

Synthesis and Structural Characterization of $[\text{Cu}(\text{SC}_6\text{H}_4\text{-}o\text{-SiMe}_3)]_{12}$, an Unusual Example of a 'Paddle-Wheel' Dodecametallic Thiolate Cluster

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Treatment of $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ with the sterically-hindered thiolate ligand 2-(trimethylsilyl)benzenethiol, $\text{HSC}_6\text{H}_4\text{-}o\text{-SiMe}_3$, affords red-orange crystals of $[\text{Cu}(\text{SC}_6\text{H}_4\text{-}o\text{-SiMe}_3)]_{12}$, a dodecametallic thiolate cluster with a 'paddle-wheel' $\text{C}_{12}\text{S}_{12}$ core.

The current intense interest in metal thiolate co-ordination chemistry¹ reflects both their biological significance and the structural diversity associated with this fundamental metal-ligand type. The tendency of Cu^{I} and Ag^{I} to form cage structures in $[\text{M}_x(\text{SR})_y]^{n-}$ complexes, rather than mono-

nuclear or non-molecular complexes, has been documented.²⁻⁷ Furthermore, manipulation of the thiolate substituent R has been shown to effect steric and electronic control of aggregation.^{3,4}

As part of our continuing investigations of the influence of

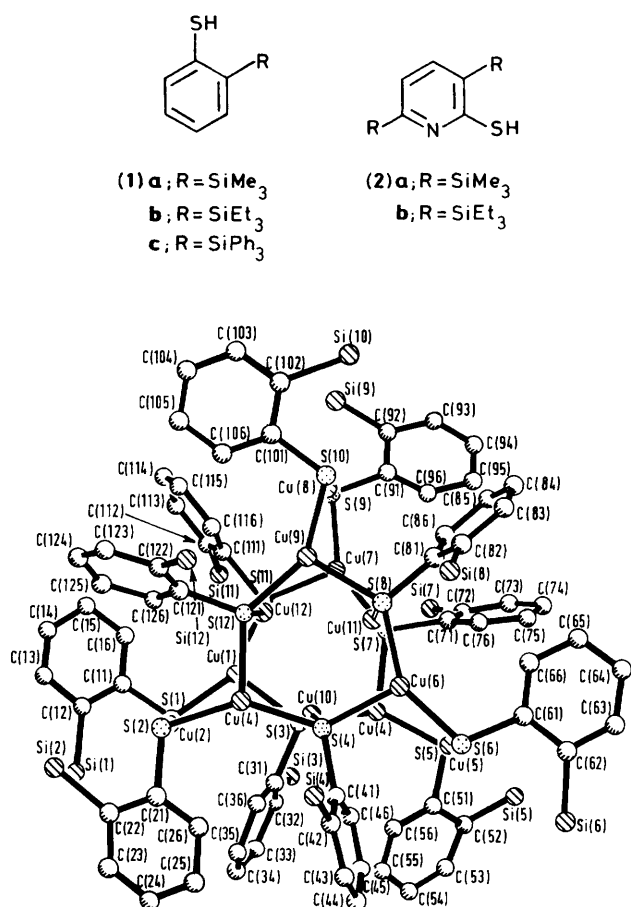


Figure 1. ORTEP view of the structure of $[\text{Cu}(\text{SC}_6\text{H}_4\text{-}o\text{-SiMe}_3)_{12}]$ showing the atom-labelling scheme. Methyl groups have been omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Cu(10)–Cu(3), Cu(10)–Cu(4), Cu(11)–Cu(6), Cu(11)–Cu(7), Cu(12)–Cu(1), Cu(12)–Cu(9) 2.745(11) (av.); Cu(2)–Cu(3), Cu(2)–Cu(1), Cu(8)–Cu(7), Cu(8)–Cu(9), Cu(5)–Cu(4), Cu(5)–Cu(6) 2.934(11) (av.); Cu(10)–Cu(1), Cu(10)–Cu(6), Cu(11)–Cu(4), Cu(11)–Cu(9), Cu(12)–Cu(7), Cu(12)–Cu(9) 3.170(11) (av.); Cu(10)–Cu(11), Cu(10)–Cu(12) 