate moieties have been shown to recreate many of the properties of the naturally occurring compounds.[6,7]

Tetradentate ligands can be designed in a vast number of structural permutations and from a tremendous variety of motifs. Depending on the structural features of these ligands, they can be designed to force the resultant metal complexes into specific desired geometries. We particularly are interested in exploiting the properties of the biphenyl moiety in designing new ligand sets due to the fact that the two aromatic rings in the parent biphenyl are not coplanar, but instead have a dihedral angle between the rings of 42°. A further increase in the dihedral angle between the rings can be anticipated if bulky substituents also are present on the rings due to the steric effects of the substituents. Most importantly in our studies is the fact that substituents on the adjacent phenyl rings of the biphenyls will be forced out of plane and the resultant metal complexes modified from a planar-based geometry towards a more tetrahedral-like geometry. Metals such as copper(II), which have Jahn–Teller distortions present, prefer planar-based geometries so copper(II) complexes formed from these biphenyl-based ligands will have to balance the tension between the preferences of the ligand set with those of the metal ion. The use of biphenyl-based ligands has resulted in the synthesis of a variety of metal complexes with interesting properties due to the presence of the biphenyl moiety[8–13] or dinaphthyl systems.[14]

As part of our efforts towards synthesizing multidentate ligands and their copper complexes,[15] we report here the synthesis of two N_2S_2 ligands, 2,2′-bis-(4-methylimidazol-5-ylmethylsulfanyl)biphenyl (N_2S_2-mim) and 2,2′-bis-(2-pyridylmethylsulfanyl)biphenyl (N_2S_2-mpy), and their complexation with copper(II) precursors. The electrochemical properties of the complexes were studied and the molecular structure of the $[Cu(N_2S_2\text{-mpy})]ClO_4{\cdot}CH_3CN$ complex was determined by X-ray diffraction. In order to assess whether the biphenyl ring is influencing the geometry around the copper atom, we also have prepared the NS ligand, 1-methyl-4-(2-pyridylmethylsulfanyl)-benzene (NS-mpy), in which the biphenyl ring is absent along with its copper complexes. Additionally, we report the properties of the N_4 ligand, 2,2′-bis-(2-pyridylmethylamino)biphenyl (N_4-mpy), in which the sulfurs have been replaced by nitrogens to determine how essential the sulfurs are to the properties of the complexes.



N_2S_2-mim

N_2S_2-mpy

N_4-mpy

N, S-mpy

Experimental

General

All reagents and solvents were purchased from commercial sources and used as received unless noted otherwise. 2,2′-Disulfanyl-1,1′-biphenyl and 2,2′-diamino-1,1′-biphenyl were prepared by the literature methods.[16,17] Melting points were obtained with the use of a Fisher-Johns apparatus and are uncorrected. The C, H, and N chemical analyses were performed at Desert Analytical, Tucson, AZ. Metal contents were determined complexometrically by indirect titration with Na_2H_2edta and zinc acetate after destruction of the sample with concentrated nitric acid.[18] The IR spectra were recorded on a Nicolet 5ZDX instrument, mass spectra at the Nebraska Center for Mass Spectrometry in Lincoln, NE, and ^{1}H and ^{13}C NMR on a Varian Unity 300 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^{-1} 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 *vs.* a zero-leakage Ag^+–AgCl reference electrode (SDR2, World Precision Instruments, Sarasota, FL). The potential of this reference was measured daily *vs.* an aqueous saturated calomel electrode (SCE) and an appropriate correction made so that the $E^{\circ\prime}$ values for each complex could be reported *vs.* SCE. A platinum wire served as the auxiliary electrode. The electrochemical cell consisted of a glass vial of *ca.* 10.0 cm^3 volume with a fitted Teflon cap. All solutions were purged 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.

