

Molecular structure and reactivity of a copper(I) tetramer

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A homoleptic copper(I) tetramer, [Cu(PhTt)]₄ **1, is synthesized using phenyltris[(methylthio)methyl]borate, PhTt⁻; X-ray analysis shows the four copper ions are nearly coplanar and each resides in an approximately tetrahedral environment; although **1** is stable towards O₂, H₂O and CO, it reacts with PPh₃, pyridine, or [NEt₄]SPh to yield the corresponding monomer, [Cu(PhTt)L] (L = PPh₃, py **3**, [NEt₄]SPh **4**).**

We have been investigating the coordination chemistry and reactivity of a series of poly[(methylthio)methyl]borates which serve as S₃⁻, face-capping ligands, *via* the synthesis and characterization of a range of metal complexes.¹ For example, [NBu₄][Mo(RTt)(CO)₃] was prepared by addition of [NBu₄][RTt] to [Mo(C₇H₈)(CO)₃].[†] Protonation with HBF₄ yielded the neutral molybdenum hydride, [Mo(RTt)(CO)₃H]. Alternatively, reaction of [NBu₄][RTt] with divalent metal ions, M = Fe, Ni or Co, yielded the six-coordinate M[RTt]₂ complexes.² During the course of these studies, we aimed to extend the synthesis to Cu^{II}. However, Cu^{II} is reduced by these ligands as evidenced by bleaching of Cu^{II} solutions upon addition of [NBu₄][RTt] or [NBu₄][PhTt].² In contrast, reaction of 1,4,7-trithiacyclononane (ttcn) with Cu^{II} does not result in reduction as evidenced by the isolation of [Cu(ttcn)₂]²⁺.^{3,4} However, employing [Cu(MeCN)₄]BF₄, a homoleptic copper(I) tetramer, [Cu(PhTt)]₄ **1** was isolated in good yield. The synthesis, characterization and reactivity of **1** is the subject of the present report.

Reaction of [NBu₄][PhTt] (0.25 g, 0.49 mmol) with [Cu(MeCN)₄][BF₄] (0.15 g, 0.49 mmol) in acetone resulted in precipitation of a white solid. The product was identified as **1** based on its ¹H NMR spectrum, analytical data and X-ray diffraction analysis.[‡] The ¹H NMR spectrum contained three aliphatic resonances consistent with two magnetic environments for the (methylthio)methyl chelates. Dissolution of **1** in CHCl₃ followed by Et₂O diffusion yielded colourless, block crystals suitable for X-ray analysis.[§] The molecular structure of **1**·solv is presented in Fig. 1. The coordination sphere about each Cu^I ion is similar and roughly tetrahedral: S–Cu–S angles range from 94.29(9) to 124.06(11)° with an average of 109.5°. Each borate ligand is oriented such that one sulfur is in a μ₂ position and the remaining two sulfurs are terminally ligated to adjacent metal ions. Consequently, the Cu^I ions and bridging S atoms form an eight-membered ring. The four Cu^I ions are essentially planar with the bridging sulfurs displaced alternately above and below the Cu₄ plane. The Cu atoms deviate from a least-squares plane as follows: Cu(1) 0.076 Å, Cu(2) –0.078 Å, Cu(3) 0.081 Å, Cu(4) –0.080 Å. The average Cu–S_t distance (2.297 Å) is as expected, shorter than the average Cu–S_b distance, 2.314 Å. The Cu···Cu distances are 4.256, 4.234, 4.062 and 4.298 Å and the average S–Cu–S angle is 117.0°. Copper(I) tetramers may be classified into two structural types, tetrahedral and planar, defined by the arrangement of the metal ions. To our knowledge, there is one other structurally characterized planar complex with bridging thioethers, [Cu₄(ddtp)₂Br₄].⁵ In this compound, the metal ions are bridged alternatively by a μ-thioether and two μ-Br⁻. Consequently, there are distinctly

different Cu···Cu distances: for Cu ions bridged by 2 Br⁻, Cu···Cu 2.71 Å for Cu ions bridged by S, Cu···Cu 5.24 Å. The longer Cu···Cu distance relative to **1** results from long Cu–S bonds (av. 2.66 Å) and an obtuse S–Cu–S angle (160.6°). Crumbliss *et al.* have prepared a planar copper(I) tetramer with bridging thioether ligands resulting in a Cu₄S₄ eight-membered ring similar to **1**.⁶

