

# Tetrameric thienylcopper and pentanuclear thienylcuprate

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## Abstract

The reaction between 2-bromothiophene and magnesium with subsequent addition of copper(I) chloride in tetrahydrofuran followed by dioxane yields thienylcopper,  $[\text{Cu}_4(\text{C}_4\text{H}_3\text{S})_4]$  (**1**). Without the addition of dioxane, magnesium thienylcuprate(I),  $[\text{Mg}(\text{THF})_6][\text{Cu}_5(\text{C}_4\text{H}_3\text{S})_6]_2$  (**2**) is formed. Both copper(I) complexes are oligomeric and are bridged by the thienyl ligands solely through carbon donors, thus lacking Cu–S bonds. The former compound, **1**, is tetranuclear with a square-planar copper core and Cu–Cu distances of 2.453(3) and 2.507(3) Å, and 2.464(2) and 2.489(2) Å within the two crystallographically independent molecules, respectively; there is a weak Cu⋯S interaction of 3.118(5) Å between these two molecules. The anion of **2** is a *closo* trigonal bipyramidal cluster of copper atoms in which the (ax)–(eq) edges are bridged by the thienyl ligands. Thus the Cu(ax)–Cu(eq) distances bridged by carbon are short, 2.497(5) and 2.503(5) Å, indicative of three-centre Cu–C–Cu two-electron bonds, whereas the Cu(eq)⋯Cu(eq) and Cu(ax)⋯Cu(ax) distances are considerably longer at 3.135(7) and 3.423(8) Å, respectively. The lack of participation of sulfur in bonding within the  $[\text{Cu}_5(\text{C}_4\text{H}_3\text{S})_6]^-$  cluster is discussed. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Thienylcopper; Thienylcuprate; X-ray crystal structure determination

## 1. Introduction

Despite much interest in homoleptic arylcopper(I) clusters, few of these have been isolated and fully characterized in the solid state. Thus, as far as neutral, unsolvated species are concerned, the structures of only seven have so far been documented, namely mesitylcopper(I), which is known to have a pentagonal core [1], but which has recently also been isolated in tetrameric form with a square-planar core [2], (2,4,6-triisopropylphenyl)copper [3], *o*-vinylphenylcopper [4] and pentamethylphenylcopper [5], all of which also have square planar copper(I) cores. Recently, trimeric  $[\text{CuC}_6\text{H}_3\text{Ph}_2(2,6)]_3$ , Ph = phenyl, and dimeric  $[\text{CuC}_6\text{H}_3\text{Mes}_2(2,6)]_2$ , Mes = mesityl, have been reported [6]. Anionic arylcopper species isolated include monomeric  $[\text{CuMes}_2]^-$  [7],  $[\text{CuPh}_2]^-$  [8] and the  $[\text{Cu}_3\text{Ph}_6]^-$  cluster, whose structure has been determined in both the  $[\text{Li}(\text{THF})_4]^+$  and  $[\text{Li}(\text{PMDTA})(\text{THF})]^+$  salts (PMDTA = pentamethyldiethylenetriamine) [9], and also more

recently in connection with the synthesis and characterization of the  $[\text{Cu}_3\text{Ph}_2(\text{PMDTA})_2]^+$  cation [10]. Phenylcopper(I) has been isolated as the dimethylsulfide solvate and in this form has a square-planar tetranuclear copper(I) core [11]. In DMS solution, however, phenylcopper would appear to be an equilibrium mixture of  $(\text{CuPh})_3$  and  $(\text{CuPh})_4$  [12]. The structure of unsolvated phenylcopper in the solid state is as yet unknown, although it is generally assumed to be polymeric.

Coupling of 2-thienylcopper, an aromatic heterocyclic analogue of phenylcopper, with halogenoarenes has been demonstrated to be an effective organometallic extension [13] of the classical Ullmann biaryl synthesis. More recently, both lithium methyl(2-thienyl)cuprate and 2-thienylcopper have been shown to be effective in the promotion of conjugate addition to  $\alpha,\beta$ -unsaturated carbonyl compounds [14]. Moreover, lithium 2-thienylcyanocuprate has been found to be an excellent precursor for mixed organocuprates [15]. 2-Thienylcopper, itself, is insoluble in most organic solvents, which has been interpreted as indicating the presence of a polymeric structure [13]. Although it would be possible to envisage a thienylcopper polymer

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without copper(I)–sulfur interactions, the existence of a Cu–S bond between copper(I) and the uncharged sulfur donor of an adjacent thienyl ligand has been debated, owing to the number of such interactions that have been documented, albeit with stronger Lewis bases. Such examples include the tetranuclear copper(I) complex between mesitylcopper and tetrahydrothiophene [1] and adducts between dimethylsulfide and copper(I) alkyls [16] and copper(I) aryls [17].

