



Note

Preparation and X-ray characterization of two-coordinate Cu(I) complex of aliphatic thiolato ligand: Effect of steric bulk on coordination features

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ABSTRACT

We have synthesized in a single-step procedure from available copper(I) precursor at RT two Cu(I) thiolato clusters of the formula $[\text{Cu}_4(\mu\text{-SCH}(\text{CH}_3)_2)_6]^{2-}$ and $[\text{Cu}_5(\mu\text{-SC}(\text{CH}_3)_3)_6]^-$ as revealed by X-ray crystallography, where increased steric bulk leads to a bigger cage with some two-coordinate metal centers. In addition, we identified a mononuclear two coordinate thiolato complex with the bulkier ligand, of the formula $\text{NET}_4[\text{Cu}(\text{SC}(\text{CH}_3)_3)_2]$. This is only the second example of such a complex of an aliphatic ligand that is structurally characterized. The X-ray structure reveals an S–Cu–S angle of 176.7–179.5°, with Cu–S distances of 2.14 Å.

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1. Introduction

The recent interest in copper metallochaperone proteins and their X-ray crystallographic analysis have redrawn attention towards copper(I) chemistry [1–14]. These proteins exhibit a conserved motif of MTCXXC (single letter abbreviation of amino acids, 'X' represents any amino acid), where the two cysteine residues bind to the copper(I) center with a coordination number of as low as two. Whereas several thiolato-bridged Cu(I) clusters are known, particularly of the Cu_4S_6 [15–25] and Cu_5S_6 [25–29] cores, the later exhibiting both three-coordinate and two-coordinate Cu(I) centers, only three examples are known in the literature of two-coordinate mononuclear thiolato Cu(I) complexes [25,29,30], two of which include an aromatic thiophenolato ligands. We have recently reported the effect of the ligand steric bulk on the coordination features of both mononuclear and polynuclear Cu(I) complexes of aromatic thiophenolato ligands [25]. Herein, we present the preparation and X-ray crystallographic characterization of two Cu(I) complexes of aliphatic thiolato ligands, as well as the second example of a two coordinate mononuclear coordination site with an aliphatic ligand that is structurally characterized.

2. Results and discussion

Reacting isopropylthiol with equivalent amounts of NaH and stirring for 5 h, followed by addition of half equivalent of the commercially available copper(I) precursor Cu^1Cl previously stirred with approximately one equivalent of NET_4Cl in THF for 5 h at RT, and allowing them to stir overnight, gave a colorless solution. Slow addition of diethylether in portions over a few days to the filtered THF solution of the product kept at -35°C afforded single crystals suitable for X-ray crystallography. The structure of the product **1** is presented in Fig. 1, and a list of selected bond lengths and angles is given in Table 1.

The structure features a Cu_4S_6 core which may be regarded as a tetrahedron of Cu atoms inscribed within an octahedron of thiolato ligands [15–25]. In this cluster, each thiolato ligand bridges the edges of the copper tetrahedron, and each copper center is tri-coordinated with a highly planar geometry pronounced by $359.7\text{--}359.8^\circ$ as the sum of angles around the copper center, with total of two NET_4^+ counter ions. The position of the carbon atoms of the S–C bonds reduce the symmetry of the complex from T_d to C_3 , since only for one Cu(I) center, a propeller-type geometry is observed (Fig. 1, Cu(2)), while for the rest, the carbon atoms on two of the thiolato ligands face opposite directions [16,25]. The range of Cu–S bond lengths of 2.24–2.31 Å and that of the S–Cu–S angles of $110\text{--}129^\circ$ with a mean value of 119.9° [16] are somewhat narrower than the equivalent ones reported for similar structures, mostly obtained from Cu(II) precursors with higher ligand/metal