Compound **1** is inert to CO, O₂ and H₂O over several hours in CH₂Cl₂ and the CV of **1** supports its stability towards O₂. At a scan speed of 0.200 V s⁻¹, **1** exhibits two irreversible one-electron oxidations at 0.720 and 0.910 V (vs. Fc–Fc⁺).[¶] However, **1** does react with pyridine, PPh₃ or [NEt₄]SPh to yield the corresponding monomer, [Cu(PhTt)L], Scheme 1. In a typical experiment, 1 equiv. of L was added to **1** in CH₂Cl₂ and allowed to stir for 4 h. Recrystallization from toluene–pentane (acetone–pentane for **4**) yielded spectroscopically pure materials.[‡] ¹H NMR serves as a diagnostic marker for monomer formation. The three (methylthio)methyl arms of the borate which are in terminal and bridging positions in **1** are magnetically equivalent in C₃ symmetric [Cu(PhTt)L] resulting in only two aliphatic resonances. Ultimate conformation of monomer formation was obtained from X-ray diffraction analysis of **2** (Fig. 2).[§] The Cu^I ion is coordinated to three sulfur

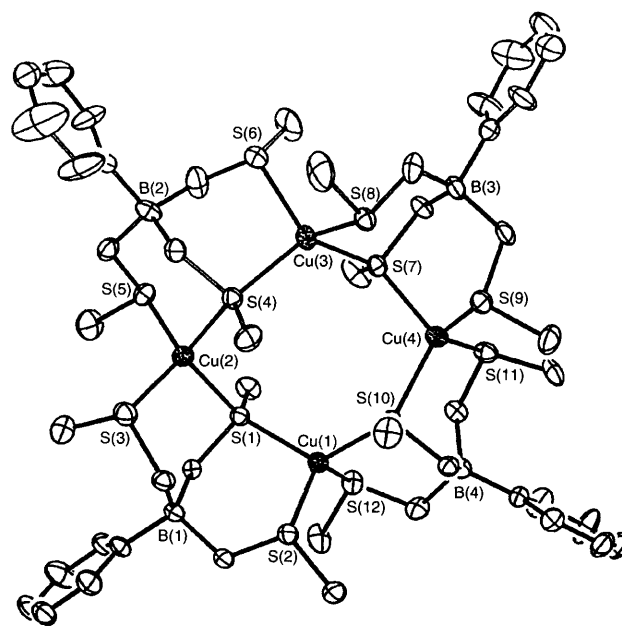


Fig. 1 ORTEP diagram of [Cu(PhTt)]₄·solv, **1**·solv, with labelling scheme and 35% thermal ellipsoids. Hydrogen atoms, apparent solvent atoms and minor disordered contributions of the sulfur atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Cu(1)–S(2) 2.294(2), Cu(1)–S(12) 2.296(2), Cu(2)–S(5) 2.273(2), Cu(2)–S(3) 2.298(3), Cu(3)–S(6) 2.301(3), Cu(3)–S(4) 2.302(2), Cu(4)–S(9) 2.275(2), Cu(4)–S(11) 2.291(3), Cu(4)–S(7) 2.313(2), Cu(4)–S(10) 2.327(2), Cu(2)–S(1)–Cu(1) 133.7(1), Cu(3)–S(4)–Cu(2) 132.5(1), Cu(3)–S(7)–Cu(4) 123.5(1), Cu(1)–S(10)–Cu(4) 135.5(1).