When the sulfur atom bears a negative charge, as in a thiolate, numerous compounds tailored for specific purposes can be prepared, as demonstrated by the work of van Koten and co-workers [18]. The structural chemistry and reactivity, and catalytic activity of copper(I) arenethiolates, in particular, has consequently attracted much attention [18] and thiolate complexes of copper(I), lithium, and magnesium are the subject of a recent review [19].

Against this background, our interest was to prepare thienylcopper and to determine its crystal struc-

ture. We report here the preparation and structural characterization of thienylcopper(I), and also of the thienylcuprate(I) anion, demonstrating both to be oligomeric rather than polymeric.

## 2. Results and discussion

Two synthetic routes were explored: the reaction between 2-bromothiophene and magnesium with subsequent addition of an equimolar amount of copper(I) chloride, and the reaction between thienyllithium, prepared from butyllithium and thiophene, and copper(I) chloride [13], THF being used as solvent in both cases. Colourless, cubic-shaped crystals of  $[\text{Cu}_4(\text{C}_4\text{H}_3\text{S})_4] \cdot 0.5\text{THF}$  (**1**) were obtained by the first synthetic route, following the addition of dioxane, whereas attempts to obtain single crystals by the second preparative method [13] failed. Without the addition of dioxane, the first synthetic route yielded colourless cubes of  $[\text{Mg}(\text{OC}_4\text{H}_8)_6][\text{Cu}_5(\text{C}_4\text{H}_3\text{S})_6]_2$  (**2**). Both compounds are extremely labile: **1** decomposes immediately on exposure to the atmosphere but can be stored in the mother-liquor at 4°C for less than 24 h, and for 4–5 days at –18°C; **2** is stable under argon, and in the mother-liquor but turns deep red and decomposes after a few seconds of exposure to the atmosphere.

As is seen from Fig. 1, neutral thienylcopper is tetrameric with a square planar  $\text{Cu}_4$  core, there being two crystallographically independent  $[\text{Cu}_4(\text{C}_4\text{H}_3\text{S})_4]$  molecules in the unit cell of **1**. The core of molecule 2, i.e. that comprising Cu(3) and Cu(4) is closer to that of a regular square plane than that of molecule 1 (cf. Table 1). In each of these molecules one crystallographically independent thienyl ligand exhibits orientational disorder. The major crystallographic difference between the two  $[\text{Cu}_4(\text{C}_4\text{H}_3\text{S})_4]$  molecules is that, in molecule 1, the sulfur atoms (or for the disordered ring the major component of sulfur) of the adjacent, non-symmetry related thienyl ligands are displaced from the copper square plane in the same direction, whereas in molecule 2, the reverse situation occurs. However, chemically molecules 1 and 2 are equivalent since both tetramers can be described by the *cis* isomer in Fig. 2. All four possible isomers, for a  $\text{Cu}_4\text{R}_4$  square-planar core with non-symmetrically substituted aryl ligands, are shown in Fig. 2 and it is conceivable that the crystallographic disorder displayed by **1** originates from isomeric mixtures. It has been reported [20] that 2-methylphenylcopper exhibits analogous isomerism in solution and that interconversion is rapid at ambient temperature in toluene. The edges of the copper cores, 2.453(3) and 2.507(3) Å for molecule 1 and 2.464(2) and 2.489(2) Å for molecule 2, are of comparable magnitude to those in other

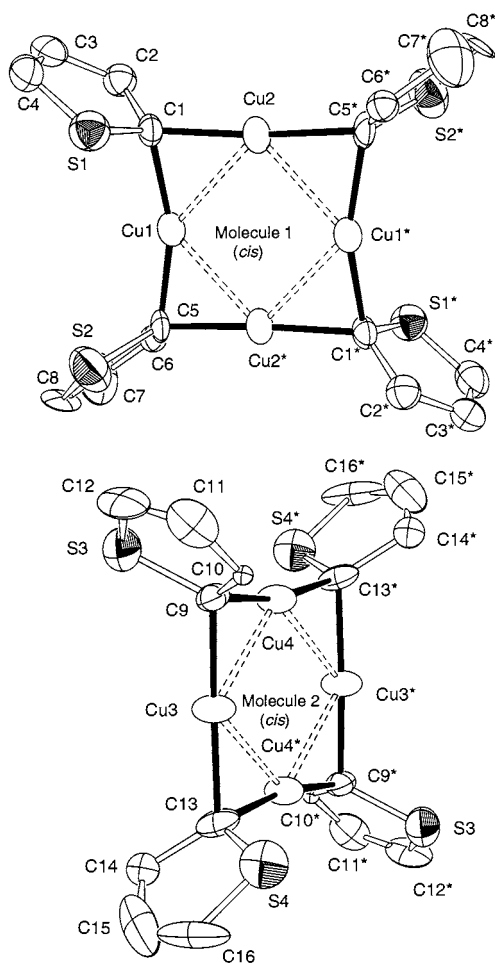


Fig. 1. The two crystallographically independent molecules of  $[\text{Cu}_4(\text{C}_4\text{H}_3\text{S})_4]$  in **1**, showing the crystallographic numbering. Only one of the two possible orientations of the disordered thienyl group in each molecule is shown. Thermal ellipsoids enclose 50% probability.

