Synthesis and Structural Characterization of $[Cu(SC_6H_4\text{-}o\text{-}SiMe_3)]_{12}$, an Unusual Example of a 'Paddle-Wheel' Dodecametallic Thiolate Cluster

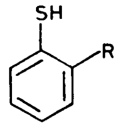
Eric Block,* Michael Gernon, Hyunkyu Kang, Shuncheng Liu, and Jon Zubieta*

Department of Chemistry, State University of New York at Albany, Albany, NY 12222, U.K.

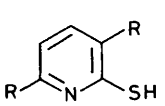
Treatment of $[Cu(MeCN)_4]PF_6$ with the sterically-hindered thiolate ligand 2-(trimethylsilyl)benzenethiol, $HSC_6H_4\text{-}o\text{-}SiMe_3$, affords red-orange crystals of $[Cu(SC_6H_4\text{-}o\text{-}SiMe_3)]_{12}$, a dodecametallic thiolate cluster with a 'paddle-wheel' $C_{12}S_{12}$ core.

The current intense interest in metal thiolate co-ordination chemistry[1] 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 $[M_x(SR)_y]^{n-}$ complexes, rather than mononuclear 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



(1)a; R = $SiMe_3$
b; R = $SiEt_3$
c; R = $SiPh_3$



(2)a; R = $SiMe_3$
b; R = $SiEt_3$

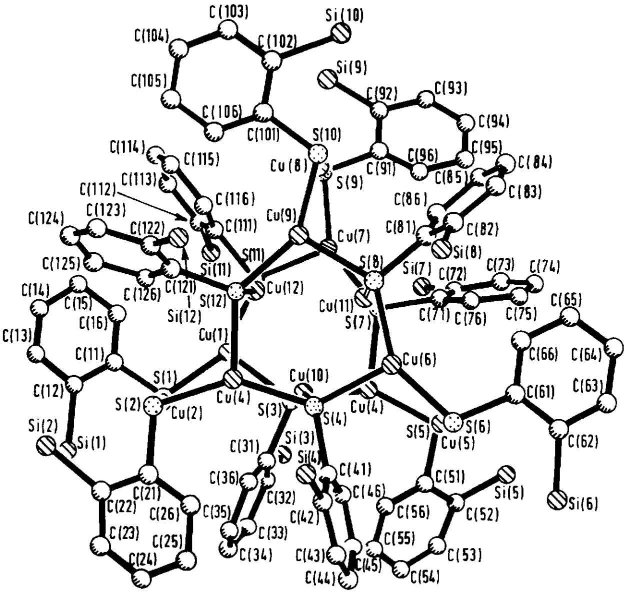


Figure 1. ORTEP view of the structure of $[Cu(SC_6H_4\text{-}o\text{-}SiMe_3)]_{12}$ showing the atom-labelling scheme. Methyl groups have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(10)–Cu(3), Cu(10)–C(4), Cu(11)–Cu(6), Cu(11)–Cu(7), Cu(12)–Cu(1), Cu(12)–Cu(9) 2.745(11) (av.); 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**), $[Cu(SC_6H_4\text{-}o\text{-}SiMe_3)]_{12}$, 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)tetrahydropyran with t-butyl-lithium in tetrahydrofuran (THF)–hexamethylphosphoramide (HMPA), followed by chlorotrimethylsilane and mercuric chloride–hydrogen sulphide. Addition of (**1a**) to a solution of $[Cu(CH_3CN)_4]PF_6$ in methanol under argon afforded a yellow-brown solid, which was recrystallized from CH_2Cl_2–methanol in 47% yield.†