Synthesis of ligands

2,2′-Bis(4-methylimidazol-5-ylmethylsulfanyl)biphenyl (N_2S_2-mim). To acetic acid (250 cm^3) was added 2,2′-disulfanylbiphenyl (1.00 g, 4.6 mmol) and 4-methyl-5-imidazolemethanol hydrochloride (1.40 g, 9.2 mmol). The solution was refluxed for 4 h. Hot ethanol (15 cm^3) was added and the solution cooled to room temperature. Sodium hydroxide (10 mol dm^{-3}) was added until the pH reached 8 and then water (50 cm^3) was added. The yellowish precipitate that formed was collected and crystallized from ethyl acetate–hexane to give white crystals (1.32 g, 70.6%), mp 238–240 °C. Mass spectrum (FAB MS): *m*/*z* (relative intensity) 407 (12), 307 (10), 216 (14), 176 (10) and 133 (100). HRMS (FAB, *m*-nitrobenzyl alcohol): calc. for $C_{22}H_{23}N_4S_2$ ($[M + H]^+$) 407.1364, found 407.1359. δ_H ($CDCl_3$) 2.15 (6 H, s), 5.14 (4 H, s), 7.23–7.70 (8 H, m), 7.50 (2 H, s) and 9.26 (2 H, broad).

2,2′-Bis(2-pyridylmethylsulfanyl)biphenyl (N_2S_2-mpy). To a solution of 2-chloromethylpyridine hydrochloride (1.50 g, 9.2 mmol) in water (50 cm^3) was added a solution of 2,2′-disulfanylbiphenyl (1.00 g, 4.6 mmol) in EtOH (50 cm^3). After both reactants were completely dissolved, the solution was stirred for 5 min followed by the addition of 10 mol dm^{-3} NaOH (1 cm^3). The solution turned from clear to a light pink. It was refluxed and stirred for 24 h. After cooling to room temperature, the solvent was evaporated at reduced pressure. Light yellow crystals were obtained which were recrystallized from MeOH to give white crystals (1.57 g, 85.3%), mp 71–72 °C, (lit.,[12] 70 °C). Mass spectrum (FAB MS): *m*/*z* (relative intensity) 401 (100), 308 (52), 276 (26) and 132 (78). HRMS (FAB): calc. for $C_{24}H_{21}N_2S_2$ ($[M + H]^+$) 401.1068, found 401.1151. δ_H ($CDCl_3$) 4.16 (4 H, s), 7.12–7.32 (8 H, m) and 7.36–7.55 (6 H, m), 8.48 (2 H, d) (Found: C, 71.40; H, 5.30; N, 6.80. $C_{12}H_{10}NS$ requires C, 71.96; H, 5.04; N, 6.99%).

2,2′-Bis(2-pyridylmethylamino)biphenyl (N_4-mpy). To a solution of 2,2′-diaminobiphenyl (1.0 g, 5.43 mmol) in EtOH (50 cm^3) was added a solution of 2-chloromethylpyridine hydrochloride (3.56 g, 21.7 mmol) in water (15 cm^3). A 10 mol dm^{-3} NaOH solution was added dropwise to the solution until the pH reached 9. A change from a light yellow to a red-orange was observed at pH 8. The solution was stirred at room temperature and NaOH added over 5 d to maintain the pH at 8–9. During this time precipitation of an off-white solid occurred. The reaction was complete when the pH no longer dropped below 8. The precipitate was collected by filtration and recrystallized from EtOH resulted in white crystals (1.51 g, 75.9%), mp 135–136 °C (lit.,[8b] 137 °C). Mass spectrum (FAB MS): *m*/*z* (relative intensity) 367 (100), 274 (35), 195 (23) and 180 (29). HRMS (FAB) calc. for $C_{24}H_{23}N_4$ ($[M + H]^+$) 366.1922, found 366.1923. δ_H ($CDCl_3$) 1.62 (2 H, broad s), 4.48 (4 H, s), 6.61–6.83 (8 H, m), 7.04–8.50 (6 H, m) and 8.53 (2H, d) (Found: C, 79.00; H, 5.84; N, 15.62. $C_{12}H_{11}N_2$ requires C, 78.65; H, 6.06; N, 15.28%).