Table 1  
Selected interatomic distances (Å) and interatomic angles (°) for  
[Cu<sub>4</sub>(C<sub>4</sub>H<sub>3</sub>S<sub>4</sub>)]·0.5THF<sup>a</sup>

Molecule 1		Molecule 2	
<i>Interatomic distances</i>			
Cu(1)–Cu(2)	2.507(3)	Cu(3)–Cu(4)	2.464(2)
Cu(1)–Cu(2 <sup>i</sup> )	2.453(3)	Cu(3)–Cu(4 <sup>ii</sup> )	2.489(2)
Cu(1)–C(1)	1.97(1)	Cu(3)–C(9)	1.98(1)
Cu(2)–C(1)	1.95(1)	Cu(4)–C(9)	1.95(1)
Cu(1)–C(5)	1.99(1)	Cu(3)–C(13)	1.98(1)
Cu(2 <sup>i</sup> )–C(5)	2.00(1)	Cu(4 <sup>ii</sup> )–C(13)	1.96(1)
Cu(1)···Cu(1 <sup>i</sup> )	3.353(4)	Cu(3)···Cu(3 <sup>ii</sup> )	3.516(4)
Cu(2)···Cu(2 <sup>i</sup> )	3.660(4)	Cu(4)···Cu(4 <sup>ii</sup> )	3.488(4)
Cu(2)···Cu(3)	3.187(3)	Cu(2)···S(3)	3.118(5)
<i>Interatomic angles</i>			
Cu(2)–Cu(1)–Cu(2 <sup>i</sup> )	95.00(8)	Cu(4)–Cu(3)–Cu(4 <sup>ii</sup> )	89.51(8)
Cu(1)–Cu(2)–Cu(1 <sup>i</sup> )	85.00(8)	Cu(3)–Cu(4)–Cu(3 <sup>ii</sup> )	90.49(8)
C(1)–Cu(1)–C(5)	162.8(5)	C(9)–Cu(3)–C(13)	164.8(6)
C(1)–Cu(2)–C(5 <sup>i</sup> )	167.0(6)	C(9)–Cu(4)–C(13 <sup>ii</sup> )	166.9(5)
Cu(1)–C(1)–Cu(2)	79.5(5)	Cu(3)–C(9)–Cu(4)	77.6(5)
Cu(1)–C(5)–Cu(2 <sup>i</sup> )	75.9(5)	Cu(3)–C(13)–Cu(4 <sup>ii</sup> )	78.3(5)

<sup>a</sup> Symmetry code: (i) 2–x, –y, –z; (ii) 1.5–x, –0.5–y, –z; (iii) 1–x, y, 1.5–z.

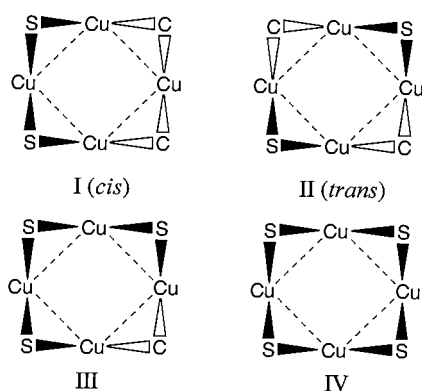


Fig. 2. Possible configurational isomers for a square planar thienylcopper(I) tetramer. Note that the *ipso* carbons of the aryl ligands are omitted for clarity. The triangles only show the orientation of the thienyl ligands and are not meant to indicate any bonding interaction between Cu and S.

square-planar homoleptic copper aryls [2–4] and slightly longer than that, 2.413(2) Å, recently found in pentamethylphenylcopper, the core of which is perfectly square-planar [5].