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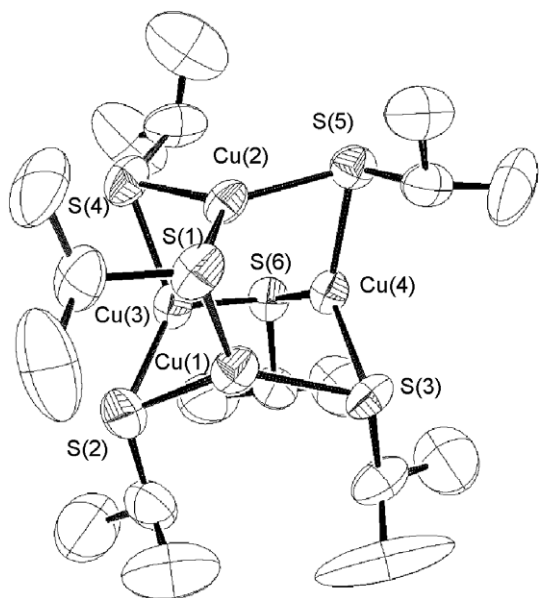


Fig. 1. ORTEP drawing of $[\text{Cu}_4(\mu\text{-SCH}(\text{CH}_3)_2)_6]^{2-}$ **1** at 50% probability ellipsoids (H atoms and disordered counter ions were omitted for clarity).

Table 1
Selected bond lengths (Å) and angles (°) for $[\text{Cu}_4(\mu\text{-SCH}(\text{CH}_3)_2)_6]^{2-}$ (**1**)

Lengths		Angles	
Cu(1)–S(3)	2.278(2)	S(3)–Cu(1)–S(2)	128.27(10)
Cu(1)–S(2)	2.291(2)	S(3)–Cu(1)–S(1)	119.50(9)
Cu(1)–S(1)	2.307(2)	S(2)–Cu(1)–S(1)	112.06(9)
Cu(2)–S(4)	2.242(2)	S(4)–Cu(2)–S(1)	120.79(9)
Cu(2)–S(1)	2.244(3)	S(4)–Cu(2)–S(5)	119.48(11)
Cu(2)–S(5)	2.273(3)	S(1)–Cu(2)–S(5)	119.54(10)
Cu(3)–S(2)	2.286(3)	S(2)–Cu(3)–S(6)	128.75(11)
Cu(3)–S(6)	2.301(3)	S(2)–Cu(3)–S(4)	119.58(10)
Cu(3)–S(4)	2.303(2)	S(6)–Cu(3)–S(4)	111.37(11)
Cu(4)–S(6)	2.268(3)	S(6)–Cu(4)–S(3)	129.33(10)
Cu(4)–S(3)	2.286(2)	S(6)–Cu(4)–S(5)	120.02(11)
Cu(4)–S(5)	2.305(3)	S(3)–Cu(4)–S(5)	110.45(10)
Cu(1)···Cu(2)	2.721	Cu(2)–S(1)–Cu(1)	73.44(8)
Cu(1)···Cu(3)	2.713	Cu(3)–S(2)–Cu(1)	72.72(7)
Cu(2)···Cu(3)	2.748	Cu(1)–S(3)–Cu(4)	73.01(7)
		Cu(2)–S(4)–Cu(3)	74.39(8)
		Cu(2)–S(5)–Cu(4)	74.08(8)
		Cu(4)–S(6)–Cu(3)	72.72(9)

stoichiometric ratio, and the Cu···Cu distances are also in a rather narrow range of 2.71–2.75 Å with no significant structural evidence for copper–copper interaction [15–19,23,25]. The Cu–S–Cu angles are of a somewhat narrower range as well, with values between 72.7° and 74.4°. In addition, these values deviate only slightly from the ideal values of 2.64 Å for Cu···Cu distance and 2.29 Å for Cu–S distance in such cores, [15,23] which suggests small influence of the *i*Pr groups.