and one phosphorus in a distorted tetrahedral geometry.⁷ The facial coordination of the borate results in a small average S–Cu–P angle of 121.1°. Consequently, the average S–Cu–P angle of 121.1°, is greater than in an idealized tetrahedron. The average Cu–S bond distance of 2.337 Å is longer than the Cu–S₁ distance in **1** and similar to the Cu–S₆ distance. While **1** and **2** are stable to O₂, on standing CH₂Cl₂ solutions of **3** or **4** become blue-green upon exposure to O₂ after several hours. The CV of **4** displayed two irreversible oxidation processes at 0.120 and 1.33 V (vs. Fc–Fc⁺, $\nu = 0.050 \text{ V s}^{-1}$).[¶] Studies aimed at determining the composition of the oxidized species are in progress.

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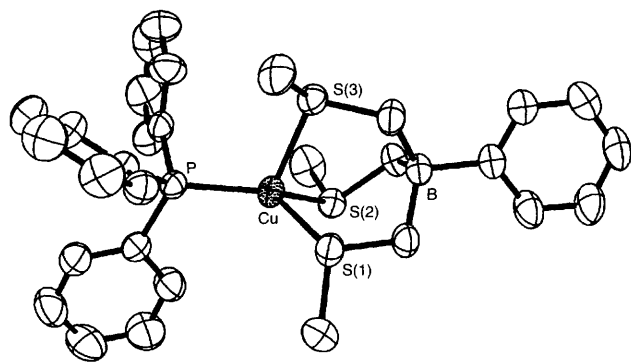
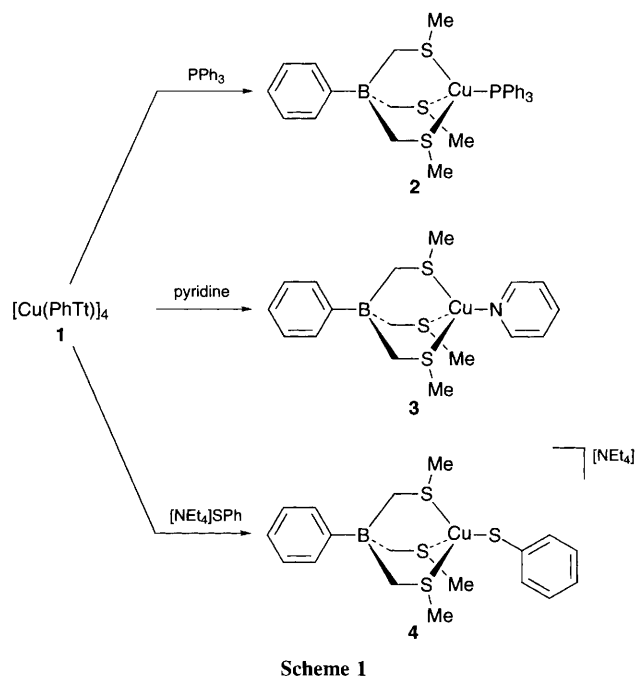


Fig. 2 ORTEP diagram of [Cu(PhTt)(PPh₃)] **2**, with labelling scheme and 35% thermal ellipsoids. Hydrogen atoms and minor disordered contributions of the sulfur atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Cu–S(1) 2.330(1), Cu–S(2) 2.323(1), Cu–S(3) 2.357(1), Cu–P 2.201(1), S(2)–Cu–S(1) 96.36(4), S(2)–Cu–S(3) 98.37(4), S(1)–Cu–S(3) 91.34(4), P–Cu–S(1) 131.40(4), P–Cu–S(2) 120.30(4), P–Cu–S(3) 111.49(4).

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Footnotes

† Abbreviations: RTt[−], tetrakis[(methylthio)methyl]borate; PhTt[−], phenyltris[(methylthio)methyl]borate; ddtp, 1,5-bis(3',5'-dimethylpyrazolyl)-3-thiapentane.