1-Methyl-4-(2-pyridylmethylsulfanyl)benzene (NS-mpy). To a solution of *p*-thiocresol (3.61 g, 29.1 mmol) in 95% EtOH (75 cm^3) was added 2-chloromethylpyridine hydrochloride (4.77 g, 29.1 mmol) dissolved in water (60 cm^3). The mixture was stirred and refluxed for 24 h. The solution was extracted with $CHCl_3$ (3 × 50 cm^3) and the organic phase dried over Na_2SO_4, filtered, and the solvent evaporated under reduced pressure. The resultant oil was dissolved in hot ethyl acetate and hexane added to induce crystallization. Shiny white needle-like crystals appeared overnight (3.40 g, 54.3%), mp 183–185 °C. δ_H ($CDCl_3$) 4.04 (2 H, s), 7.02–7.25 (4 H, m), 7.31–7.46 (3 H, m) and 8.08 (1 H, d) (Found: C, 72.18; H, 5.98; N, 6.77. $C_{13}H_{13}NS$ requires C, 72.51; H, 6.10; N, 6.50%).

Synthesis of copper complexes

[Cu(N_2S_2-mim)]ClO_4 1. A solution of N_2S_2-mim (0.10 g, 0.25 mmol) in MeOH (10 cm^3) was treated with $[Cu(H_2O)_6][ClO_4]_2$ (0.093 g, 0.25 mmol) in MeOH (10 cm^3), filtered and allowed to stand at room temperature whereupon colorless crystals precipitated over a period of two weeks. The crystals were collected and washed with cold MeOH. Mass spectrum (FAB MS): *m/z* (relative intensity) 469 (100), 406 (65), 311 (31), 186 (18) and 154 (29) (Found: C, 46.59; H, 4.36; Cu, 11.29; N, 10.01. $C_{22}H_{22}ClCuN_4O_4S_2$ requires C, 46.39; H, 3.90; Cu, 11.16; N, 9.83%).

[Cu(N_2S_2-mim)]BF_4 2. A solution of N_2S_2-mim (0.10 g, 0.25 mmol) in MeOH (10 cm^3) was treated with $[Cu(H_2O)_6][BF_4]_2$ (0.086 g, 0.25 mmol) in MeOH (10 cm^3), filtered and allowed to stand at room temperature whereupon colorless crystals precipitated overnight. The crystals were collected and washed with cold MeOH. Mass spectrum (FAB MS): *m/z* (relative intensity) 469 (86), 406 (100), 311 (51) and 186 (15) (Found: C, 47.18; H, 3.65; Cu, 11.36; N, 10.32. $C_{22}H_{22}BCuN_4F_4S_2$ requires C, 47.44; H, 3.99; Cu, 11.41; N, 10.06%).

[Cu(N_2S_2-mpy)]ClO_4 3. A solution of N_2S_2-mpy (0.10 g, 0.25 mmol) in MeOH (15 cm^3) was added to a solution of $[Cu(H_2O)_6][ClO_4]_2$ (0.093 g, 0.25 mmol) in MeOH (10 cm^3) turning from blue to pale yellow almost instantly. Colorless crystals formed over 48 h, were collected and washed with cold MeOH. Crystals suitable for determination were grown by vapor diffusion of diethyl ether into an MeCN solution of the complex. Mass spectrum (FAB MS): *m/z* (relative intensity) 565 (25), 563 (38), 464 (45), 401 (100), 364 (32), 307 (65) and 176 (52) (Found: C, 51.84; H, 3.63; N, 4.83. $C_{24}H_{20}ClCuN_2O_4S_2$ requires C, 51.15; H, 3.58; N, 4.97%).

[Cu(N_2S_2-mpy)]BF_4 4. A solution of N_2S_2-mpy (0.10 g, 0.25 mmol) in MeOH (15 cm^3) was added to a solution of $[Cu(H_2O)_6][BF_4]_2$ (0.086 g, 0.25 mmol) in MeOH (10 cm^3) turning from light blue to colorless almost instantly. Colorless crystals formed overnight, were collected and washed with cold MeOH. Mass spectrum (FAB MS): *m/z* (relative intensity) 464 (35), 401 (100), 371 (27), 307 (76) and 176 (66) (Found: C, 52.46; H, 3.88; N, 4.91. $C_{24}H_{20}BCuF_4N_2S_2$ requires C, 52.32; H, 3.67; N, 5.08%).