3.077(7) (av.); digonal Cu–doubly bridging thiolate S [e.g. Cu(2)–S(1)] 2.160(9) (av.); digonal Cu–triply bridging thiolate S [e.g. Cu(10)–S(4)] 2.200(9) (av.); trigonal planar Cu–doubly bridging thiolate S [e.g. Cu(3)–S(2)] 2.210(10) (av.); trigonal planar Cu–triply bridging thiolate S [e.g. Cu(1)–S(3)] 2.253(10) (av.) and 2.309(10) (av.), alternating within each Cu_3S_3 central ring; S–Cu–S (digonal Cu) 174.7(5) (av.) [Cu(2), Cu(5), Cu(8) sites] and 163.6(6) (av.) [Cu(10), Cu(11), Cu(12) sites]; S–Cu–S (trigonal planar Cu) 107.5(9) (av.) and 143.6(8) (av.).

ligand steric demands on the degree of aggregation of homoleptic metal thiolate complexes, we have prepared a new class of sterically-hindered thiolate ligands, of which (1) and (2) are representative examples. Herein, we report the synthesis and structure of the Cu^{I} complex with (1a), $[\text{Cu}(\text{SC}_6\text{H}_4\text{-}o\text{-SiMe}_3)_{12}]$, a polycyclic, dodecanuclear cage complex exhibiting both linear and trigonal planar Cu–thiolate co-ordination.

The 2-(trimethylsilyl)benzenethiol ligand (1a) was prepared by the treatment of 2-(phenylthio)tetrahydrofuran with *t*-butyl-lithium in tetrahydrofuran (THF)–hexamethylphosphoramide (HMPA), followed by chlorotrimethylsilane and mercuric chloride–hydrogen sulphide. Addition of (1a) to a solution of $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ in methanol under argon

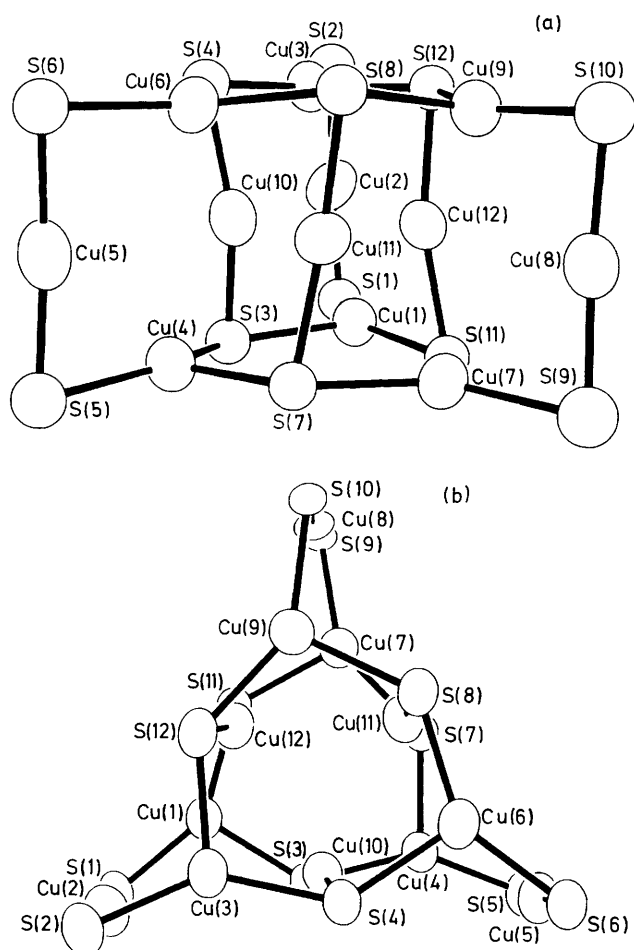


Figure 2. (a) The $\text{C}_{12}\text{S}_{12}$ core viewed normal to the plane of the Cu_3S_3 interior rings. (b) The $\text{Cu}_{12}\text{S}_{12}$ viewed with the normal to the Cu_3S_3 rings in the plane of the page, showing the octanuclear Cu_4S_4 framework of the 'paddle-wheels'.

