Synthesis and Structure of the First Indium–Copper Cluster, $[Cu_6In_3(SEt)_{16}]^-$ and its Possible Relevance to $CuInS_2$

Wakgari Hirpo, Sandeep Dhingra and Mercouri G. Kanatzidis*

Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, East Lansing, MI 48824, USA

The cluster $(Ph_4P)[Cu_6In_3(SEt)_{16}]$ has been prepared by the reaction of $[Cu(CH_3CN)_4]PF_6$ with $(Ph_4P)[In(SEt)_4]$ and its crystal structure shows an adamantoid framework.

Despite recent developments in homoleptic metal-thiolate chemistry, a quick literature survey reveals that *heterometallic* metal thiolate complexes are conspicuously absent.[1] Our interest in mixed metal-thiolate and selenolate compounds stems from the need to develop single-source precursors for $CuInS_2$ and $CuInSe_2$, the latter being a leading low cost photovoltaic material for direct solar energy conversion.[2] Thin film photovoltaic devices based on $CuInSe_2$ have now achieved 12% efficiency while devices based on $CuInS_2$, a potentially cheaper, lighter and less toxic material, lag behind at 7%.[2] The reasons for this are not entirely understood but there are increasing indications of a greater number of defects in its crystal structure.[2] To date, thin films of $CuInQ_2$ ($Q = S$, Se) have been deposited by a number of physical techniques including evaporation of $CuInSe_2$ powder with coevaporation of Se,[3] evaporation from the binary compounds,[4] Cu_2Se, In_2Se_3, three source coevaporation from the elements,[5] ion beam sputtering of polycrystalline $CuInSe_2$,[6] molecular beam epitaxy[7] and spray pyrolysis.[8] All these techniques involve high temperatures. The films obtained usually suffer from high defect density and non-stoichiometry, both detrimental to device performance. Development of suitable precursors should provide milder synthetic routes and better materials. Reports on soluble one-source precursor compounds for low temperature preparation of $CuInQ_2$ with atomic Cu : In ratio of 1 : 1, however, are scarce.[9] For these reasons we are exploring the thiolate (and selenolate) chemistry of Cu and In. Herein, we report a novel mixed Cu–In thiolate polynuclear cluster $(Ph_4P)[Cu_6In_3(SEt)_{16}]$, **1**, featuring a remarkable adamantoid structural framework, which is an important addition to the metal-thiolate family of compounds because it is the first compound to contain metal heteroatoms from different groups in the periodic table.

Reaction of $[Cu(CH_3CN)_4]PF_6$[10a] with $(Ph_4P)[In(SEt)_4]$

(prepared *in situ* from $InCl_3$, 4NaSEt and Ph_4PCl), produces the yellow crystalline complex **1** in 40% yield.† The compound crystallizes from $CH_3OH–CH_3CN$ mixture as a Ph_4P^+ salt‡ and is sparingly soluble in most common organic solvents.

The structure of the nona-nuclear $[Cu_6In_3(SEt)_{16}]^-$, **I**, anion is shown in Fig. 1. It is composed of three fused distorted adamantane cages consisting of three tetrahedral Cu atoms, three trigonal planar Cu atoms and three tetrahedral In atoms 'glued' together by four triply bridging, nine double bridging and three terminal thiolates. The three adamantane cages share Cu atoms which cluster together to form a central $[Cu_6(SEt)_4]^{2+}$ core. This hexanuclear core consists of three tetrahedral and three trigonal planar Cu atoms. To form the entire cluster the $[Cu_6(SEt)_4]^{2+}$ core is capped with three tripodal $[(\mu\text{-SEt})_3InSEt]^-$ units. The three tetrahedral Cu atoms, each from the three adamantane cores, are bridged by one of the triply bridging thiolates. The remaining three tridentate thiolates bridge two trigonal and one tetrahedral Cu atoms. All doubly bridging thiolates however, bridge In and Cu atoms. A pseudo threefold axis passes through the only sulfur atom S(8) shared by the three adamantane cores and perpendicular to the plane containing the three tetrahedral copper atoms Cu(1), Cu(3) and Cu(6).