Unlike (2,4,6-triisopropylphenyl)copper [3] and *o*-vinylphenylcopper [4], in which the Cu<sub>4</sub>C<sub>4</sub> rings are puckered, such that alternate C<sub>ipso</sub> atoms lie 0.4 Å above and below the copper plane, in both [Cu<sub>4</sub>(C<sub>4</sub>H<sub>3</sub>S<sub>4</sub>)] molecules in **1** the C<sub>ipso</sub> atoms lie, within the limits of experimental error, in the plane formed by the four copper atoms. This situation is similar to that found for the tetranuclear form of mesitylcopper [2] and in pen-

tamethylphenylcopper [5], in which the C<sub>ipso</sub> ligand atoms are exactly coplanar with the metal core. In consequence, the C<sub>ipso</sub> ligand atoms in [Cu<sub>4</sub>(C<sub>4</sub>H<sub>3</sub>S<sub>4</sub>)] are relatively symmetrically positioned with respect to the copper(I) atoms to which they are bonded, as is evident from the Cu–C distances and Cu–C<sub>ipso</sub>–Cu angles (cf. Table 1), which are similar to those found for [Cu<sub>4</sub>(Mes)<sub>4</sub>] [2] and [Cu<sub>4</sub>{C<sub>6</sub>(CH<sub>3</sub>)<sub>5</sub>}<sub>4</sub>] [5]. All four crystallographically independent thienyl groups are planar; in molecule 1 the thienyl rings are inclined to the eight-membered Cu<sub>4</sub>C<sub>4</sub> entity at angles of 73 and 86°, whereas in molecule 2 the corresponding angles are 83 and 84°.

There is one intermolecular Cu···S distance, Cu(2)···S(3) = 3.118(5) Å, which is comparable in magnitude to the shortest intramolecular Cu···S contacts within [Cu<sub>4</sub>(C<sub>4</sub>H<sub>3</sub>S<sub>4</sub>)] of 3.000(6), 3.112(6), 3.128(5) and 3.158(5) Å. Although the relatively short Cu(2)···S(3) distance might be interpreted as indicating a very weak intermolecular interaction, it can hardly be seen as indicating a regular Cu–S bond. As in the tetranuclear form of mesitylcopper [2] and in pentamethylphenylcopper [5], the THF solvent molecule in **1** is completely separated from the [Cu<sub>4</sub>(C<sub>4</sub>H<sub>3</sub>S<sub>4</sub>)] molecules.

The crystal-structure determination of **2** showed the compound to be [Mg(OC<sub>4</sub>H<sub>8</sub>)<sub>6</sub>][Cu<sub>5</sub>(C<sub>4</sub>H<sub>3</sub>S<sub>4</sub>)<sub>6</sub>]<sub>2</sub>, the anion of which is a pentanuclear homoleptic thienylcuprate(I) cluster. As is seen from Fig. 3, the pentanuclear [Cu<sub>5</sub>(C<sub>4</sub>H<sub>3</sub>S<sub>4</sub>)<sub>6</sub>]<sup>–</sup> cluster has a trigonal bipyramidal copper(I) core, in which the Cu(eq)–Cu(ax) distances, 2.479(5) and 2.503(5) Å, are very much shorter than the Cu(eq)···Cu(eq) and Cu(ax)···Cu(ax) interactions, which are 3.135(7) and 3.423(8), respectively (cf. Table 2). The core is thus very similar to that of the [Cu<sub>5</sub>Ph<sub>6</sub>]<sup>–</sup> anion [9]. The six thienyl groups bridge the Cu(eq)–Cu(ax)

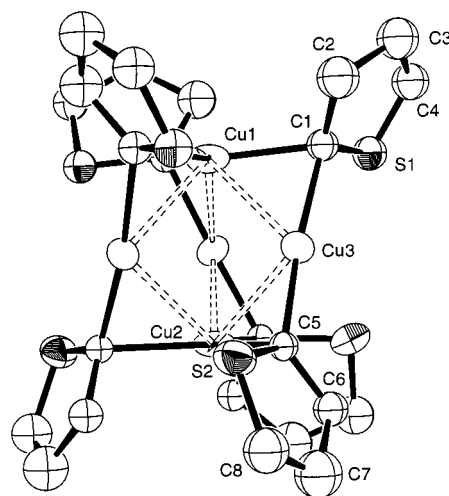


Fig. 3. The thienylcuprate(I) cluster in **2**, showing the crystallographic numbering. Cu···Cu interactions are depicted as dashed bonds and only one of the two possible orientations of the disordered thienyl group is shown. Thermal ellipsoids enclose 50% probability.

