Inorganica Chimica Acta, *167* (1990) 147–148

Inorganica Chimica Acta
LETTER

The Crystal and Molecular Structure of a Tetranuclear Copper Thiolate Cluster, $[Cu\{SC_6H_3\text{-}2,6\text{-}(SiMe_3)_2\}]_4$

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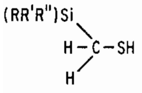
(Received August 28, 1989; revised November 3, 1989)

Metal-thiolate coordination chemistry continues to be of significant interest by virtue of its biological relevance and the structural diversity associated with this fundamental metal–ligand type [1]. The tendency of Cu(I) and Ag(I) to form cage structures in $[M_x(SR)_y]^{n}\bar{n}$ complexes has been firmly established [2–12]. The range of available thiolate ligands can be substantially increased through attachment of single or multiple silyl functions to methanethiol (**1**–**3**) thiophenol (**4** and **5**) and pyridinethiol (**6** and **7**). Such manipulation of the thiolate substituent R will effect steric and electronic control of aggregation [3, 4].



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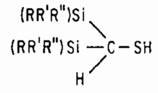

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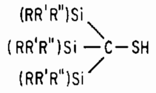

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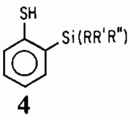

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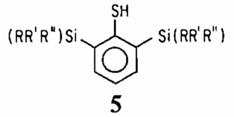

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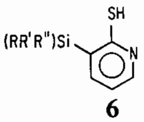

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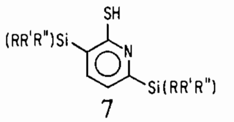

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We have recently described the structure of $[Cu(SC_6H_4\text{-}2\text{-}SiMe_3)]_{12}$ (**8**), a dodecanuclear cage complex with a 'paddlewheel' $Cu_{12}S_{12}$ core [10]. Furthermore, as illustrated in Fig. 1, we have shown that functionalizing the thiolate by introducing a pyridine nitrogen donor in the analogous pyridine-2-thiol-3-$SiMe_3$ ligand resulted in a hexanuclear copper complex $[Cu(SC_5H_3N\text{-}3\text{-}SiMe_3)]_6$ (**9**) which retains the Cu_3S_3 faces of the central core previously described for **8** but exploits the pyridine N-donors to complete the coordination geometry [11]. In an effort to extend these studies on the influence of steric substituents on copper thiolate structures, the Cu(I) complex of **5** was synthesized and structurally characterized.

Addition of **5** to a solution of $[Cu(CH_3CN)_4]PF_6$ in methanol under argon afforded a yellow solid, which was recrystallized from CH_2Cl_2 methanol in 57% yield. The complex $[Cu\{SC_6H_3\text{-}2,6\text{-}(SiMe_3)_2\}]_4$

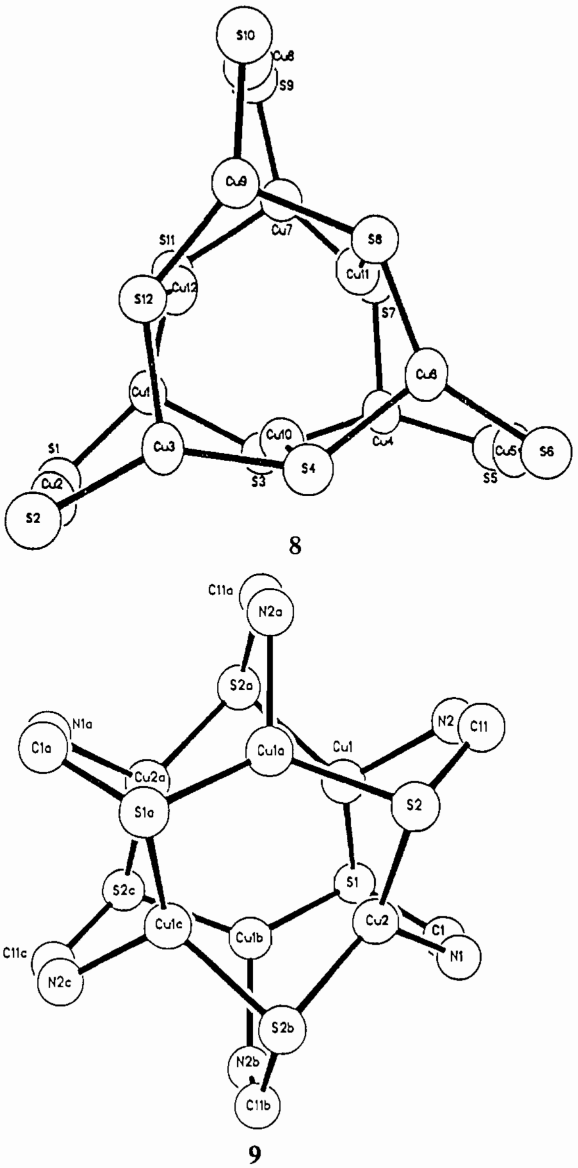

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Fig. 1. Schematic representations of the copper-thiolate sulfur cores of $[Cu(SC_6H_4\text{-}2\text{-}SiMe_3)]_{12}$ and $[Cu(SC_5H_3N\text{-}3\text{-}SiMe_3)]_6$.