The Cu–S bond distances are influenced predominantly by the metal coordination type rather than by the binding modes of the sulfur atoms. Thus, Cu–S bond distances around the trigonal copper atoms range from 2.19 to 2.26 Å and are shorter than those around the tetrahedral Cu atoms, which range from 2.30 to 2.48 Å, in agreement with a trend observed earlier.[11] The In–S bond distances (2.44–2.49 Å) are in the range found for other tetrahedral In thiolate complexes.[12] All the In–S bond distances for the terminal thiolates are shorter than those of the bridging In–S bonds in accordance with an observation reported earlier for $(In_4S_{10})^{8-}$ anion.[13]

Unlike the related metal-thiolate structures with adamantane building blocks, in which the metal coordination is always tetrahedral,[14] $[Cu_6In_3(SEt)_{16}]^-$ contains trigonal planar Cu atoms. The single adamantane structure of $[Cu_4(SPh)_6]^{2-}$ is another example with trigonal planar Cu atoms.[15] Fig. 2 shows a view of the cluster in which the three trigonal planar Cu atoms are readily visible. The presence of the trigonal planar Cu atoms has actually prevented the anion from capping an additional $[(\mu\text{-SEt})_3InSEt]^-$ to form $[Cu_6In_4(SEt)_{20}]^{2-}$, **II**, which would probably have the known four-fused adamantoid structure of $[M_{10}Q_4(SPh)_{16}]^{4-}$ (Q = S, Se, M = Zn, Cd),[14c,d] or that of the proposed structure of the neutral $Cd_{10}(SPh)_{20}$.[16] The structural relationship between **I** and **II** is illustrated in Fig. 3. With a high sulfide-to-thiolate ratio, the recently reported $[M_{10}S_{16}(SPh)_4]^{6-}$ (M = In, Ga), are additional members of the same family of the decameric clusters.[17] Thus, **I** with a 'missing' $In(SEt)_4^-$, may be considered to have a unique truncated tetrahedron structure. It is also remarkable that the central core of **I** is exclusively built with a copper thiolate cluster '$Cu_6(SEt)_4$' with no evidence of scrambling between In and Cu atoms. The driving force for Cu metal clustering in this molecule is not clear since the long Cu–Cu distances (ranging from 3.18 to 3.35 Å) prevent any attractive $d^{10}–d^{10}$ interactions[15] from taking place. However, it may be related to the desire of the In^{3+} atoms to move as far away from each other as possible in order to minimize electrostatic repulsions.

Unfortunately, the atomic ratio of Cu : In is 2 : 1 and thus **I** is not suitable as a precursor to $CuInS_2$. However, the value of

