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A Hexanuclear Copper Arylselenolate: Synthesis, Structure and Proposal for its Rearrangement

Dietmar Ohlmann,^a Hans Pritzkow,^b Hansjörg Grützmacher,^{*a} Mitchell Anthamatten^c and Rainer Glaser^{*c}

^a Institut für Anorganische und Analytische Chemie, Albertstraße 21, D-79104 Freiburg, Germany

^b Anorganisch Chemisches Institut der Universität, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

^c Department of Chemistry, University of Missouri-Columbia, Columbia, Missouri 65211, USA

Copper(I) oxide reacts with selenol 2,4,6-Pr₃C₆H₂-SeH in ethanol to give the hexanuclear copper(I) selenolate {Cu[Se(2,4,6-Pr₃C₆H₂)]₆ of **6**, the solid state structure of which consists of a disordered Cu₆ octahedron embedded in an antiprism formed by six selenium centres of the selenolate residues; this leads us to propose an exchange mechanism for the equilibration of all copper positions.

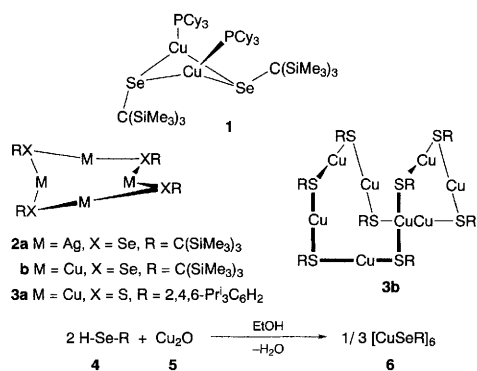
Despite the potential of copper selenolates and tellurolates as precursors for copper selenides and tellurides¹ and as reagents in organic synthesis,² structural information on these compounds remains limited. Recently, Arnold *et al.* determined the structure of the phosphane complexed copper arylselenolate [(PCy₃)CuSeC(SiMe₃)₃]₂ **1** and the silver selenolate Ag[SeC(SiMe₃)₃]₂ **2a** which is a tetramer in the solid state.³ Based on similar IR spectra, the authors concluded that the analogous copper complex Cu[SeC(SiMe₃)₃]₂ **2b** has a comparable structure.

For the preparation of a copper(I) selenolate we chose the readily available selenol 2,4,6-Pr₃C₆H₂-SeH **4**.⁴ Furthermore, the corresponding copper(I) thiolates are well known to exist as μ₂-sulfur bridged tetrameric **3a** and octameric **3b** Cu–S cycles in the solid state.⁵ When selenol **4** is reacted with freshly prepared copper(I) oxide **5** in ethanol (Scheme 1) a coloured reaction mixture results from which {Cu[Se(2,4,6-Pr₃C₆H₂)]₆ **6** precipitates as a greenish-yellow crystalline solid.†

Recrystallisation from *n*-hexane yields bright orange crystals of **6** suitable for a single crystal structure analysis which was performed at a temperature of –65 °C.‡ In contrast to the proposed structure of **2b**, a hexameric copper(I)–selenium Cu₆Se₆ cluster is formed (Fig. 1) rather than a heterocycle with μ₂-bridging selenium centres.

Hexameric copper clusters are well known and have been observed in various copper(I) hydride phosphane complexes, mixed copper(I) aryl alkynes, heterometallics like Cu₆[ReH₇(PPh₃)₂]₄²⁺, copper(I) pyridine thionato complexes and copper(I) iodides.⁶ The refinement in P1 yielded very high anisotropic temperature factors for two copper atoms which are disordered and refined by two split atoms for each of the pairs Cu(2)/Cu(4A) and Cu(3)/Cu(5A) [shown as filled and open circles, Fig. 1(b)]. In order to describe the novel structure of **6** we chose the selenium atoms as edges of a distorted antiprism with the atoms Se(1)–Se(2)–Se(3) and Se(1A)–Se(2A)–Se(3A) facing top and bottom, respectively (mean Se–Se distance 4.14 Å). Both triangles are linked by somewhat longer Se–Se distances (mean 4.58 Å). A severely distorted Cu₆ octahedron is embedded into this antiprism. The Cu–Cu contacts vary