We made numerous attempts to prepare and characterize a mononuclear structure of the isopropylthiolato ligand. Unfortunately, we did not obtain crystals suitable for X-ray crystallography under various reaction conditions and crystallization conditions employed. Nevertheless, NMR techniques revealed indications for formation of a different compound that is difficult to purify when the reaction was initiated at lower temperature and a ratio of 1:4 metal-to-ligand was employed. Although no clear evidence was obtained as to its exact structure, we suspect this compound to be the mononuclear three-coordinate complex, as our previous studies with thiophenolato ligands suggested that the cage of a

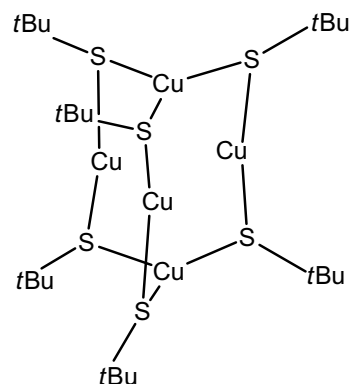
Cu_4S_6 core is normally obtained with ligands of mediocre steric bulk that may lead only to three-coordinate complexes [25]. We thus increased the steric bulk by employing the *tert*-butylthiolato ligand in an attempt to obtain two-coordinate Cu(I) centers.

Reacting the Cu(I) salt with *tert*-butylthiol previously stirred with NaH in a similar manner gave two types of compounds over time, **2** and **3**. Single crystals of both products were obtained from a THF/diethylether solution at -35°C , and the structures were resolved by X-ray crystallography.

The structure of **2** features a trigonal bi-pyramid of copper atoms within a trigonal antiprism of μ_2 -thiolato ligands, with a D_3 symmetrical core [25,27,28]. This cluster is identical to a structure previously published, where the complex was obtained from a Cu(II) precursor through in situ reduction by the thiolato ligand [26]. A schematic representation of this cluster is given in Scheme 1.

The structure of **3** (Fig. 2, Table 2), however, features a two-coordinate mononuclear copper(I) anionic center with one NEt_4^+ counter ion. Approximately linear S–Cu–S angles are observed for the two anions in the asymmetric unit, of 176.7° and 179.5° . The Cu–S bond distances of 2.14 Å are similar to those of known structures [25,29,30]. Interestingly, the two *t*-Bu groups do not face opposite directions, but rather are located on approximately perpendicular vectors on both anions in the asymmetric unit, which raises the possibility of Cu–S π interactions through perpendicular metal orbitals. Compound **3** may be obtained more selectively when a 1:4 metal-to-ligand ratio is employed and the reaction is initiated at -30°C and allowed to warm to RT overnight, conditions that also appeared to favor formation of a mononuclear species with the isopropylthiolato ligand, as discussed above.

In conclusions, we observed that consistently with our previous results, [25] the size of the thiolato ligand influences the coordination features of the Cu(I) center. Bigger cluster cores are obtained for larger ligands, which may also lead to two-coordinate Cu(I)



Scheme 1.

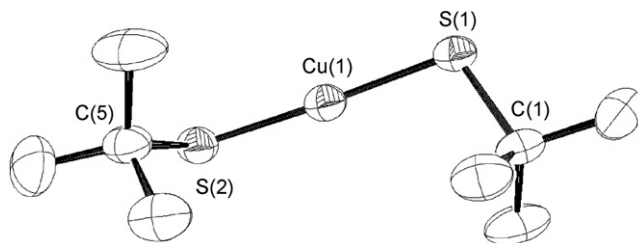


Fig. 2. ORTEP drawing of one of the anions $[\text{Cu}(\text{SC}(\text{CH}_3)_3)_2]^-$ **3** in the asymmetric unit at 50% probability ellipsoids (second anion, H atoms and counter ions were omitted for clarity).