Table 2  
Selected interatomic distances (Å) and angles (°) for  
[Mg(OC<sub>4</sub>H<sub>8</sub>)<sub>6</sub>][Cu<sub>5</sub>(C<sub>4</sub>H<sub>3</sub>S)<sub>6</sub>]<sub>2</sub> (2)<sup>a</sup>

Interatomic distances			
Cu(1)–Cu(3)	2.479(5)	Cu(2)–Cu(3)	2.503(5)
Cu(1)–C(1)	2.12(3)	Cu(3)–C(1)	2.05(3)
Cu(2)–C(5)	2.12(2)	Cu(3)–C(5)	1.94(2)
Cu(1)···Cu(2)	3.423(8)	Cu(3)···Cu(3')	3.135(7)
Interatomic angles			
Cu(3)–Cu(1)–Cu(3')	78.4(2)	Cu(3)–Cu(2)–Cu(3')	77.5(2)
Cu(1)–Cu(6,7(3)–Cu(2)	86.8(2)	C(1)–Cu(1)–C(1')	119.4(2)
C(5)–Cu(2)–C(5')	120.00(2)	C(1)–Cu(3)–C(5)	173(1)
Cu(1)–C(1)–Cu(3)	72.9(9)	Cu(2)–C(5)–Cu(3)	76.2(9)

<sup>a</sup> Symmetry code: (i): 1 – y, 1 + x – y, z.

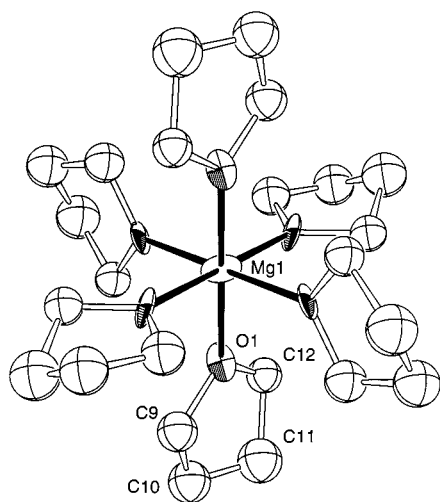


Fig. 4. The [Mg(THF)<sub>6</sub>]<sup>2+</sup> cation in **2**, showing the crystallographic numbering. Thermal ellipsoids enclose 50% probability.

edges of the trigonal bipyramid, through the carbon atoms adjacent to sulfur. The edge-bridging by the ligands is somewhat distorted towards face-capping of the trigonal bipyramid, i.e. the six carbon donor atoms are distorted from a trigonal prism towards an octahedron, probably owing to steric hindrance. There is no evidence of any bonding interaction between copper and sulfur, the shortest Cu···S distances being 3.08(1), 3.181(9), 3.255(9) and 3.26(1) Å, i.e. closely similar to the shortest intramolecular Cu···S distances in **1**.

The apical copper centres Cu(1) and Cu(2) are situated on the three-fold axis and have approximate trigonal planar coordination geometry. Thus Cu(1) is displaced 0.16 Å from the plane through C(1), C(1<sup>i</sup>) and C(1<sup>ii</sup>) (symmetry code: (i): 1 – y, 1 + x – y, z; (ii): –x + y, 1 – x, z], whereas Cu(2) is almost exactly coplanar with C(5), C(5<sup>i</sup>) and C(5<sup>ii</sup>) resulting in a C–Cu–C bond angle of 120° (cf. Fig. 1). The three equatorial copper atoms, Cu(3), are approximately lin-

early coordinated (173(1)°) by C(1) and C(5), and the bridging thienyl groups are perpendicular (both 99.8°) to the relevant Cu–C–Cu planes. The [Cu<sub>5</sub>(thienyl)<sub>6</sub>]<sup>–</sup> cluster is thus very similar to its [Cu<sub>5</sub>(Ph)<sub>6</sub>]<sup>–</sup> counterpart [9].

In both **1** and **2** the Cu–Cu distances bridged by the thienyl ligands are short — of the order of 2.4 Å — and consistent with the presence of three-centre two-electron Cu–C–Cu bonds [21]. A question often debated in connection with Cu clusters is the existence of Cu–Cu bonding [22]. Since the thienyl-bridged Cu–Cu lengths in the present clusters are of the same magnitude as the shortest Cu–Cu distances determined in [Cu<sub>10</sub>O<sub>2</sub>(Mes)<sub>6</sub>], viz. 2.376(8), 2.414(7) and 2.439(6) Å, for which bonding Cu–Cu interactions have been shown to exist [23], it seems likely that bonding Cu–Cu interactions can also be invoked here. Further support for this viewpoint is provided by recent calculations on tetranuclear and pentanuclear copper(I) clusters with bridging aryl groups, which provide clear evidence for the presence of Cu–Cu bonds [24]. In [Cu<sub>5</sub>(thienyl)<sub>6</sub>]<sup>–</sup>, as in [Cu<sub>5</sub>(Ph)<sub>6</sub>]<sup>–</sup> [9], the longer Cu(eq)···Cu(eq) and Cu(ax)···Cu(ax) interactions are probably essentially non-bonding.