between 2.534(3) and 2.830(3) Å. These distances lie well within the range of those observed in phosphane-stabilized copper selenide clusters.¹ The Cu(1) [and Cu(1A)] centre is trigonal planar coordinated by Se(1), Se(2), Se(3) [sum around Cu(1) 359.8°] with typical Cu–Se bond lengths between 2.370(2) and 2.412(2) Å. The copper atoms Cu(4) and Cu(5) [Fig. 1(a)] are coordinated in a nearly linear fashion by two selenium atoms [Se(2)–Cu(4)–Se(3A) 165.63(7); Se(1)–Cu(5)–Se(2A) 158.97(7)°] each with a short and a longer bond [Cu(4)–Se(3A) 2.143(2), Cu(4)–Se(2) 2.500(2); Cu(5)–Se(2A) 2.273(2), Cu(5)–Se(1) 2.404(2) Å]. The coordination geometry of copper atom Cu(2) is most remarkable. Apart from two Cu–Se bonds [Cu(2)–Se(2A) 2.331(2), Cu(2)–Se(3) 2.503(2) Å; Se(2A)–Cu(2)–Se(3) 144.71(8)°], Cu(2) has a bonding contact [2.244(5) Å] to the *ipso*-carbon atom C(16A) of the aryl ring bonded to Se(2A). This contact is longer than the electron-deficient three-centre copper carbon bonds in oligomeric copper–aryl compounds [*ca.* 2.06 Å],⁷ but comparable to



Scheme 1

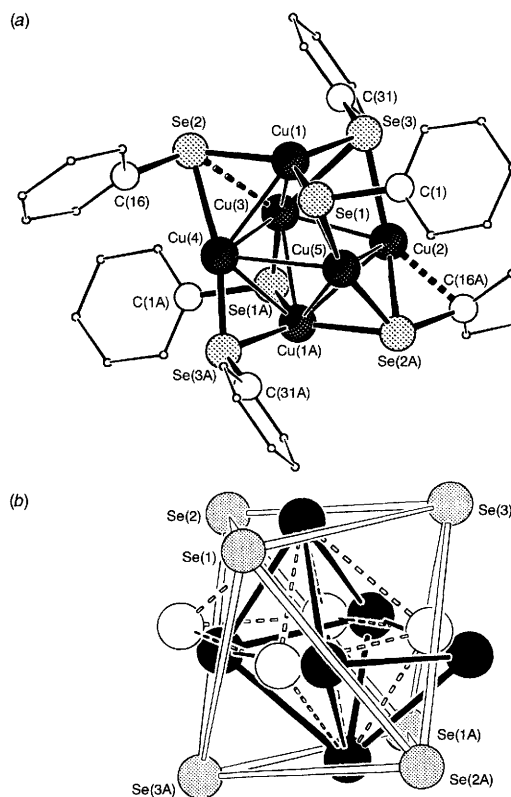


Fig. 1 (a) Molecular structure of **6**. One position of the disordered copper atoms Cu(2), Cu(3), Cu(4) and Cu(5) is shown. Hydrogen atoms and isopropyl groups are omitted for clarity. Selected relevant bond lengths and angles are given in the text. (b) Arrangement of the disordered Cu₆ core within the distorted antiprism of selenium centres. Copper atoms are shown as shaded and open circles to illustrate the assumed disorder of Cu(2/3/4/5).

distances in copper–hydrocarbon π -complexes (2.15–2.34 Å).⁸ This copper–carbon bond is most likely responsible for opening of the Cu(2)–Cu(1) bond within the Cu₆ core [Cu(1)–Cu(2) 3.455(3) Å]. The dislocation of Cu(2) is best visualized as the result of a copper atom displaced from its triangular face of the Se₆ antiprism [Fig. 1(b)]. While Cu(1) lies almost perfectly in the plane defined by Se(1)–Se(2)–Se(3) (deviation 0.055 Å), and atoms Cu(3), Cu(4) and Cu(5) are displaced towards the centre of the Se₆ core [Cu(3) 0.189, Cu(4) 0.088, Cu(5) 0.233 Å], the atom Cu(2) lies far outside the Se(1A)–Se(2A)–Se(3) plane by 0.605 Å. The withdrawing effect of C(16A) on Cu(2) is further transmitted to Cu(3), which forms a rather short bond to Cu(2) [2.534(3) Å] but a long bond to Se(2) of 2.829(3) Å. This causes Se(2) to lose its μ_3 -bridging mode of the Cu(1)–Cu(3A)–Cu(4A) triangle. In turn, however, the selenium atom Se(3) has developed considerably into a μ_3 -bridging centre capping the copper atoms Cu(1), Cu(2) and Cu(3) [Se(3)–Cu(1) 2.412(2), Se(3)–Cu(2) 2.503(2), Se(3)–Cu(3) 2.663(2) Å].