[Cu(N_4-mpy)][ClO_4]$_2$ 5. A solution of N_4-mpy (0.50 g, 1.4 mmol) in EtOH (25 cm^3) was treated with $[Cu(H_2O)_6][ClO_4]_2$ (0.50 g, 1.4 mmol) in EtOH (25 cm^3), filtered and allowed to stand at room temperature whereupon dark green crystals precipitated. Mass spectrum (FAB MS): *m/z* (relative intensity) 429 (38), 307 (28), 219 (7) and 154 (100) (Found: C, 45.59; H, 3.75; Cu, 10.45; N, 8.70. $C_{24}H_{22}Cl_2CuN_4O_8$ requires C, 45.83; H, 3.53; Cu, 10.10; N, 8.90%).

[Cu(N_4-mpy)][BF_4]$_2$ 6. A solution of N_4-mpy (0.50 g, 1.4 mmol) in EtOH (25 cm^3) was treated with $[Cu(H_2O)_6][BF_4]_2$ (0.47 g, 1.4 mmol) in EtOH (25 cm^3), filtered and allowed to stand at room temperature whereupon green crystals precipitated. Mass spectrum (FAB MS): *m/z* (relative intensity) 429 (72), 307 (43), 219 (18) and 154 (100) (Found: C, 47.95; H, 3.83; Cu, 10.22; N, 9.09. $C_{24}H_{22}B_2CuF_8N_4$ requires C, 47.75; H, 3.68; Cu, 10.53; N, 9.28%).

[Cu(NS-mpy)$_2$][ClO_4]$_2$ 7. A solution of NS-mpy (0.30 g, 1.4 mmol) in absolute EtOH (10 cm^3) was treated with $[Cu(H_2O)_6][ClO_4]_2$ (0.24 g, 0.70 mmol) in absolute EtOH (10 cm^3), filtered and allowed to cool to room temperature. Large brown crystals formed which were filtered off and washed with cold EtOH. Mass spectrum (FAB MS): *m/z* (relative intensity) 493 (23), 371 (8), 307 (31), 216 (32) and 154 (100) (Found: C, 45.05; H, 3.79; N, 4.04. $C_{26}H_{26}Cl_2CuN_2O_8S_2$ requires C, 45.60; H, 4.14; N, 4.13%).

[Cu(NS-mpy)$_2$][BF_4]$_2$ 8. A solution of NS-mpy (0.30 g, 1.4 mmol) in absolute EtOH (10 cm^3) was treated with $[Cu(H_2O)_6][BF_4]_2$ (0.24 g, 0.70 mmol) in absolute EtOH (10 cm^3), filtered and allowed to cool to room temperature. Large brown crystals formed which were filtered off and washed with cold EtOH. Mass spectrum (FAB MS): *m/z* (relative intensity) 493 (100), 310 (26), 278 (82) and 216 (77) (Found: C, 46.33; H, 3.78; N, 3.73. $C_{26}H_{26}B_2CuF_8N_2S_2$ requires C, 46.76; H, 3.93; N, 4.20%).

Crystal structure determination for [Cu(N_2S_2-mpy)]ClO_4·MeCN 3

Crystallographic data are collected in Table 1. Systematic absences in the diffraction data indicated either of the monoclinic space groups *Cc* or *C*2/*c*. Although the cation possesses nearly perfect twofold symmetry, only the non-centrosymmetric alternative can be stoichiometrically correct. In *Cc* the asymmetric unit consists of one copper(I) cation, one ClO_4^- counter ion and a molecule of acetonitrile, the recrystallization solvent. This choice is supported by the distribution of *E* values and by the chemically reasonable results of refinement. Corrections for absorption were made empirically. The structure was solved by direct methods and refined with all non-hydrogen atoms anisotropic. Hydrogen atoms were introduced as idealized contributions. At this point the refinement converged at $R(F) = 12.6\%$, but difficulties in assigning the correct absolute structure led us to consider the possibility of racemic twinning. The inclusion of a racemic twin model in further refinement reduced *R*(*F*) to 4.4%. All computations used SHELXTL 5.03 software.[19]

CCDC reference number 186/1453.