It is also possible to view the [Cu<sub>5</sub>(thienyl)<sub>6</sub>]<sup>–</sup> anion as a cage of five copper(I) centres, to which 12 bonding electrons are contributed by the carbon donors of the six thienyl ligands, thus resulting in a *closo* trigonal bipyramidal cluster. It has been shown that the (ax)–(eq) bonds within such trigonal bipyramidal clusters are appreciably stronger than the (eq)···(eq) or (ax)···(ax) interactions [25]. This is entirely consistent with the ligands bridging the (ax)–(eq) edges. Moreover, this approach would also explain the lack of additional Cu–S interactions, since the number of bonding electrons required for a *closo* trigonal bipyramidal cluster is already met.

It is interesting that it is possible to replace one [26] or both [27] of the axial copper(I) centres in [Cu<sub>5</sub>(Ph)<sub>6</sub>]<sup>–</sup>, by magnesium [26] or lithium [26,27] and retain the overall trigonal bipyramidal cluster geometry, with preservation of the Cu(ax)–Cu(eq) bonding interactions. In **2**, magnesium is not incorporated in the cluster, but is present as the Mg(THF)<sub>6</sub><sup>2+</sup> cation (Fig. 4). This cation is a completely symmetrical octahedron, as in [Mg(THF)<sub>6</sub>][Cu<sub>5</sub>(viph)<sub>2</sub>Br<sub>4</sub>]<sub>2</sub>·THF, (viph = *o*-vinylphenyl) [4], and not axially distorted as in [Mg(THF)<sub>6</sub>]-[MoOCl<sub>4</sub>(THF)<sub>2</sub>]<sub>2</sub> [28]. Moreover the Mg–O bond length, 2.04(2) Å, in [Mg(THF)<sub>6</sub>][Cu<sub>5</sub>(C<sub>4</sub>H<sub>3</sub>S)<sub>6</sub>]<sub>2</sub> is identical to that found in [Mg(THF)<sub>6</sub>][Cu<sub>5</sub>(viph)<sub>2</sub>Br<sub>4</sub>]<sub>2</sub>·THF [4].

In conclusion, the present study shows that, contrary to previous belief, thienylcopper is not polymeric. Rather it is a tetrameric species, with a square-planar core, exhibiting the short Cu–Cu distances typically associated with three-centre two-electron Cu–C–Cu bonds. The thienylcuprate(I) anion is also oligomeric and very similar to the phenyl analogue: [Cu<sub>5</sub>(Ph)<sub>6</sub>]<sup>–</sup>

[9,10]. Calculations on phenyl derivatives of copper demonstrate that square-planar and pentagonal copper cores are energetically equally favourable [24]. Experimental support for this viewpoint has recently been provided by an investigation of the delicate balance between pentameric and tetrameric mesitylcopper species in solution [2]. Although the solid-state structure of unsolvated phenylcopper is as yet unknown, the wealth of evidence now available on related species suggests that it can be isolated as a discrete tetramer.

### 3. Experimental

#### 3.1. Synthesis and spectroscopy

##### 3.1.1. General data

All operations were carried out under argon using low-temperature methodology [29] or standard Schlenk techniques (centrifugation was preferred to filtration). Solvents were distilled under argon from sodium–benzophenone immediately prior to use. Copper(I) chloride was purified according to literature methods [30]. Commercial 2-bromothiophene was degassed and used without further purification. NMR spectra were recorded on a Varian XL 400 spectrometer with a measuring frequency of 400 MHz  $^1\text{H}$  in THF- $d_8$ . The infrared spectrum of **2** was recorded on a Mattson Polaris spectrometer, using Nujol mulls, NaCl windows, with a resolution of  $2\text{ cm}^{-1}$  and 10–100 scans.

##### 3.1.2. Preparation of $[\text{Cu}_4(\text{C}_4\text{H}_3\text{S})_4]\cdot 0.5\text{THF}$ (**1**)

2-Bromothiophene (1.63 g, 10.0 mmol) was slowly added to a slight excess of magnesium (0.27 g, 11.0 mmol) in 20 ml THF. The reaction started immediately and was allowed to proceed under stirring for 12 h. After centrifugation, the solution was diluted with 20 ml THF and copper(I) chloride (0.99 g, 10.0 mmol) was added at  $0^\circ\text{C}$ . The solution was kept at  $0^\circ\text{C}$  for 1 h, and then allowed to warm gradually to room temperature (r.t.), whereupon a yellow solution and white precipitate were formed. Dioxane (7 ml) was slowly added to the mixture resulting in a red solution and a brown precipitate. After centrifugation of this mixture, colourless cubic-shaped crystals of  $[\text{Cu}_4(\text{C}_4\text{H}_3\text{S})_4]\cdot 0.5\text{THF}$  were deposited at  $4^\circ\text{C}$  from the red solution. The crystals decompose immediately on exposure to the atmosphere but can be stored, without extensive decomposition, in the mother-liquor at  $4^\circ\text{C}$  for approximately 24 h, and for 4–5 days at  $-18^\circ\text{C}$ . Crystals of **1** are sparingly soluble in THF.  $^1\text{H}$ -NMR (THF- $d_8$ ,  $20^\circ\text{C}$ )  $\delta$  7.02 (dd),  $\delta$  7.36 (d), 7.68(d). Many attempts were made to record the IR spectrum, both at ambient temperature and at temperatures of ca.  $-100^\circ\text{C}$  of **1**. These were, however, not successful, owing to decomposition of the sample.

