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Mononuclear N₃S(thioether)-Ligated Copper(II) Methoxide Complexes: Synthesis, Characterization, and Hydrolytic Reactivity

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Mononuclear copper(II) methoxide complexes supported by N₃S(thioether) chelate ligands having two internal hydrogen bond donors have been prepared, comprehensively characterized, and evaluated for hydrolytic reactivity.

Mononuclear copper(II) complexes having a unidentate alkoxide ligand are rare,[1] with examples being limited to fluoroalkoxide derivatives.[2] To our knowledge, terminal methoxide ligation on copper(II) has been identified only in complexes wherein the $-OCH_3$ ligand is coordinated to a single copper ion in a multicopper system.[3] As a portion of our continuing work directed at examining how ligand effects influence the chemistry of mononuclear metal alkoxide species,[4] we report herein the preparation, characterization, and hydrolytic reactivity of two novel N₃S(thioether)-ligated copper(II) methoxide complexes.

Treatment of the N₃S(thioether) ligands pbnpa (*N*-2-(phenylthio)ethyl-*N*,*N*-bis(6-neopentylamino-2-pyridyl-methyl)amine)[5] and ebnpa (*N*-2-(ethylthio)ethyl-*N*,*N*-bis(6-neopentylamino-2-pyridylmethyl)amine)[4] with equimolar amounts of $Cu(ClO_4)_2 \cdot 6H_2O$ and $Me_4NOH \cdot 5H_2O$ in dry methanol, followed by workup and crystallization from MeOH/Et₂O, yielded the mononuclear methoxide complexes **1** ([(pbnpa)Cu$-OCH_3$]ClO₄) and **2** ([(ebnpa)Cu$-$OCH₃]ClO₄) (Scheme 1).

ORTEP views of the cationic portions of **1** and **2** are shown in Figure 1.[6] The overall geometry of the copper centers in the complexes differs, with **1** exhibiting a nearly perfect square pyramidal geometry ($\tau = 0.01$),[7] whereas **2** is distorted trigonal bipyramidal ($\tau = 0.84$).[7] Differences in geometry have also been observed for simple copper(II) chloride derivatives of the pbnpa/ebnpa ligands, with the $-$SPh complex ([(pbnpa)Cu$-$Cl]ClO₄) being more square pyramidal ($\tau = 0.25$),[7] and the $-$SEt complex [(ebnpa)Cu$-$Cl]ClO₄ closer to trigonal bypyramidal ($\tau = 0.63$).[7] Despite the differences in geometry, **1** and **2** exhibit identical Cu$-$O bond lengths that fall on the short end of the range known for terminal alkoxides on copper(II) (1.89$-$1.97 Å).[2,3] The Cu$-$N bond lengths in **1** and **2** are also similar, albeit the Cu$-$N$_{py}$ distances are slightly longer in **2**. Notably different are the Cu$-$S distances, with **1** having a weak Cu(1)$-$S(1) interaction (2.704(1) Å), whereas in **2** the Cu(1)$-$S(1) interaction is ~0.29 Å shorter, and is comparable to that found in a copper(II) complex of the N₃S ligand *N*-(2-methylthio)-ethyl-*N*,*N*-bis(2-pyridylethyl)amine (2.335(2) Å).[8]

For spectroscopic comparison, as well as subsequent reactivity studies, we prepared the corresponding hydroxide complexes **3** ([(pbnpa)Cu$-$OH]ClO₄) and **4** ([(ebnpa)Cu$-$OH]-ClO₄, Scheme 1) using a synthetic route very similar to that for the methoxide derivatives, with the only difference being that the reactions were performed in acetonitrile solution. Representations of the cationic portions of **3** and **4** are shown in Figure 2. The Cu$-$S distances in the hydroxide derivatives are longer, with the Cu(1)⋯S(1) distance in **3** (2.813(1) Å) being outside the sum of the ionic radii of copper(II) (CN = 5) and S²⁻ (~2.5 Å), but within the sum of the van der Waals radii (~3.2 Å), indicating that a weak Cu(II)$-$SR₂ interaction is present.[9] It is worth noting that structurally characterized examples of mononuclear Cu$-$OH species are rare, with only four having been previously reported, none

