



Note

Copper(II) complexes of aliphatic tridentate amine/dithioether ligands – Synthesis and molecular structures

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ARTICLE INFO

Article history:

Received 13 February 2012

Accepted 16 April 2012

Available online 25 April 2012

Keywords:

Mixed donor ligands
Sulfur donor function
Tridentate ligands
Copper

ABSTRACT

Three new tridentate ligands (**1–3**) featuring a central secondary amine linked by ethylene bridges to two thioether donor functions with *S*-methyl or *S*-benzyl substituents have been synthesized and reacted with copper(II) chloride or copper(II) nitrate. The resulting complexes of type $[\text{CuX}_2(\text{L})]$ (L = amine-dithioether ligand) **6**, **7**, and **9** exhibit a square-pyramidal coordination geometry with the nitrogen and sulfur donor groups of the tridentate ligand occupying three of the basal binding sites at the metal ion. Two chloro (**6** and **7**) or a nitrate ligand (**9**) originating from the metal precursor salt complete the coordination sphere of the copper(II) ion. The apical donors are bonded with significantly longer bond distances compared to identical donors in the basal plane. The weakly bound apical chloro ligand of **6** can be abstracted with silver(I) nitrate effecting the formation of the dinuclear complex **10** featuring a nitrate ligand coordinated to two copper(II) centers in a bridging fashion. For all copper(II) complexes the observed Cu–S bond distances are very similar and not significantly influenced by alteration of the alkyl group at the thioether donor function.

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1. Introduction

As essential part of many biological systems copper exhibits a diverse and fascinating coordination chemistry. In particular the intensely blue colored Cu^{II} -sites of cupredoxins like azurin or plastocyanin have interested chemists for many years due to their exceptional spectroscopic and structural properties [1]. In the active centers of these enzymes the copper(II) ion is coordinated by two histidine nitrogen atoms and a cystein thiolato donor. The copper coordination sphere is usually completed by one or two weakly bound ligands resulting in a distorted tetrahedral or trigonal-bipyramidal complex geometry [2]. In many cupredoxins these additional ligands are thioether donors, e.g. methionine residues. An often observed problem during the synthesis of model compounds for copper(II) enzymes is the facile oxidation of thiolato ligands to the corresponding disulfides by the metal center [3]. One approach to prevent this undesired reaction is the substitution of the thiolato donor function by a more stable thioether group [4].

N-centered tripodal ligands are frequently used to model the active sites of metallo proteins [5] and various symmetric and asymmetric tripodal ligands containing different donor functions [6] including a number of ligands of type $\text{N}[(\text{CH}_2)_x\text{-SH}]_3$ have been described [6e–i]. Complexes bearing N-centered tripodal aliphatic

triamines exhibit a variation of the geometric parameters depending on the lengths of the ligand arms [7]. Recently we reported on a series of copper(I) complexes with tris(ω -benzylmercaptoalkyl) amine ligands [8]. The geometry at the metal center turned out to be highly dependent on the ligand arm lengths and can be gradually adjusted from trigonal-pyramidal (exclusively ethylene spacers) to tetrahedral (exclusively propylene spacers). For related complexes with tripodal ligands featuring thioether donor functions a significant dependence of the structural and spectroscopic properties on the alkyl or aryl substituents of the thioether was observed [9,10]. Berreau et al. synthesized copper(II) complexes with N-centered tripodal ligands with two pyridyl and one thioether donor group [9]. While the complex with an ethyl thioether substituent exhibits the trigonal-bipyramidal geometry, the analogous compound with an aromatic phenyl thioether is square-pyramidal. The Cu–S bond distances differ significantly with values of 2.418(1) Å for the ethyl and 2.701(1) Å for the phenyl derivative.

Herein, we report on the coordination chemistry towards copper(II) of three novel ligands with thioether donors. The syntheses of the tridentate ligands featuring a secondary amine and two thioether donor functions with different substituents as well as the preparation and molecular structures of their copper(II) complexes are presented and discussed. Some complexes of related ligands with two thiolato donor functions have been described previously [11].

