



A CuN₂S₂ core with a high potential copper(II/I) couple. Use of a surface modified electrode and generation of five coordinate copper(I)



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ABSTRACT

Using the 1:2 condensate of benzil dihydrazone and 2-(methylthio)benzaldehyde as a ligand (L), a cationic copper(I) complex [CuL]PF₆·0.5THF (THF ≡ tetrahydrofuran; **1**) is synthesized. The X-ray crystal structure of the desolvated species [CuL]PF₆ has been determined and is found to contain a CuN₂S₂ core. The corresponding copper(II) complex could not be obtained. The cyclic voltammograms of **1** at a Pt or a glassy carbon electrode show features of adsorption, but it shows a quasireversible Cu(II/I) couple at a gold electrode modified by thiocyanate. The redox potential is 0.79 V versus NHE. Complex **1** reacts with PPh₃ in CH₂Cl₂ in 1:1 M proportion and subsequent addition of *n*-hexane yields [CuL(PPh₃)]PF₆·0.25*n*-hexane·4H₂O (**2**). Our bp86/6–311g(2d,p) calculations indicate two plausible structures **A** and **B** for the cation in **2**. In **A**, copper(I) is 5-coordinate with a trigonal bipyramidal N₂S₂P coordination sphere (the P atom and an azine N occupy the apices) and in **B**, the metal has a tetrahedral N₂SP coordination sphere with one of the two S atoms of L remaining uncoordinated. Binding of PPh₃ to the metal in [CuL]⁺ is theoretically exothermic; structure **B** is energetically more stable than **A** by 4.5 kcal mol⁻¹. In solution there exists an equilibrium between **A** and **B**. From variable temperature ¹H NMR of **2**, an average ΔH⁰ value of –2.8 kcal mol⁻¹ is obtained for the equilibrium thus showing that enthalpy wise **B** is more stable than **A** which matches well with the DFT results. The equilibrium is not favoured entropically. Existence of the equilibrium is also apparent in the ³¹P NMR of **2**.

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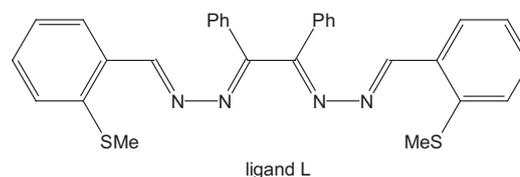
1. Introduction

The type 1 copper centers in biologically occurring blue copper proteins have Cu(II/I) potential in the range 0.26–1.00 V versus NHE [1–3]. Actually, the redox potential E⁰ of a Cu(II/I) couple [Eq. (1)] is expected to be negative since Cu(I) cannot have crystal



field stabilization energy while Cu(II) can. The E⁰ of the Cu(II/I) couple in aqueous medium is only 0.13 V versus NHE [4]. However, it should be remembered that Cu(I) disproportionates in water [5]. Extensive studies on low molecular weight copper complexes having a CuN₄ core have revealed that factors like π-acidity which preferentially stabilizes copper(I) and factors like tetrahedral distortion which destabilizes copper(II) increase the Cu(II/I) potential [4,6–10]. The highest Cu(II/I) potential attained so far for a CuN₄ core is 1.79 V versus NHE [11]. Some type 1 coppers have N₂S₂ coordination sphere. Consequently, CuN₂S₂ cores also have

been much studied [12–17]. In these cases, the highest E⁰ for the couple (1) reported to date is 1.12 V versus NHE [14]. Herein we report a novel copper(I) complex having a CuN₂S₂ core and some of its chemistry. The ligand L used is depicted below.



2. Results and discussion

The ligand L is a 1:2 condensate of benzil dihydrazone and 2-(methyl-thio)benzaldehyde (L). Its X-ray crystal structure is shown in Fig. 1. The conformation of the ligand in the solid state is clearly not suitable for coordination to a metal. On binding to a metal S(1) and N(18) donor atoms form a six-membered chelate