Results and discussion

Synthesis

The N_2S_2-mim ligand was prepared by treating 2,2′-disulfanylbiphenyl with 4-methyl-5-imidazolemethanol hydrochloride. Imidazolylmethylation of thiols has been shown to occur for a variety of thiols,[20] and we anticipated the procedure would lead smoothly to products here. The importance of this method in preference to others for incorporating imidazoles into multidentate ligands is that the imidazole ring is functionalized at the five position rather than the one or two position. Since the imidazole on histidine found in biological systems is also linked through this position, systems with this substitution pattern should have properties closer to the protein bound metalloproteins. The N_2S_2-mpy and NS-mpy ligands were synthesized using the substitution reaction between a thiol and 2-chloromethylpyridine under basic conditions; N_2S_2-mpy was reported previously by Serratrice and co-workers.[12]

The N_4-mpy ligand was synthesized using the well known reaction between a primary amine and 2-chloromethylpyridine. In this case only one pyridylmethylene arm adds to each primary amine. This is probably a result of the precipitation of the product as it is formed under the reaction conditions used. This ligand previously was made *via* the reaction of 2,2′-diaminobiphenyl with pyridine-2-carbaldehyde in the presence of zinc dust.[8b] Further condensation of the N_4-mpy ligand with 2-chloromethylpyridine or other aromatic amines to form N_6 ligands has been successful and will be reported elsewhere. Characterization of the ligands by a combination of ^1H, ^{13}C NMR, elemental analysis, fast atom bombardment or high resolution FAB MS confirmed the structures proposed.

The complexes **1**–**8** were prepared in straightforward fashion from the appropriate ligand. Treatment of N_4-mpy with copper(II) salts led to isolation of copper(II) complexes with the formula $[Cu(N_4\text{-mpy})]X_2$ where $X = ClO_4$ or BF_4. These

Table 1 Crystallographic data for [Cu(N_2S_2-mpy)]ClO_4·Me_4CN **3**

Formula	$C_{26}H_{23}ClCuN_3O_4S_2$
Formula weight	604.58
Crystal system	Monoclinic
Space group	*Cc* (no. 9)
a, b, c/Å	14.0927(5), 14.0871(6), 13.7574(6)
β/°	105.1415(13)
V/Å^3, Z	2636.4(2), 4
D_x/g cm^{-3}	1.523
μ(Mo-Kα)/cm^{-1}	11.3
T/°C	−50(2)
Reflections collected	4510
Independent reflections	3573
Transmission coefficients	0.944–0.834
$R(F)$, $R(wF^2)$ (%)	4.35, 10.12

complexes were analysed by a combination of elemental analysis, IR spectroscopy, FAB MS and electrochemistry. Likewise, treatment of NS-mpy with copper(II) salts led to isolation of the copper(II) complexes [Cu(NS-mpy)$_2$][ClO_4]$_2$ or [Cu(NS-mpy)$_2$][BF_4]$_2$. These complexes are formulated as being four-co-ordinate with two ligands per copper as evidenced by their mass spectra and elemental analysis data.

In comparison to the results found for ligands N_4-mpy and NS-mpy, treatment of the N_2S_2-mim or N_2S_2-mpy with [Cu(H_2O)$_6$][ClO_4]$_2$ or [Cu(H_2O)$_6$][BF_4]$_2$ in MeOH led to an immediate change in the solution from blue to very pale yellow signifying reduction of the oxidation state of the metal. Crystallization of the complexes led to isolation of colorless or off-white crystals of [Cu(N_2S_2-mim)]ClO_4 **1**, [Cu(N_2S_2-mim)]BF_4 **2**, [Cu(N_2S_2-mpy)]ClO_4 **3**, and [Cu(N_2S_2-mpy)]BF_4 **4**. These complexes are air stable indefinitely. Their formulation as copper(I) species was confirmed by analytical methods, and for **3**, by X-ray crystallography. Elemental analysis data were consistent with the presence of only one perchlorate or tetrafluoroborate counter ion in each. Serratrice and co-workers[12] previously had prepared **3** and saw a similar result. Repeated attempts to isolate X-ray quality crystals of **1** or **2** have been unsuccessful.