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0020-1693/90/$3.50

(10) crystallized in the monoclinic space group $P2_1/c$; $a = 16.965(2)$, $b = 19.096(3)$, $c = 21.987(4)$ Å; $\beta = 95.13(1)°$, $V = 7094.6(10)$ Å^3, $Z = 4$, $D_{calc} = 1.19$ g cm^{-3}. Structure solution and refinement were based on 3614 reflections with $F_o \geqslant 6\sigma(F_o)$ (Mo Kα, λ = 0.71073 Å (8451 total reflections collected) to give final residuals of 0.0981 and 0.0993 for R and R_w, respectively.

The structure of **10** is illustrated in Fig. 2 and selected bond lengths and angles are given in the caption. The structural core is seen to consist of an eight-membered Cu_4S_4 ring, with the aryl groups disposed in an alternating pattern above and below the centroid of the Cu_4S_4 cycle. The Cu_4S_4 unit is distinctly folded about the S2———S4 axis, such that the dihedral angle between the S2–Cu3–S3–Cu4–S4 and S2–Cu2–S1–Cu1–S4 planes is 134.0°. The folded M_4S_4 geometry is similar to that observed for the $[Ag(SR)]_4$ units of the bis-cyclic structures reported for $\{[Ag(SC_6H_4\text{-}o\text{-}SiMe_3)]_4\}_2$ [12] and $\{[AgSCH(SiMe_3)_2]_4\}_2$ [3]. However, in contrast to the silver-thiolate structures, the increased steric bulk of the ligand prevents secondary Cu–S interactions required to expand the Cu coordination sphere and to induce further aggregation.

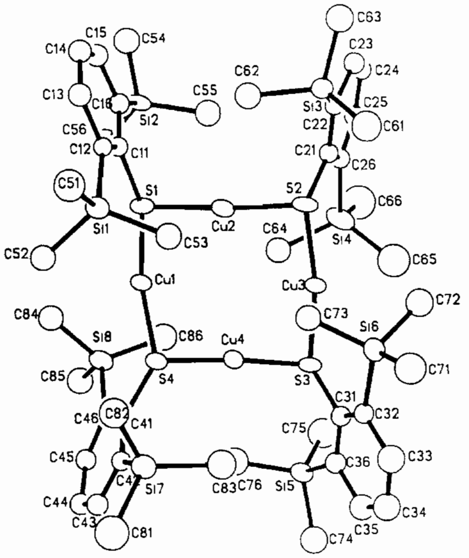

Fig. 2. ORTEP view of the structure of $[Cu(SC_6H_3\text{-}2,6\text{-}SiMe_3)]_4$, showing the atom-labelling scheme. Selected bond lengths (Å) and angles (°): Cu1–S1, 2.134(8); Cu1–S4, 2.150(8); Cu2–Si, 2.154(9); Cu2–S2, 2.150(9); Cu3–S2, 2.153(9); Cu3–S3, 2.150(9); Cu4–S3, 2.164(9); Cu4–S4, 2.145(9); S1–Cu1–S4, 168.9(3); S1–Cu2–S2, 175.4(4); S2–Cu3–S3, 169.7(3); S3–Cu–S4, 174.1(3); Cu1–S1–Cu2, 83.7(3); Cu2–S2–Cu3, 92.3(3); Cu3–S3–Cu4, 82.9(3); Cu1–S4–Cu4, 92.4(3).

A comparison of the structure of **10** with that previously reported for **8** illustrates the dramatic structural consequences of increased steric hindrance of ligand substituents. Whereas **8** exhibits a dodecanuclear core with six trigonal planar CuS_3 sites and six linear CuS_2 sites, the structure of **10** is tetranuclear with exclusively digonally coordinated Cu centers. We are currently extending our structural studies to other members of the class of sterically-hindered thiols **1**–**7** and to their chemistry with Group Ib and IIb elements and with the metals of Groups IIIa–Va.

Acknowledgement

This work was supported by a grant from the National Institute of Health (GM2256610).

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*On the structures of $[CuSCH(SiMe_3)_2]_4$ and $[CuSC(SiMe_3)_3]_3$.