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ring as do S(2) and N(23) and this conformation is illustrated in the structure of the hexafluorophosphate salt of the copper(I) complex of L. As isolated from the reaction of L with $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ in equimolar proportion in tetrahydrofuran (THF) under N_2 atmosphere at room temperature, the copper(I) complex is $[\text{CuL}]\text{PF}_6 \cdot 0.5\text{THF}$ (**1**). Its single crystals are obtained by direct diffusion of *n*-hexane into a dilute dichloromethane solution of the complex as $[\text{CuL}]\text{PF}_6$. The structure of the cation $[\text{CuL}]^+$ is shown in Fig. 2. The metal is in a distorted four coordinate tetrahedral environment. Least squares plane calculations show that the two six-membered chelate rings have r.m.s. deviations of 0.061, 0.084 Å and intersect at an angle of $76.3(1)^\circ$. The two Cu–N distances are 2.008(4), 2.004(4) Å and the Cu–S distances 2.229(1), 2.242(1) Å. The two methyl groups on the sulfur atoms occupy different conformations (Fig. 2). The torsion angles C(1)–S(1)–Cu(1)–S(2) and S(1)–Cu(1)–S(2)–C(2) are $19.2(2)^\circ$ and $-123.9(2)^\circ$, respectively. Interestingly, from the reactions of copper(II) salts (perchlorate, nitrate, acetate, chloride) with L, only the unreacted ligand is recovered and the oxidation state of the metal remains unchanged.

We have studied the electrochemical behavior of **1** by cyclic voltammetry (CV) in CH_2Cl_2 . At a platinum or a glassy carbon electrode it shows features of adsorption (Fig. 3), a common phenomenon for compounds containing S atoms. To circumvent it we have performed the CV at a gold electrode modified by thiocyanate by dipping it in a 1 mmol dm^{-3} aqueous solution of KSCN for 30 s [18]. The copper(I) complex shows a quasireversible Cu(II/I) couple with a moderately high E^0 of 0.79 V versus NHE. Use of surface modified electrodes is common in studies of the electron transfer proteins and enzymes [19–21], but we are not aware of any report of examining the electrochemical behavior of a coordination complex at a surface modified electrode.

The copper(I) complex **1** reacts with triphenylphosphine at room temperature in CH_2Cl_2 in 1:1 molar proportion under N_2 atmosphere and subsequent addition of *n*-hexane yields $[\text{CuL}(\text{PPh}_3)]\text{PF}_6 \cdot 0.25n\text{-hexane} \cdot 4\text{H}_2\text{O}$ (**2**). We have not been able to grow single crystals of this phosphine adduct. We have therefore investigated the structure of the cation in **2** theoretically using density functional theory. Two plausible structures **A** and **B** emerge from our bp86/6-311g(2d,p) calculations [22] – Fig. 4. In **A**, copper(I) is five coordinate with a trigonal bipyramidal $\text{N}_2\text{S}_2\text{P}$

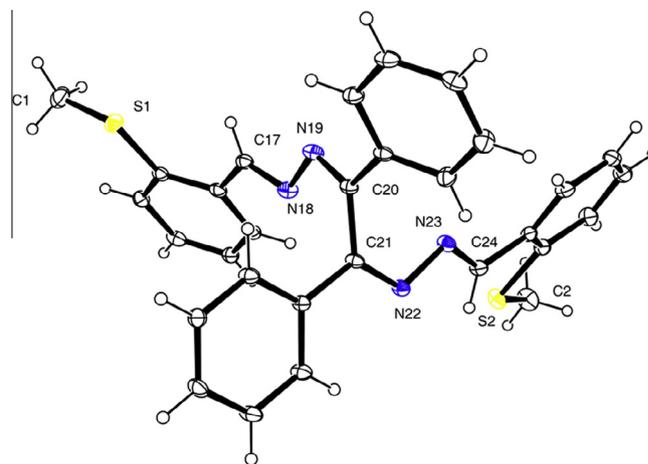


Fig. 1. The structure of L with ellipsoids at 30% probability. Torsion angle N(19)–C(20)–C(21)–N(22) is $96.6(2)^\circ$.