Table 2
Selected bond lengths (Å) and angles (°) for $[\text{Cu}(\text{SC}(\text{CH}_3)_2)_2]^-$ (**3**)

Lengths		Angles	
Cu(1)–S(1)	2.1380(7)	S(1)–Cu(1)–S(2)	176.69(2)
Cu(1)–S(2)	2.1410(6)	S(3)–Cu(1)–S(2)	179.54(3)
Cu(2)–S(3)	2.1434(6)		
Cu(2)–S(4)	2.1422(6)	C(1)–S(1)–S(2)–C(5)	78.7

centers. In particular, we observed that consistently, steric crowding that allows formation of Cu_5S_6 core structures may also lead to two-coordinate mononuclear complexes. The mononuclear two-coordinate Cu(I) complex may be regarded as a structural model of the active site of copper metallochaperone proteins.

3. Experimental

Isopropylthiol (97%) and *tert*-butylthiol (98%) were purchased from Aldrich Chemical Company Inc. and Fluka Inc., respectively, and used without further purification. Tetraethylammonium chloride (98%) was purchased from Sigma Inc. and used without further purification. Copper chloride (CuCl) (97%) was purchased from Fluka Inc. and used without further purification.

All syntheses that required dry atmosphere were performed in an M. Braun dry-box or under nitrogen atmosphere using Schlenk line techniques. THF and diethylether were distilled from K/benzophenone under nitrogen and stored in the dry box.

X-ray diffraction data were obtained with Bruker Smart Apex diffractometer, running the SMART software package. After collection, the raw data frames were integrated by the SAINT software package. The structures were solved and refined using the SHELXTL software package. NMR data were recorded using AMX-300 or AMX-400 MHz Bruker spectrometer. Elemental analysis was performed in the microanalytical laboratory in our institute.

3.1. $[\text{NEt}_4]_2[\text{Cu}_4(\mu\text{-SCH}(\text{CH}_3)_2)_6]$ (**1**)

A solution of isopropylthiol (0.79 mmol) in THF (2 ml) was added to a solution of sodium hydride (0.75 mmol) in THF (2 ml) at RT and under nitrogen atmosphere. A solution of tetraethylammonium chloride (0.39 mmol) in THF (2 ml) was added to a solution of copper(I) chloride (0.35 mmol) in THF (2 ml) at RT and under nitrogen atmosphere. The solutions were allowed to stir separately in sealed flasks for 5 h. The reaction solution of the copper salt was then added to the reaction solution of the ligand and the reaction mixture was stirred overnight. The product was filtered, the THF was removed under reduced pressure, to give **1** in 25% yield. Colorless crystals were obtained from THF/diethylether at -35°C . Anal. Calc. for $\text{C}_{34}\text{H}_{82}\text{S}_6\text{N}_2\text{Cu}_4$: C, 42.29; H, 8.56; N, 2.90. Found: C, 42.45; H, 8.78; N, 3.05%. ^1H NMR (400 MHz, CD_3CN , Me_4Si , 25°C): δ 3.15 (q, $J = 7.6$ Hz, 16H, NCH_2CH_3), 3.00 (m, 6H, $\text{SCH}(\text{CH}_3)_2$), 1.27 (d, $J = 5.6$ Hz, 36H, $\text{SCH}(\text{CH}_3)_2$), 1.21 (tt, $J = 7.2$, 2.0 Hz, 24H, NCH_2CH_3).

3.2. Crystal data for (**1**)

Compound **1** was crystallized from THF/diethylether at -35°C . The asymmetric unit contains one anion and two cations, one of which is disordered. $[\text{C}_{18}\text{H}_{20}\text{S}_6\text{Cu}_4][\text{C}_{16}\text{H}_{20}\text{N}_2]$, $M = 956.54$, monoclinic, $a = 41.228(5)$, $b = 17.524(2)$, $c = 16.5737(19)$ Å, $\beta = 104.150(2)^\circ$, $U = 11611(2)$ Å³, $T = 173(2)$ K, $\lambda = 0.71073$, space group $\text{C}2/c$, $Z = 8$, $\mu(\text{Mo K}\alpha) = 1.681$ mm⁻¹, 60915 reflections measured, 12684 unique ($R_{\text{int}} = 0.0476$). $R(F_o^2)$ for $[I > 2\sigma(I)] = 0.1149$, R_w for $[I > 2\sigma(I)] = 0.3486$.