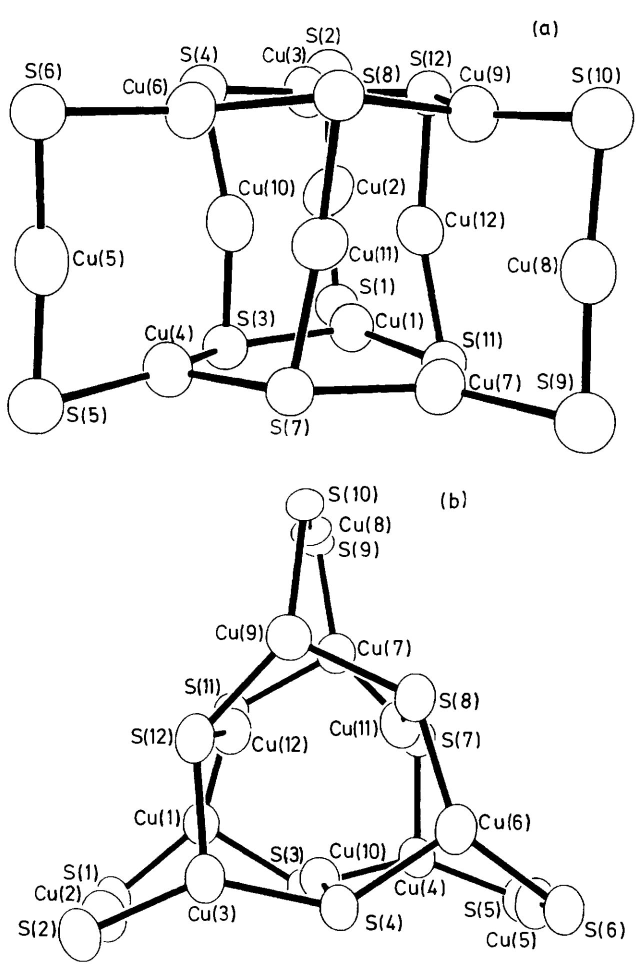


Figure 2. (a) The $C_{12}S_{12}$ core viewed normal to the plane of the Cu_3S_3 interior rings. (b) The $Cu_{12}S_{12}$ viewed with the normal to the Cu_3S_3 rings in the plane of the page, showing the octanuclear Cu_4S_4 framework of the 'paddle-wheels'.

The unique molecular geometry of the discrete dodecametallic cluster is shown in Figure 1, while Figure 2 presents two views of the $Cu_{12}S_{12}$ 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 $[Cu(SR)_2]$ 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 $C_{108}H_{156}Si_{12}Cu_{12}$. ^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, $\beta = 93.58(1)°$, $U = 14416.0(11)$ Å^3, $Z = 4$. Solution and refinement based on 5645 reflections with $F_0 \geqslant 6\sigma(F_0)$ (8436 collected; $+h$, $+k$, $\pm l$ with $2 \leqslant 2\theta \leqslant 45°$, 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.

$Cu_{12}S_{12}$ array is reminiscent of the molecular geometry of $[2_3](1,3,5)$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 linear[4] and trigonal planar geometries[7] 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 $[Cu(SC_6H_4\text{-}o\text{-}SiMe_3)]_{12}$ 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.

This work was supported by a grant (to E. B. and J. Z.) from the National Institutes of Health (Grant GM2256609).

Received, 28th March 1988; Com. 8/01241E

References

1 I. G. Dance, *Polyhedron*, 1986, **5**, 1037; P. G. Blower and J. R. Dilworth, *Coord. Chem. Rev.*, 1987, **76**, 121.
2 P. Gonzalex-Duarte, S. Sola, J. Vives, and X. Solans, *J. Chem. Soc., Chem. Commun.*, 1987, 1641, and references therein.
3 K. Tang, M. Aslam, E. Block, T. Nicholson and J. Zubieta, *Inorg. Chem.*, 1987, **26**, 1488, and references therein.
4 Q. Yang, K. Tang, H. Liao, Y. Han, Z. Chen, and Y. Tang, *J. Chem. Soc., Chem. Commun.*, 1987, 1076.
5 K. L. Tang, Q. C. Yang, J. P. Yang, H. Liao, and Y. Q. Tang, personal communication on the structures of $[CuSCH(SiMe_3)_2]_4$ and $[CuSC(SiMe_3)_3]_3$.
6 G. Henkel, P. Betz, and B. Krebs, *Angew. Chem., Int. Ed. Eng.*, 1987, **26**, 145.
7 J. R. Nicholson, I. L. Abrams, W. Clegg, and C. D. Garner, *Inorg. Chem.*, 1985, **24**, 1092.
8 P. M. Keehn in 'Cyclophanes,' ed. P. M. Keehn and S. M. Rosenfeld, Academic Press, New York, 1983, vol. 1, pp. 69—239; A. W. Hanson, *Cryst. Struct. Commun.*, 1980, **9**, 1243.