afforded a yellow-brown solid, which was recrystallized from CH_2Cl_2 –methanol in 47% yield.[†]

The unique molecular geometry of the discrete dodeca-metallic cluster is shown in Figure 1, while Figure 2 presents two views of the $\text{Cu}_{12}\text{S}_{12}$ core. The structure is best described as a molecular 'paddle-wheel'. The central cylinder of the paddle-wheel is constructed from two nearly parallel but staggered (*ca.* 10°) Cu_3S_3 rings, bridged by Cu(10), Cu(11), and Cu(12). The 'paddles' are provided by the exocyclic, bridging $[\text{Cu}(\text{SR})_2]$ groups [Cu(2)–S(1)–S(2), Cu(5)–S(5)–S(6), Cu(8)–S(9)–S(10)]. In a gross geometric sense, the

[†] Satisfactory elemental analyses (C,H) were obtained for $\text{C}_{108}\text{H}_{156}\text{Si}_{12}\text{Cu}_{12}$. ^1H n.m.r. (CD_2Cl_2): δ –0.14 and 0.39 (methyl H from two distinct environments), 6.49–8.28 (complex multiplets, phenyl protons). ^{13}C n.m.r. (CD_2Cl_2): δ –0.031 and 2.179 (methyl C), 124.36–142.43 (phenyl C).

Crystal data: Monoclinic, space group $P2_1/n$, $a = 17.220(2)$, $b = 30.564(4)$, $c = 27.446(3)$ Å, $\beta = 93.58(1)^\circ$, $U = 14416.0(11)$ Å³, $Z = 4$. Solution and refinement based on 5645 reflections with $F_0 \geq 6\sigma(F_0)$ (8436 collected; $+h$, $+k$, $\pm l$ with $2 \leq 2\theta \leq 45^\circ$, Mo- $K\alpha$, $\lambda = 0.71073$ Å) to give $R = 0.064$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

$\text{Cu}_{12}\text{S}_{12}$ array is reminiscent of the molecular geometry of $[\text{2}_3](1,3,5)\text{cyclophane}$.⁸ Alternatively, the structure may be described as an exterior S_6 trigonal prism enclosing an interior S_6 trigonal prism, with digonal and trigonal planar Cu atoms bridging the thiolate centres.

There are three distinct Cu types: the trigonal planar Cu centres in the Cu_3S_3 heterocycles, the digonal Cu atoms bridging the triangular faces of the exterior S_6 trigonal prism, and the interior digonal Cu centres bridging the Cu_3S_3 rings. This variety in Cu co-ordination type is reflected in the significant differences in the Cu–S bond lengths and S–Cu–S bond angles associated with the structure (see Figure 1 caption). Although both linear⁴ and trigonal planar geometries⁷ are known for copper–thiolate clusters, it is unusual to find both types of co-ordination in the same molecule. Although sterically encumbered ligands have been shown to favour linear co-ordination for Cu^{I} ,^{4,5} the structure of $[\text{Cu}(\text{SC}_6\text{H}_4\text{-}o\text{-SiMe}_3)]_{12}$ demonstrates that modification in the substituent geometry or bulk may effect pronounced structural changes. We are currently extending these investigations to related ligand types (**1b,c**) and (**2a,b**) in an effort to tune the steric effects and to elucidate the consequences of substituent variation on the degree of cluster aggregation.

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