Spontaneous reduction of Cu^{II} upon complexation to ligand sets typically occurs when sterically demanding ligands which contain sulfur are present.[21–27] Addison and co-workers[21] have shown that in N_2S_2 macrocyclic ligands the ability of the ligand to provide a tetrahedral environment around Cu^{I} stabilizes that structure at the expense of the copper(II) form. A similar situtation exists here for complexes **1–4**. The autoreduction process for N_2S_2 ligands with Cu^{II} is thought to occur through the copper-catalysed oxidation of the solvent or *via* ligand involvement of a sulfur radical cation.[26,27] The solvent oxidation mechanism may be working in our case since changing the solvent from MeOH to MeCN slows down the reduction process. In MeCN the reaction mixture slowly becomes colorless over the course of 24 h rather than instantaneously as is found in MeOH.

Structure of [Cu(N_2S_2-mpy)]ClO_4·MeCN

X-ray quality crystals of complex **3**·MeCN were obtained by recrystallizing the complex from acetonitrile–diethyl ether. The complex crystallizes in the space group *Cc*. Crystal, data collection and refinement parameters are given in Table 1 and selected bond angles and lengths in Table 2. A view of the cationic portion of the complex is depicted in Fig. 1, including the atomic numbering scheme. The Cu^{I} is co-ordinated by two pyridyl nitrogens and two thioether sulfurs. The co-ordination geometry around the copper atom can best be described as distorted tetrahedral with the bond angles ranging from 87.5 to 136.3°. Our goal was to enforce a tetrahedral geometry on the copper *via* the use of the N_2S_2-mpy biphenyl-based ligand and the crystallographic results confirm this approach. However, as noted above, the complex has stabilized itself by spontaneous reduction from Cu^{II} to Cu^{I} thereby minimizing the unfavorable steric constraints. The Cu–N bond lengths are essentially identical (1.966 and 1.967 Å) and fall within the norms for many other four-co-ordinated copper(I)-pyridine bond lengths.[28] The Cu–S bond lengths (2.428 and 2.459 Å) also can be considered as normal.[29]

Table 2 Selected bond lengths (Å) and bond angles (°) for [Cu(N_2S_2-mpy)]ClO_4·MeCN **3**

Cu(1)–N(1)	1.966(6)	Cu(1)–N(2)	1.967(5)
Cu(1)–S(1)	2.428(2)	Cu(1)–S(2)	2.459(2)
N(1)–Cu(1)–N(2)	136.3(2)	N(1)–Cu(1)–S(1)	125.76(13)
N(2)–Cu(1)–S(1)	87.5(2)	N(1)–Cu(1)–S(2)	86.52(14)
N(2)–Cu(1)–S(2)	116.76(13)	S(1)–Cu(1)–S(2)	101.20(5)

Dihedral angles

Phenyl/phenyl 83.0

Mean Plane S(1)–C(12)–C(11)–N(2)–Cu(1) and mean plane S(2)–C(6)–C(5)–N(1)–Cu(1) 89.4

Plane S(1)–Cu(1)–N(2) and plane S(2)–Cu(1)–N(1) 67.4

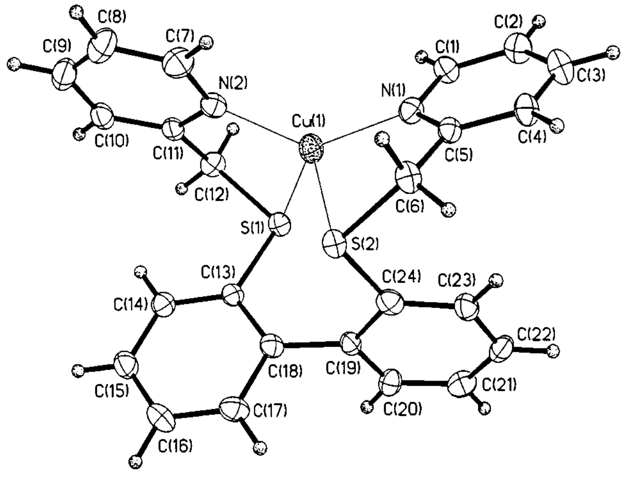


Fig. 1 Molecular structure and atom-labelling scheme for [Cu(N_2S_2-mpy)]ClO_4·MeCN.