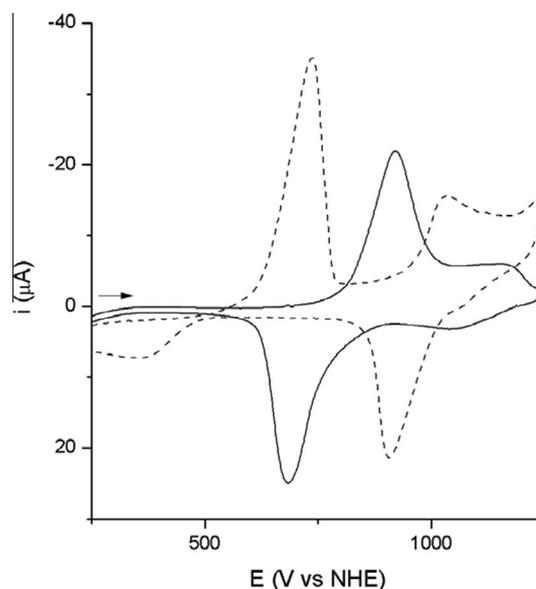


Fig. 3. The cyclic voltammograms of $[\text{CuL}]\text{PF}_6 \cdot 0.5\text{THF}$ (**1**) at a glassy carbon electrode (dashed line) and at a thiocyanate modified Au electrode (full line) in CH_2Cl_2 (1 mmol dm^{-3}). Scan rate, 50 mV s^{-1} ; supporting electrolyte, 0.1 mol dm^{-3} TBAP. The arrow indicates the start of scan.

coordination sphere (apical positions are occupied by the P atom and an azine N) and in **B**, the metal is four coordinate with a tetrahedral N_2SP coordination sphere (one of the S ends is dangling). While binding of a PPh_3 to $[\text{CuL}]^+$ is theoretically found to be exothermic, structure **B** is energetically more stable than **A** by $4.5 \text{ kcal mol}^{-1}$ indicating an equilibrium of the type



in solution. Existence of such an equilibrium is indeed found in the ^1H NMR spectrum of **2** in CD_2Cl_2 (Fig. 5). Two types of imino protons are expected – one for the four coordinate species and another for the five coordinate one. In fact, they appear as two distinct signals at 8.39 and 8.30 ppm with different intensities. The signal at 8.30 ppm is assigned to the imino proton of the four coordinate species **B**. From variable temperature NMR studies, a plot of $-\text{RTln}K$ versus temperature T (Fig. 6) yields a ΔH^0 value (intercept) of $-3.2 (\pm 0.7) \text{ kcal mol}^{-1}$. This means that **B** is enthalpically more stable than **A** by $3.2 \text{ kcal mol}^{-1}$. Consequently Eq. (2) is favoured by

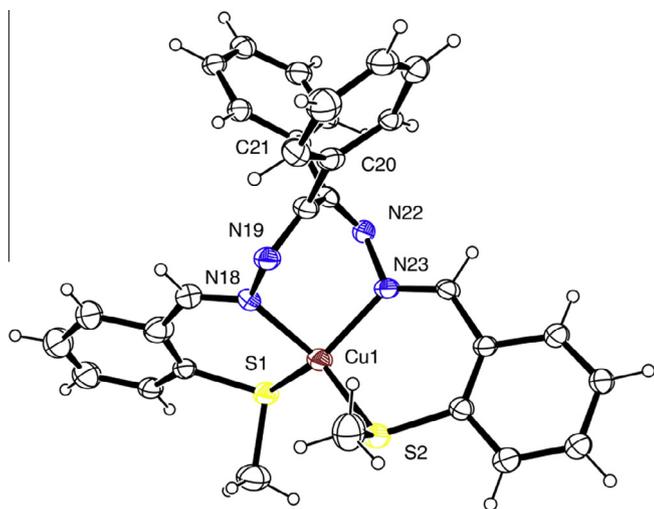


Fig. 2. The structure of cation $[\text{CuL}]^+$ with ellipsoids at 30% probability. Selected bond distances (Å) and angles ($^\circ$): Cu(1)–N(18) 2.008(4), Cu(1)–N(23) 2.004(4), Cu(1)–S(1) 2.229(1), Cu(1)–S(2) 2.242(1), N(23)–Cu(1)–N(18) $93.14(15)$, N(23)–Cu(1)–S(1) $125.20(11)$, N(18)–Cu(1)–S(1) $97.73(11)$, N(23)–Cu(1)–S(2) $98.66(12)$, N(18)–Cu(1)–S(2) $123.29(11)$, S(1)–Cu(1)–S(2) $118.25(5)$, N(19)–C(20)–C(21)–N(22) $-64.6(2)$.

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