##### 3.1.3. Preparation of $[\text{Mg}(\text{THF})_6][\text{Cu}_5(\text{C}_4\text{H}_3\text{S})_6]_2$ (**2**)

2-Bromothiophene (1.63 g; 10.0 mmol) was slowly added to a slight excess of magnesium (0.27 g; 11.0 mmol) in 20 ml THF, and the resulting mixture was stirred and cooled for 12 h. After centrifuging of the mixture, the brown solution was removed, diluted with 20 ml THF and cooled to  $0^\circ\text{C}$  whereupon copper(I) chloride (0.99 g; 10.0 mmol) was added. The reaction was allowed to proceed at  $0^\circ\text{C}$  for 1 h. On gradual heating to r.t. a yellow solution and a white precipitate were formed. The mixture was centrifuged and the solution was cooled to  $4^\circ\text{C}$  whereupon colourless crystals were deposited in approximately 25% yield; these crystals turn red immediately on exposure to the atmosphere. Crystals of **2** are fairly soluble in THF.  $^1\text{H}$ -NMR (THF- $d_8$ ,  $20^\circ\text{C}$ ):  $\delta$  6.97 (d),  $\delta$  7.20 (s), 7.66(d). IR ( $\text{cm}^{-1}$ , Nujol mull, NaCl windows): 1343 w, 1303 w, 1189 m, 1074 w, 1019 s, 960 w, 918 m, 869 s, 828 s, 720 s, 712 s, 675 w.

#### 3.2. X-ray crystallography

##### 3.2.1. General data

Crystal and experimental data are summarised in Table 3. Crystals were isolated, selected and mounted using low-temperature methodology [29] under argon at  $-150^\circ\text{C}$ , and transferred in Lindemann capillaries under liquid nitrogen to a Rigaku AFC6R diffractometer. Diffracted intensities were measured at  $-110^\circ\text{C}$ , using graphite-monochromated Mo- $K_\alpha$  ( $\lambda = 0.71073\text{ \AA}$ ) radiation from a RU200 rotating anode source operated at 9 kW (50 kV, 180 mA). The  $\omega/2\theta$  scan mode was employed and stationary background counts were recorded on each side of the reflection, the ratio of peak counting time versus background counting time being 2:1. Weak reflections ( $I < 10.0\sigma(I)$ ) were rescanned up to seven times and counts accumulated to improve counting statistics. The intensities of three reflections monitored regularly after measurement of 150 reflections indicated crystal stability during data collection. Correction was made for Lorentz and polarization effects. For **1**, an empirical correction based on azimuthal scans for several reflections was made for the effects of absorption. However, for **2**, it was not possible to obtain a more satisfactory structural model from empirically corrected data, and no correction was made for the effects of absorption.

The structures were solved by direct methods (MITHRIL) [31]. Where possible, hydrogen atoms were introduced in calculated positions. Reflections were weighted according to  $w = [\sigma^2(F_o)]^{-1}$ . All calculations were carried out with the TEXSAN [32] program package. Atomic scattering factors and anomalous dispersion correction factors were taken from Ref. [33]. Structural illustrations were drawn with ORTEP3 for Windows [34]. Crystallographic data for the structural

Table 3  
Crystallographic data for  $[\text{Cu}_4(\text{C}_4\text{H}_3\text{S})_4] \cdot 0.5\text{THF}$  (**1**) and  $[\text{Mg}(\text{OC}_4\text{H}_8)_6][\text{Cu}_5(\text{C}_4\text{H}_3\text{S})_6]_2$  (**2**)