The flexibility of the biphenyl ring is manifested in the local geometry around the copper. One measure of the closeness of fit to a tetrahedron is the dihedral angle between the S(1)–Cu(1)–N(2) and S(2)–Cu(1)–N(1) planes (it would be 90° for an idealized tetrahedron). For complex **3**·MeCN this value is 67.4°. For other biphenyl-based copper(I) complexes this angle ranges from 55.1 to 91.7°.[9,10] A second measure of the tetrahedral nature of a complex is the dihedral "crossing" angle. For **3**·MeCN the dihedral angle between the S(1)–C(12)–C(11)–N(2)–Cu–(1) plane and the S(2)–C(6)–C(5)–N(1)–Cu–(1) plane is 89.4°. In other biphenyl-based copper(I) complexes, it varies from 48.9 to 74.9°.

Conformation changes also occur to the ligand upon complexation. Most notable is the dihedral angle of 83° found between the individual aromatic rings of the biphenyl moiety. This near perpendicular orientation of the rings shows how the biphenyl twists to generate the tetrahedron around the copper. This is the largest biphenyl dihedral angle reported for a copper(I) complex (between 61.6 and 73.9°).[9b,10] The non-planar nature of the rings and the ability of the ligand to twist out of planarity is a hallmark of biphenyl-based ligand sets.

Mass spectra

We have made extensive use of Fast Atom Bombardment Mass Spectrometry (FAB MS) in the analysis of copper(I) and copper(II) complexes for partial structure analysis.[15] This technique has been used to help characterize complexes **1–8** by using both the molecular ion present and the fragmentation

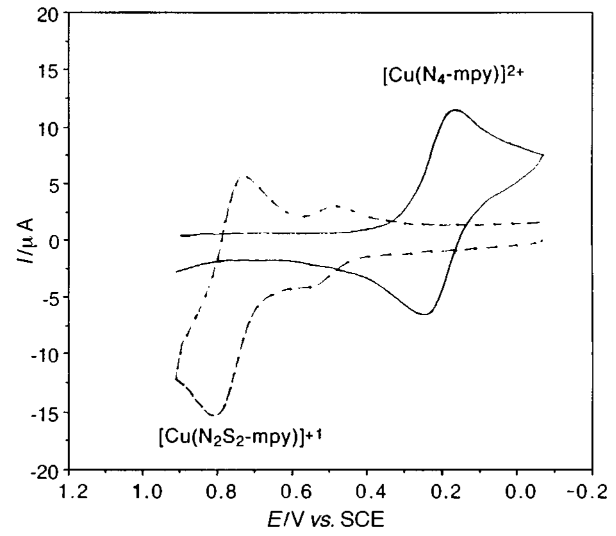


Fig. 2 Cyclic voltammograms recorded at a glassy carbon electrode in acetonitrile: (--) 0.38 mM solution of $[Cu(N_2S_2\text{-mpy})]ClO_4$ **3**, $E^{\circ\prime} = +0.77$ V *vs.* SCE, $\Delta E_p = 84$ mV; (-) 0.70 mM solution of $[Cu(N_4\text{-mpy})][ClO_4]_2$ **5**, $E^{\circ\prime} = +0.21$ V *vs.* SCE, $\Delta E_p = 88$ mV. The scan rate was 50 mV s^{-1} and the supporting electrolyte 0.10 M tetrabutylammonium hexafluorophosphate solution in both cases.

patterns obtained. The results indicate the presence of the intact cation in all cases. For example, it is found at *m*/*z* 469 for **1** and 464 for **3**. The fragmentation patterns found for complexes **1–8** are also consistent with the presence of their respective ligands and counter ions.

Electrochemistry

The reduction potentials for complexes **3**, **5**, and **7** were measured by cyclic voltammetry in acetonitrile at a glassy carbon electrode. The results for the experiments are shown in Fig. 2. For a 0.38 mM solution of **3**, two voltammetric waves were observed as the potential was swept in the anodic direction resulting in the oxidation of the copper(I) complex to Cu^{II}. The predominant wave has a value for $E^{\circ\prime}$ (taken as the average of the anodic and cathodic peak potentials) of +0.77 V *vs.* SCE. A value of 84 mV was observed for the peak separation, δE_p, which is indicative of a quasi-reversible heterogeneous electron transfer. The ratio of the cathodic to anodic peak currents, $i_{pc}:i_{pa}$, was nearly 1 : 1, demonstrating that the oxidized form of the complex was stable on the timescale of the voltammetric experiment. This chemical reversibility, along with the very positive value for the oxidation potential, clearly illustrates the stability the N_2S_2-mpy ligand imparts to the copper(I) complex. The smaller of the two voltammetric waves, centered near +0.50 V, is thought to be the result of an impurity in the sample. The high oxidation potential for $[Cu(N_2S_2\text{-mpy})]ClO_4$ demonstrates the ease with which the complex can be reduced and is clearly a result of the biphenyl backbone and the sulfur donors. Indeed, the $[Cu(N_2S_2\text{-mpy})]ClO_4$ reproduces the very positive potentials found for the blue copper proteins.[30]