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(1) Bradley, D. C.; Mehrotra, R. C.; Rothwell, I. P.; Singh, A. *Alkoxo and Aryloxo Derivatives of Metals*; Academic Press: San Diego, CA, 2001.
(2) (a) Jeffries, P. M.; Wilson, S. R.; Girolami, G. S. *Inorg. Chem.* **1992**, *31*, 4503. (b) Purdy, A. P.; George, C. F. *Inorg. Chem.* **1991**, *30*, 1969. (c) Purdy, A. P.; George, C. F.; Callahan, J. H. *Inorg. Chem.* **1991**, *30*, 2812.
(3) See for example: (a) Murthy, N. N.; Mahroof-Tahir, M.; Karlin, K. D. *J. Am. Chem. Soc.* **1993**, *115*, 10404. (b) Nishida, Y.; Takeuchi, M.; Takahashi, K.; Kida, S. *Chem. Lett.* **1985**, 631. (c) Nishida, Y.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1986**, 2633.
(4) Garner, D. K.; Fitch, S. B.; McAlexander, L. H.; Bezold, L. M.; Arif, A. M.; Berreau, L. M. *J. Am. Chem. Soc.* **2002**, *124*, 9970.
(5) Tubbs, K. J.; Fuller, A. L.; Bennett, B.; Arif, A. M.; Makowska-Grzyska, M. M.; Berreau, L. M. *Dalton Trans.* **2003**, 3111−3116.

(6) Please see Supporting Information for crystallographic details for **1**−**4**.
(7) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.
(8) Champloy, F.; Benali-Cherif, N.; Bruno, P.; Blain, I.; Pierrot, M.; Reglier, M.; Michalowicz, A. *Inorg. Chem.* **1998**, *37*, 3910.
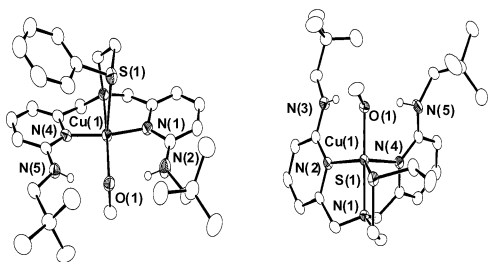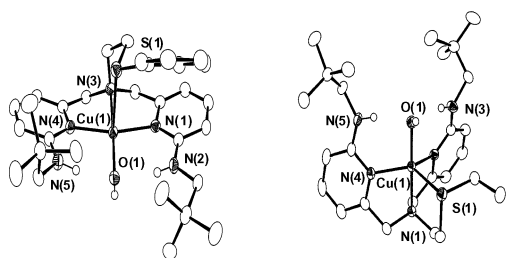
Figure 1. Representations of the cationic portions of the X-ray crystal structures of **1** (left) and **2** (right). All ellipsoids are drawn at the 50% probability level (all hydrogens except the secondary amine hydrogens not shown for clarity). Selected bond lengths: (**1**) Cu(1)−O(1) 1.915(2), Cu(1)−N(1) 2.016(2), Cu(1)−N(3) 2.051(2), Cu(1)−N(4) 2.007(2), Cu(1)−S(1) 2.704(1) Å; (**2**) Cu(1)−O(1) 1.905(2), Cu(1)−N(1) 2.033(2), Cu(1)−N(2) 2.089(2), Cu(1)−N(4) 2.113(2), Cu(1)−S(1) 2.418(1) Å.


Figure 2. Representations of the cationic portions of the X-ray crystal structures of **3** (left) and **4** (right). All ellipsoids are drawn at the 50% probability level (all hydrogens except secondary amine and hydroxyl hydrogens not shown for clarity). Selected bond lengths: (**3**) Cu(1)−O(1) 1.904(1), Cu(1)−N(1) 2.036(1), Cu(1)−N(3) 2.047(1), Cu(1)−N(4) 2.045(1) Å, Cu(1)···S(1) 2.813(1); (**4**) Cu(1)−O(1) 1.887(1), Cu(1)−N(1) 2.049(2), Cu(1)−N(2) 2.124(2), Cu(1)−N(4) 2.084(2), Cu(1)−S(1) 2.464(1) Å.