3.3. $[\text{NEt}_4][\text{Cu}_5(\mu\text{-SC}(\text{CH}_3)_2)_6]$ (**2**)

Compound **2** was synthesized in analogy to **1** in 29% yield by reacting a solution of *tert*-butylthiol (0.82 mmol) previously stirred with sodium hydride (0.88 mmol) in THF, with a solution of copper chloride (0.36 mmol) previously stirred with tetraethylammonium chloride (0.40 mmol) in THF. Yellow crystals of **2** were obtained from THF/diethylether at -35°C . Anal. Calc. for $\text{C}_{32}\text{H}_{74}\text{S}_6\text{Ncu}_5$: C, 39.10; H, 7.59; N, 1.42. Found: C, 38.99; H, 7.84; N, 1.53%. ^1H NMR (400 MHz, CD_3CN , Me_4Si , 25°C): δ 3.15 (q, $J = 7.2$ Hz, 8H, NCH_2CH_3), 1.43 (s, 54H, *t*Bu), 1.20 (tt, $J = 7.2$, 2.0 Hz, 12H, NCH_2CH_3).

3.4. $[\text{NEt}_4][\text{Cu}(\text{SC}(\text{CH}_3)_2)_2]$ (**3**)

A solution of *tert*-butylthiol (3.10 mmol) in THF (2 ml) was added to a solution of sodium hydride (3.25 mmol) in THF (2 ml) at RT and under nitrogen atmosphere. A solution of tetraethylammonium chloride (0.83 mmol) in THF (2 ml) was added to a solution of copper(I) chloride (0.76 mmol) in THF (2 ml) at RT and under nitrogen atmosphere. The solutions were allowed to stir separately in sealed flasks for 5 h. The two solutions were cooled to -30°C and the reaction solution of the copper salt was added to the reaction solution of the ligand and the reaction mixture was allowed to warm to RT overnight. The product was filtered, the THF was removed under reduced pressure, to give **3** in 58% yield. Colorless crystals of **3** were obtained from THF/diethylether at -35°C . ^1H NMR (300 MHz, CD_3CN , Me_4Si , 25°C): δ 3.16 (q, $J = 7.2$ Hz, 8H, NCH_2CH_3), 1.41 (s, 18H, *t*Bu), 1.20 (tt, $J = 7.2$, 1.8 Hz, 12H, NCH_2CH_3). UV-Vis: λ_{max} , nm (ϵ , M⁻¹ cm⁻¹). THF: 250 (700000).

3.5. Crystal data for (**3**)

Compound **3** was crystallized from THF/diethylether at -35°C . The asymmetric unit contains two anions and four cations. $[\text{C}_8\text{H}_{18}\text{S}_2\text{Cu}][\text{C}_8\text{H}_{20}\text{N}]$, $M = 372.13$, monoclinic, $a = 12.9296(14)$, $b = 20.850(2)$, $c = 16.8487(18)$ Å, $\beta = 100.280(2)^\circ$, $U = 4469.2(8)$ Å³, $T = 173(1)$ K, $\lambda = 0.71073$, space group $\text{P}2(1)/c$, $Z = 8$, $\mu(\text{Mo K}\alpha) = 1.158$ mm⁻¹, 23769 reflections measured, 9698 unique ($R_{\text{int}} = 0.0226$). $R(F_o^2)$ for $[I > 2\sigma(I)] = 0.0398$, R_w for $[I > 2\sigma(I)] = 0.1031$.

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Appendix A. Supplementary material

CCDC 672323 and 672324 contain the supplementary crystallographic data for this paper. 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.jorganchem.2008.03.002.

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