A cyclic voltammogram recorded for a 0.70 mM solution of complex **5** in acetonitrile is shown in Fig. 2. The potential was swept in the cathodic direction first with the reduction of Cu^{II} being observed at a value for $E^{\circ\prime} = +0.21$ V *vs.* SCE. This is greater than 500 mV more cathodic than the reduction potential of **3** and shows the large effect of replacing sulfur with nitrogen in this ligand. The value for ΔE_p was 88 mV, very close to that observed for **3**, demonstrating quasi-reversible kinetics for the electron transfer reaction. The ratio of the reverse to forward peak currents was again unity, indicative of the reversible regeneration of the original complex following reduction.

The cyclic voltammetry of the copper(II) complex **7** (0.44 mM), prepared from two bidentate NS-mpy ligands, is chemically reversible ($i_{pc}:i_{pa} = 1:1$), with an $E^{\circ\prime}$ value of +0.53 V *vs.* SCE. This value is intermediate between those for **3** and **5**. The value for ΔE_p was found to be 124 mV, indicating that the electron transfer to **7** is the slowest of the three complexes, but still quasi-reversible. A comparison with the voltammogram for **3** demonstrates that the absence of the biphenyl moiety in **7** results in lessened stability for the +1 oxidation state for copper. Although this decrease in stability is not nearly as extreme as the 560 mV cathodic shift that results from the replacement of sulfur by nitrogen in **5**, the presence of the biphenyl ring leads to a 0.24 V cathodic shift. The primary reason for this shift seems to be the ability of **3** to exist in a tetrahedral environment which stabilizes the copper(I) form.[31]

Conclusion

We have probed the properties of copper complexes prepared from a series of related ligands which were designed to enforce geometrical constraints on the metal atom. Our original goal was to prepare ligands which would enforce tetrahedral geometry on metal ions through the use of the biphenyl backbone. In that respect, our original premise that the biphenyl moiety would impose this geometrical outcome has proven to be correct as evidenced by the single crystal structure analysis of **3**·MeCN which revealed it to be in a pseudotetrahedral structure. However, in order to relieve the severe steric constraints placed on the copper(II) form, complexes **1–4** spontaneously reduced to Cu^I. In order to test whether the mere presence of two sulfur donors is enough to lead to the spontaneous reduction we prepared the bidentate NS-mpy analog of the N_2S_2-mpy ligand. When treated with copper(II) precursors isolation of copper(II) complexes was found. This result shows that the biphenyl backbone is necessary for the observed spontaneous reduction since the biphenyl is absent in the NS-mpy ligand.

We also wanted to probe whether the sulfurs were essential for the reduction so we prepared the all nitrogen N_4-mpy ligand. The spontaneous reduction found for complexes **1–4** does not occur when the sulfurs are replaced by nitrogen donors as in **5** and **6**. Therefore, in ligands of this type, the presence of the sulfur donors and the biphenyl ring is necessary for the spontaneous reduction process.

Cyclic voltammetry showed a significant positive shift of the Cu^{II}–Cu^I redox couple due to the presence of the sulfur donors or the biphenyl ring. It has previously been shown that the $E_{1/2}$ values become more positive as the local geometry around the copper is changed from that of a distorted plane to a distorted tetrahedron.[21] It is not surprising, then, that the $E^{\circ\prime}$ for $[Cu(N_2S_2\text{-mpy})]ClO_4$ is so positive as it includes sulfur donors and is forced into a tetrahedral environment. The synthesis of related ligands based on the biphenyl backbone are being pursued.

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