Scheme 1
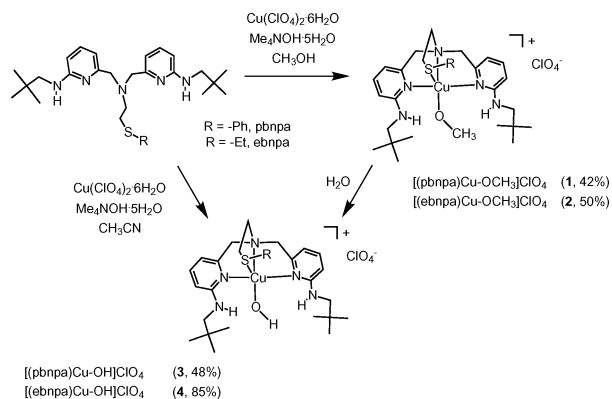
of which have sulfur ligation.[10] The Cu−O distances in **1**−**4** are all ∼1.90 Å, with little deviation resulting from the nature of the O-donor. The hydrogen-bonding interactions for the complexes having the same supporting chelate ligand (**1** and **3**, **2** and **4**) are generally similar, with the more square pyramidal pbnpa-ligated derivatives **1** and **3** exhibiting secondary hydrogen bonds having heteroatom distances that are slightly shorter than those found in the distorted trigonal

bypramidal ebnpa-ligated systems (**1/3**, N···O(1)$_{av}$ 2.70 Å; **2/4**, N···O(1)$_{av}$ 2.74 Å;) and involve slightly more acute angles (**1/3**, N−H···O(1)$_{av}$ 161°; **2/4**, N−H···O(1)$_{av}$ 165°).

The UV−visible spectra of **1**−**4** in the region of 400−1100 nm are shown in Figure S1 (Supporting Information). Most dramatic are differences for complexes having the same anionic ligand (methoxide or hydroxide) but different N$_3$S chelate ligands (e.g., **1** and **2**). Similarly to copper(II) halide and pseudohalide complexes of the pbnpa/ebnpa ligands, EPR analysis of **1**−**4** in methanol (**1** and **2**; 4 mM, 115 K) or acetonitrile (**3** and **4**; 4 mM, 115 K) revealed that all of the complexes have $g(z) > g(x,y)$ and thus a d$_{x^2−y^2}$ ground state and a square-pyramidal based geometry in solution (Figure S2, Supporting Information).[5] Notably, a second component is present in the EPR spectrum of **2**, with $A_{||}$ and $g_{||}$ values (Table S1, Figure S3, Supporting Information) consistent with increased spin delocalization on to sulfur.[11] This type of solution behavior has also been observed for the ebnpa-supported complexes [(ebnpa)Cu−X]ClO$_4$ (X = Cl or N$_3$) and likely results from geometric distortion in the [(ebnpa)Cu−X]$^+$ ions that results in a stronger Cu−S interaction.

Differences in the d−d region of UV−visible spectra were determined between the methoxide and hydroxide derivatives for each chelate ligand system, thus enabling spectroscopic monitoring of the reactivity of the methoxide derivatives with water. Addition of a single equivalent of water to acetonitrile solutions of **1** or **2** yields spectra intermediate between those of **1** and **3** (Figure S4) or **2** and **4** (Figure S5) (Supporting Information). This may be due to the formation of equilibrium mixtures involving water, as has been observed with structurally related zinc complexes.[4] However, treatment of **1** or **2** with excess water (∼49−50 equiv) in acetonitrile solution results in the clean formation of **3** or **4** as indicated by UV−vis and FTIR analysis (Figures S4 and S5).

In conclusion, novel examples of mononuclear copper(II) alkoxide complexes have been prepared, characterized, and examined for hydrolytic reactivity. Our continuing efforts focus on examining the reversibility of the hydrolysis reactions presented herein, as well as evaluating the influence of hydrogen-bonding on the chemical properties of copper alkoxide derivatives.

Supporting Information Available: Synthetic details and characterization data; UV−visible figure; EPR figure and data; UV−vis figures showing water addition reactions for **1** and **2**; four X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) (a) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. (b) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(10) (a) Fujisawa, K.; Kobayashi, T.; Fujita, K.; Kitajima, N.; Moro-oka, Y.; Miyashita, Y.; Yamada, Y.; Okamoto, K. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1797. (b) Harata, M.; Hasegawa, K.; Jitsukawa, K.; Masuda, H.; Einaga, H. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1031. (c) Berreau, L. M.; Mahapatra, S.; Halfen, J. A.; Young, V. G., Jr.; Tolman, W. B. *Inorg. Chem.* **1996**, *35*, 6339. (d) Lee, S. C.; Holm, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 11789.

(11) Peisach, J.; Blumberg, W. E. *Arch. Biochem. Biophys.* **1974**, *165*, 691.