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2. Results and discussion

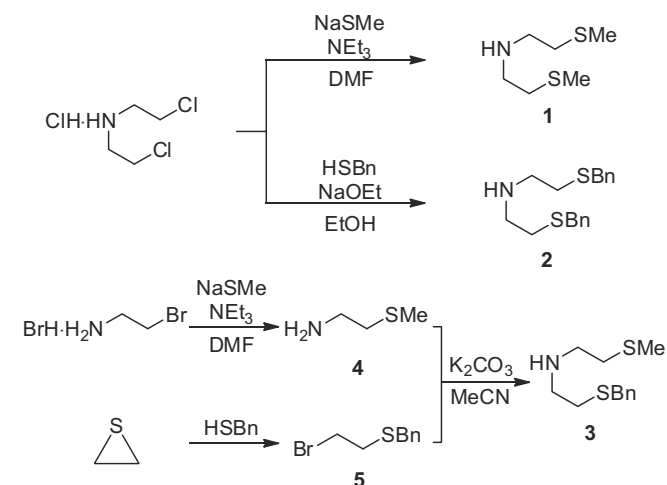
The symmetric tridentate ligands **1** and **2** were synthesized by a nucleophilic substitution of the halides of bis(2-chloroethyl)amine hydrochloride with methylthiolate or benzylthiolate [12], respectively (Scheme 1). For the preparation of the asymmetric ligand **3** bearing both methyl and benzyl thioether donor functions 2-(mercaptomethyl)ethylamine **4** was prepared from 2-bromoethylamine hydrobromide and subsequently *N*-alkylated with 2-(mercaptobenzyl)ethylbromide **5** [13]. Compounds **2** and **5** have been used previously as precursors for tripodal ligands [8].

The mononuclear copper(II) complexes [CuCl₂(**1**)] **6**, [CuCl₂(**2**)] **7**, [CuCl₂(**3**)] **8**, and [Cu(NO₃)₂(**3**)] (**9**) were prepared by the reaction of the appropriate ligands with copper(II) chloride or copper(II) nitrate dihydrate in acetonitrile (Scheme 2). Treatment of compound **6** with one equivalent of silver(I) nitrate in acetonitrile leads to the dinuclear complex [{CuCl(**1**)₂(μ-NO₃)]NO₃ **10** featuring a bridging nitrate ligand. Dark green single crystals of **6**, **7**, **9**, and **10** which were suitable for X-ray diffraction analyses have been obtained by slow diffusion of diethyl ether into saturated solutions of the complexes in acetonitrile.

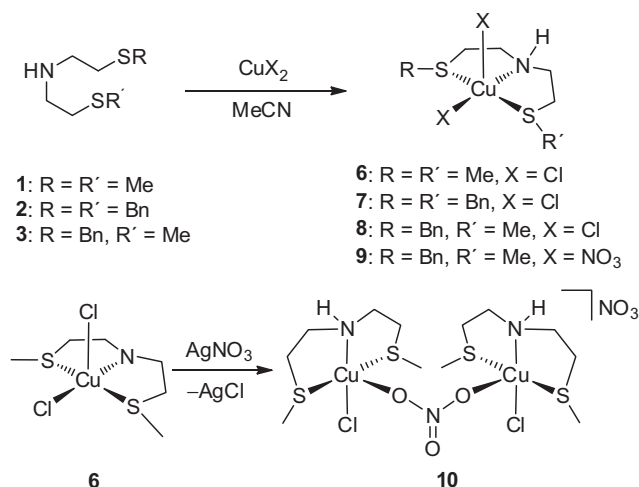
The molecular structures of complexes **6**, **7** and **9** (Figs. 1–3) confirm the proposed composition of the complexes and the coordination of the copper(II) center by the amine and the two thioether donor functions of the tridentate ligands. The remaining coordination sites at Cu^{II} are occupied by two counterions of the metal precursor salt, i.e. chloro (for **6** and **7**) or nitrate ligands (for **9**), respectively. The τ-values [14] for **6**, **7**, and **9** are ranging from 0.01 to 0.15 confirming a square-pyramidal coordination geometry at the metal centers with the nitrogen and sulfur donor functions coordinated in basal positions.