‡ *Spectroscopic data for 1*: yield 75%; ¹H NMR (CDCl₃, 400 MHz, 27 °C) δ 7.34 [(*o*-C₆H₅)B, d, 2 H], 7.20 [(*m*-C₆H₅)B, t, 2 H], 7.07 [(*p*-C₆H₅)B, t, 1 H], 2.65 (S₆CH₃, br, 3 H), 2.40 (S₁CH₃ and S₁CH₂, br, 10 H), 2.16 (S₆CH₂, br, 2 H). Anal: Calc for C₄₈H₈₀B₄Cu₄S₁₂: C, 43.04; H, 6.02. Found: C, 42.82; H, 5.86%. For **2**: yield 88%; ¹H NMR (CDCl₃, 400 MHz, 27 °C) δ 7.38 [P(C₆H₅)₃ and (*o*-C₆H₅)B, br, 17 H], 7.17 [(*m*-C₆H₅)B, t, 2 H], 7.00 [(*p*-C₆H₅)B, t, 1 H], 2.22 (BCH₂S, s, 6 H), 1.98 (SCH₃, s, 9 H). For **3**: prepared *in situ*, ¹H NMR (C₅D₅N, 400 MHz, 27 °C) δ 8.07 [(*o*-C₆H₅)B, d, 2 H], 7.46 [(*m*-C₆H₅)B, t, 2 H], 7.24 [(*p*-C₆H₅)B, t, 1 H], 2.58 (SCH₂, br, 6 H), 2.15 (SCH₃, s, 9 H). For **4**: yield 85%; ¹H NMR (CDCl₃, 400 MHz, 27 °C) δ 7.44 [(*o*-C₆H₅)S, d, 2 H], 7.39 [(*o*-C₆H₅)B, d, 2 H], 7.08 [(*m*-C₆H₅)B, t, 2 H], 6.90 [(*p*-C₆H₅)B, t, 1 H], 6.80, [(*p*-C₆H₅)S and (*m*-C₆H₅)S, m, 3 H], 2.75 (NCH₂, q, 8 H), 2.16 (SCH₃, s, 9 H), 2.01 (SCH₂, br, 6 H), 0.93 (NCH₂CH₃, t, 12 H).

§ *Crystal data for 1*: solv: C₄₈H₈₀B₄Cu₄S₁₂, *M* = 1339.30, monoclinic, space group *P*2₁/*n*, *a* = 20.433(2), *b* = 9.9551(10), *c* = 32.902(4), β = 94.137(8), *U* = 6675.1(12) Å³, *Z* = 4. Of 10937 reflections collected (Mo-Kα, 2 ≤ 2θ ≤ 22.5°, 238 K), 8738 were independent and 4773 [*F* > 4.0σ(*F*)] were observed. Attempts to model five peaks in the difference map, located away from the compound molecule, as a chemically recognizable solvent molecule were unsuccessful. These apparent solvent atoms were assigned carbon atom identities. Two sulfur atoms, S(6) and S(8), were disordered over two positions with an 80 : 20 distribution. The structure was solved by direct methods and refined anisotropically to *R*(*F*) = 0.0584 and *R*_w(*F*²) = 0.1181 with a GOF = 1.007.

For **2**: C₃₀H₃₅B₃CuPS₃, *M* = 597.08, monoclinic, space group *P*2₁/*n*, *a* = 9.034(2), *b* = 20.108(2), *c* = 16.810(3), β = 99.24(2), *U* = 3014.1(9) Å³, *Z* = 4. Of 10271 reflections collected (Mo-Kα, 2 ≤ 2θ ≤ 30°, 298 K), 8106 were independent and 4265 [*F* > 4.0σ(*f*)] were observed. The sulfur atoms were disordered in two positions with a 90 : 10 distribution. The structure was solved by direct methods and refined anisotropically to *R*(*F*) = 0.0491 and *R*_w(*F*²) = 0.1293 with a GOF = 0.900.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/41.

¶ The ferrocene–ferrocenium couple was used as the internal standard (CH₂Cl₂, 0.48 V vs. Ag–AgCl, Δ*E*_p = 0.111 V, *i*_{pc}/*i*_{pa}^{−1} = 1.0, 27 °C).

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