	$[\text{Cu}_4(\text{C}_4\text{H}_3\text{S})_4] \cdot 0.5\text{THF}$ ( <b>1</b> )	$[\text{Mg}(\text{OC}_4\text{H}_8)_6][\text{Cu}_5(\text{C}_4\text{H}_3\text{S})_6]_2$ ( <b>2</b> )
Formula	$\text{C}_{18}\text{H}_{16}\text{Cu}_4\text{O}_{0.5}\text{S}_4$	$\text{C}_{72}\text{H}_{84}\text{Cu}_{10}\text{MgO}_6\text{S}_{12}$
Formula weight	622.8	2089.9
Crystal system	Monoclinic	Trigonal
Space group	$C2/c$ (No. 15)	$R\bar{3}c$ (hex) (No. 167)
$a$ (Å)	21.389(3)	15.033(6)
$b$ (Å)	9.976(3)	
$c$ (Å)	19.647(4)	63.820(9)
$\beta$ (°)	94.42(1)	
$V$ (Å <sup>3</sup> )	4179(1)	12490(6)
$Z$	8	6
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.98	1.67
Radiation Mo-K $\alpha$ (Å)	0.71073	0.71073
$\mu$ (cm <sup>-1</sup> )	44.2	28.5
$T$ (°C)	-110	-110
Absorption correction	Empirical (psi-scans)	None
$2\theta_{\text{max}}$ (°)	50	50
No. unique reflections	3914	2760
No. observed reflections	1807	734
No. parameters refined	210	88
$R$	0.052	0.078
$R_w$	0.044	0.112
Max. residual electron density (e Å <sup>-3</sup> )	0.85	1.53
Min. residual electron density (e Å <sup>-3</sup> )	-0.72	-0.87

analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 127012 for compound **1** and no. 127013 for compound **2**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

### 3.2.2. $[\text{Cu}_4(\text{C}_4\text{H}_3\text{S})_4] \cdot 0.5\text{THF}$ (**1**)

Diffraction intensities from an orange crystal, with approximate dimensions  $0.25 \times 0.15 \times 0.10$  mm, were measured for  $5 < 2\theta < 50^\circ$ , using an  $\omega$  scan rate of  $16^\circ \text{ min}^{-1}$  and a scan width of  $(1.21 + 0.30 \tan \theta)^\circ$ . Of the 3914 unique reflections measured, 1807 had  $I > 3.0\sigma(I)$  and were considered observed. Cell constants were obtained by least-squares refinement from the setting angles of 25 reflections in the range  $25.0 < 2\theta < 32.7^\circ$ .

Two of the thienyl rings was found to be disordered and the disorder was modelled by refining S(1) and C(2), both with occupancy 0.75 and resetting C(2a) and S(1a), both with occupancy 0.25, to the positions of the former, respectively. Similarly, for the second disordered ring S(4) and C(14), both with occupancy 0.75,

were refined and C(14a) and S(4a) reset. Full-matrix least-squares refinement, including anisotropic thermal parameters for the ordered atoms, and isotropic thermal parameters for the above-mentioned disordered atoms, as well as for C(6) and C(10), gave a final  $R = 0.052$  ( $R_w = 0.044$ ) for 210 parameters and 1807 observed reflections. C(6) and C(10) were refined with isotropic thermal parameters since refinement of anisotropic displacement parameters yielded non-positive definite values, indicating slight disorder associated also with these rings. The hydrogen atoms of the THF molecule and of the ordered thienyl rings were included as a fixed contribution. The maximum and minimum values in the final difference map were 0.85 and  $-0.72 \text{ e \AA}^{-3}$ , respectively.

### 3.2.3. $[\text{Mg}(\text{THF})_6][\text{Cu}_5(\text{C}_4\text{H}_3\text{S})_6]_2$ (**2**)

Diffraction intensities from a yellow cube, with approximate dimensions  $0.10 \times 0.10 \times 0.10$  mm, were measured for  $5 < 2\theta < 50^\circ$  using an  $\omega$  scan rate of  $8^\circ \text{ min}^{-1}$  and a scan width of  $(0.42 + 0.30 \tan \theta)^\circ$ . Of the 2760 unique reflections measured, 734 had  $I > 3.0\sigma(I)$  and were considered observed. Cell constants were obtained by least-squares refinement from the setting angles of 20 reflections in the range  $11.4 < 2\theta < 16.0^\circ$ .

One of the thienyl rings was found to be disordered and the disorder was modelled by refining S(1) and C(2), both with occupancy 0.6667, and resetting C(2a) and S(1a), both with occupancy 0.3333, to the positions of the former, respectively. Full-matrix least-squares refinement, including anisotropic thermal parameters for Cu(1), Cu(2), Cu(3), S(2), Mg and O, and isotropic thermal parameters for the remaining non-hydrogen atoms, and with the hydrogen atoms of the THF groups and the ordered thienyl group as a fixed contribution in calculated positions ( $\text{C-H} = 0.95 \text{ \AA}$ ), gave a final  $R = 0.078$  ( $R_w = 0.112$ ) for 88 parameters and 734 observed reflections.

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