For complex **6** (Fig. 1) a Cu–N1 bond length of 2.045(2) Å was found. The Cu–S separations of 2.3168(6) Å (S1) and 2.3332(7) Å (S2) involving the two methylthioether groups are nearly of identical lengths and the measured values fall in the range observed for the copper(II) complex of a tripodal ligand containing an ethylthioether donor [9]. As expected for a square-pyramidal complex, the basal chloro ligand Cl2 features a significantly shorter Cu–Cl bond length (2.2763(7) Å) than the apical ligand chloro ligand Cl1 (2.4864(7) Å).

Complex **7** crystallizes with two molecules in the asymmetric unit and only one of these is depicted in Fig. 2. These two crystallographically independent molecules feature essentially identical metric parameters. Apparently due to the greater steric demand



Scheme 1. Synthesis of the tridentate ligands **1**–**3**.



Scheme 2. Synthesis of the copper(II) complexes **6**–**10**.

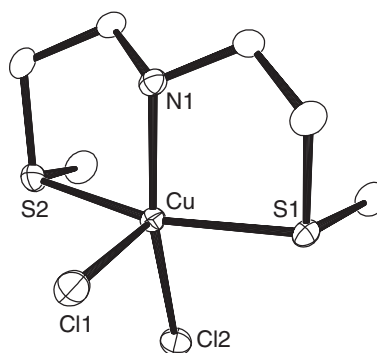


Fig. 1. Molecular structure of complex **6** (hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Cu–S1 2.3168(6), Cu–S2 2.3332(7), Cu–Cl1 2.4864(7), Cu–Cl2 2.2763(7), Cu–N1 2.045(2); S1–Cu–S2 163.76(2), S1–Cu–Cl1 92.04(2), S1–Cu–Cl2 90.08(2), S1–Cu–N1 86.95(5), S2–Cu–Cl1 102.66(2), S2–Cu–Cl2 93.19(2), S2–Cu–N1 85.36(5), Cl1–Cu–Cl2 103.20(2), Cl1–Cu–N1 93.32(5), Cl2–Cu–N1 163.31(5).

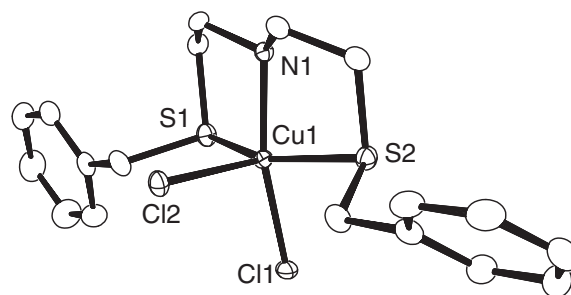


Fig. 2. Molecular structure of one of the two independent molecules of **7** in the asymmetric unit (hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°) for molecule 1 (molecule 2): Cu–S1 2.3625(9) [2.4126(9)], Cu–S2 2.3770(9) [2.4308(9)], Cu–Cl1 2.2629(9) [2.2535(9)], Cu–Cl2 2.4509(8) [2.4395(8)], Cu–N1 2.005(3) [1.999(3)]; S1–Cu–S2 156.32(3) [158.51(3)], S1–Cu–Cl1 92.21(3) [93.17(3)], S1–Cu–Cl2 102.45(3) [98.97(3)], S1–Cu–N1 85.77(8) [83.79(8)], S2–Cu–Cl1 92.63(3) [92.44(3)], S2–Cu–Cl2 99.51(3) [100.25(3)], S2–Cu–N1 83.63(8) [84.96(8)], Cl1–Cu–Cl2 99.97(3) [101.23(3)], Cl1–Cu–N1 165.13(8) [163.52(8)], Cl2–Cu–N1 94.85(8) [95.24(8)].

of the Bz–S groups, the Cu–S distances in **7** (range 2.3625(9)–2.4308(9) Å) are slightly longer than in **6** (2.3168(6)–2.3332(7) Å), while the Cu–N distances in **7** (1.999(3)–2.005(3) Å) are slightly shorter than in **6** (2.045(2) Å).

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