This leads us to propose a mechanism to explain the fluxional behaviour of the Cu₆Se₆ cluster. In the temperature range 190–300 K in [²H₈]toluene, the ¹H NMR spectrum of **6** shows only one set of signals for the selenolate groups, and the ⁷⁷Se spectrum also shows only one broadened resonance at δ –189.2. This is probably owing to high intramolecular fluctuation involving rapid exchange of the μ_2 - or μ_3 -binding modes of the selenolate ligands, although dissociation of **6** into smaller fragments and subsequent intermolecular exchange of selenolate groups cannot be ruled out with certainty. We could not determine the molecular mass in benzene solution with sufficient accuracy. However, the similar colour in solution and the solid state may indicate the same aggregation state. § A 1 : 3 mixture of **6** and free selenol **4** shows both species separately in the ¹H NMR in the temperature range 190–270 K. Above 270 K, broadening of the aromatic and isopropyl methine protons indicates slow exchange of the selenolate residues with added **4**. This again points to a relatively inert aggregate as **6** in solution while smaller fragments are expected to be more reactive. In principle, two limiting mechanisms may be discussed in which (i) either the selenium centres circulate around a Cu₆ core, or (ii) the copper atoms move within the Se₆ antiprism. A comparable (and still unsolved) problem is found in the dynamic behaviour of Fe₃(CO)₁₂.⁹ The structure of **6** points to mechanism (ii). However, if our interpretation of the results is correct, this would imply the interesting conclusion that the Cu₆ sub-cluster does not rotate intact within the Se₆ arrangement but, instead, that the exchange of the copper positions is facilitated by additional copper–carbon contacts. By this mechanism, all selenium centres within the rigid selenium framework may likewise adopt either a μ_2 - or a μ_3 -bonding mode. If averaged positions for the disordered copper atoms are assumed, one obtains a more regular Cu₆Se₆ cluster **7**, which corresponds in our model to the transition state of the arrangement. In **7**, two μ_3 -selenium atoms [*i.e.* Se(2), Se(2A)] occupy opposite faces and four μ_2 -selenium atoms [*i.e.* Se(1), Se(1A), Se(3), Se(3A)] bridge adjacent edges of the Cu₆ cluster. The copper centres Cu(2), Cu(3), Cu(4) and Cu(5) lie in one plane and Cu(1) and Cu(1A) (1.97 Å above and below) are slightly displaced from the centroid of this plane. None of the copper atoms show an extraordinary displacement from one of the selenium triangular faces. In any case, the structures of copper(I) selenolates are obviously very sensitive to slight electronic and steric changes of the selenolate ligands which can cause a transition from a heterocycle like **2b** to a cluster as in **6**.

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Footnotes

† Preparation of compound **6**: Freshly prepared Cu₂O is suspended in degassed ethanol and 2,4,6-triisopropylphenylselenol is added at 0 °C. The reaction mixture is warmed to room temp. and stirred for 3 h. The copper selenolate **6** precipitates as a greenish-yellow solid. All volatiles were removed in a vacuum (0.01 torr) and *n*-hexane was added to the residue. Some brownish insoluble material was removed by filtration at 40 °C and washed three times with *n*-hexane. The combined *n*-hexane phases were kept at –20 °C. Large yellow crystals of **6** were collected after 24 h. Compound **6** can be handled briefly in air, but should be stored under an inert atmosphere under exclusion of light. Mp (decomp.) > 105 °C. ¹H NMR (C₆D₆): δ 1.11 (d, *J*(HH) 6.8 Hz, 12 H, Me of *o*-Prⁱ), 1.21 (d, *J*(HH) 6.8 Hz, 6 H, Me of *p*-Prⁱ), 2.81 (sept., *J*(HH) 6.8 Hz, 1 H, CH of *p*-Prⁱ), 4.00 (sept., *J*(HH) 6.8 Hz, 2 H, CH of *o*-Prⁱ), 6.89 (s, 2 H, aromatic CH). ¹³C NMR (C₆D₆): δ 24.3 (s, Me of *o*-Prⁱ), 24.4 (s, Me of *p*-Prⁱ), 34.4 (s, CH of *o*-Prⁱ), 37.1 (s, *p*-CH), 122.2 (s, *m*-C), 128.3 (s, C–Se), 147.5 (s, *o*-C), 150.8 (s, *p*-C). ⁷⁷Se NMR (CDCl₃): δ –189.2(s).

‡ Crystal data for **6**: [(C₁₅H₂₃)Se]₆Cu₆·xC₆H₁₄, *M* = 2161.2, triclinic, space group *P* $\bar{1}$, *a* = 13.880(9), *b* = 14.283(8), *c* = 14.330(9) Å, α = 79.34(5), β = 65.34(5), γ = 80.07(5)°, *V* = 2523 Å³, *Z* = 1, crystal size 0.2 × 0.4 × 0.8 mm, μ = 34.5 mm^{–1}, 8877 reflections measured (Mo-K α , ω -scan, 2 θ (max) = 50°, empirical absorption correction (0.44 < *T* < 0.836). The structure was solved by direct methods and refined by the least-squares method based on all *F*² with all reflections (SHELXL93; G. M. Sheldrick, Göttingen, 1993). Refinement in *P* $\bar{1}$ yielded normal anisotropic temperature factors for all atoms but two Cu atoms which were split and refined in two positions. Hydrogen atoms were included in calculated positions, methyl groups were refined as rigid groups. Final *R* values were *R*1 = 0.040 (for 6877 observed reflections) and *wR*2 = 0.116 (for all reflections). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ The copper(I) arylselenolate **6** is orange–yellow in solution and in the solid state, while the copper(I) alkylselenolate **2b** cited above is colourless. This is comparable to the observation that the tetramer **3a** of CuS(2,4,6-Prⁱ₃C₆H₂) is colourless (Cu–Cu *ca.* 2.70 Å) while the octamer **3b** (Cu–Cu 2.70–3.04 Å) is yellow. The bathochromic shifts observed in the higher aggregates are probably an effect of the extended σ -Cu–S(Se) bonding framework, thus providing supporting evidence for the supposed tetrameric structure of **2b** with μ_2 -bridging selenolates.

References

- For recent theoretical and synthetic work on molecular CuS/Se clusters, see: A. Schäfer and R. Ahlrichs, *J. Am. Chem. Soc.*, 1994, **116**, 10686; S. Dehnen, A. Schäfer, D. Fenske and R. Ahlrichs, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 746 and references cited therein; bulky selenolates as precursors for CdSe have been described: M. Bochmann, K. J. Webb, J. E. Hails and D. Wolverson, *Eur. J. Solid State Inorg. Chem.*, 1992, **29**, 155.
- A. P. Kozikowski and A. Ames, *Tetrahedron*, 1985, **41**, 4821; H. Suzuki, H. Abe and A. Osuka, *Chem. Lett.*, 1981, **1**, 151.
- P. J. Bonasia, G. P. Mitchell, F. J. Hollander and J. Arnold, *Inorg. Chem.*, 1994, **33**, 1797.
- M. Bochmann, K. J. Webb, M. B. Hursthouse and M. Mazid, *J. Chem. Soc., Dalton Trans.*, 1991, 2317.
- I. Schröter-Schmid and J. Strähle, *Z. Naturforsch., Chem. Sci. B*, 1990, **45**, 1537.
- R. C. Stevens, M. R. Lean, R. Bau and T. F. Koetzle, *J. Am. Chem. Soc.*, 1989, **111**, 3472; T. H. Lemmen, K. Folting, J. C. Huffman and K. G. Caulton, *J. Am. Chem. Soc.*, 1985, **107**, 7914; E. Wehman, G. van Koten, J. T. B. Jastrzebski, M. A. Rottevel and C. H. Stam, *Organometallics*, 1988, **7**, 1477; R. W. M. ten Hoedt, J. G. Noltes, G. Van Koten and A. L. Spek, *J. Chem. Soc., Dalton Trans.*, 1978, 1800; L. F. Rhodes, R. L. Bansemer, K. Folting, J. C. Huffman and K. G. Caulton, *Inorg. Chim. Acta*, 1992, **191**, 31 and references cited therein; S. Kitagawa, M. Munakata, H. Shimono, S. Matsuyama and H. Masuda, *J. Chem. Soc., Dalton Trans.*, 1990, 2105 and references cited therein; F. M.-H. Abadi, H. Hartl and J. Fuchs, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 514.
- Review: G. van Koten, *J. Organomet. Chem.*, 1990, **400**, 283 and references cited therein.
- See: C. Zybilla and G. Müller, *Organometallics*, 1987, **6**, 2489; C. J. Brown, P. J. McCarthy, I. D. Salter, K. P. Armstrong, M. McPartlin and H. R. Powell, *J. Organomet. Chem.*, 1990, **394**, 711, and references cited therein.
- For a recent account, see: D. Braga, F. Creponi, L. J. Farrugia and B. F. G. Johnson, *J. Chem. Soc., Dalton Trans.*, 1994, 2911.