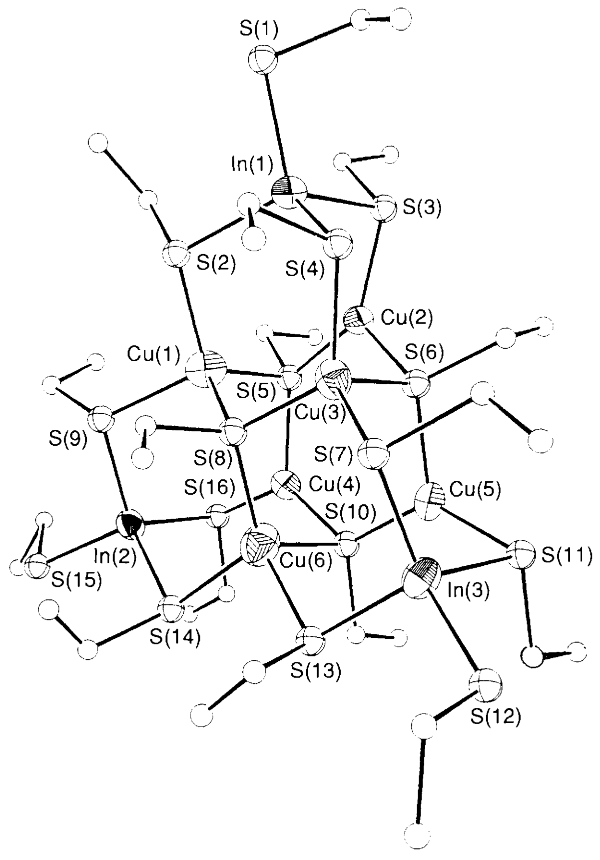


Fig. 1 ORTEP plot of $[Cu_6In_3(SEt)_{16}]^{-1}$ (I) with labelling scheme. Selected bond distances (Å) and angles (°). In(1)–S(1) 2.44(1), In(1)–S(3) 2.49(1), Cu(1)–S(5) 2.31(1), Cu(1)–S(2) 2.37(2), Cu(2)–S(6) 2.26(1), Cu(3)–S(4) 2.37(1), Cu(3)–S(8) 2.29(1), Cu(4)–S(10) 2.21(1), Cu(4)–S(16) 2.24(1), Cu(5)–S(6) 2.26(1), Cu(5)–S(10) 2.22(1), Cu(6)–S(8) 2.28(1), Cu(6)–S(14) 2.43(1), Cu(6)–S(13) 2.48(1); S(5)–Cu(4)–S(10) 115.4(4), In(1)–S(2)–Cu(1) 107.7(5), In(1)–S(4)–Cu(3) 103.8(4), In(3)–S(7)–Cu(3) 104.9(4), Cu(3)–S(8)–Cu(6) 109.8(5), Cu(2)–S(5)–Cu(4) 124.7(6), In(2)–S(9)–Cu(1) 105.8(4), In(3)–S(13)–Cu(6) 105.4(4), S(14)–In(2)–S(16) 104.3(3), Cu(3)–S(6)–Cu(5) 100.8(4), Cu(4)–S(10)–Cu(5) 124.2(6).

---

† (a) A mixture of 0.76 g (9.05 mmol) NaSEt in 50 ml of methanol and 0.85 g (2.25 mmol) Ph_4PCl was stirred for a few minutes; 0.5 g (2.26 mmol) $InCl_3$ was then added and the mixture stirred for *ca.* 30 min and filtered. After adding 20 ml of acetonitrile to the filtrate, 0.84 g (2.25 mmol) $[Cu(CH_3CN)_4]PF_6$,[10a] was finally added and the mixture stirred for 3 h and filtered. The colourless filtrate was concentrated under vacuum. When yellow microcrystals started forming, the solution was left to cool overnight at −10 °C. Yield of $[Ph_4P][Cu_6In_3(SEt)_{16}]$ was 40%, based on Cu. Using $[Cu(CH_3CN)_4]BF_4$[10b] instead of the PF_6^- salt reproducibly gives similar results. However, several attempts to prepare **1** by mixing the exact ratios of the reagents as they appear in the formula failed. The hierarchy of addition of reagents is also important in that the $[Ph_4P][In(SEt)_4]$ must be formed first to avoid precipitation of insoluble copper thiolates (*i.e.* $[CuSR]_n$,[14b]).

‡ *Crystal data*: $[Ph_4P][Cu_6In_3(SEt)_{16}]$, triclinic, $P\bar{1}$ with a = 15.184(11), b = 16.836(11), c = 17.661(9) Å, α = 92.31(5), β = 112.90(5), γ = 103.74(6)°, V = 3995(4) Å^3, Z = 2, D_c = 1.697 g cm^{-3} and μ = 28.6 cm^{-1}. Single crystal X-ray diffraction data were collected (at −110 °C) on a Nicolet P3 four-circle diffractometer (Mo-Kα radiation), with θ/2θ scan, $3° < 2\theta < 40°$, and 3003 reflections with $F_o^2 > 3\sigma(F_o^2)$. An empirical absorption correction (DIFABS, N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, 39, 158) was applied. The number of variables were 412, and final R/R_w = 8.2/9.8%. The structure was solved with SHELXS-86 and was refined with the TEXSAN Structure Analysis Package (Molecular Structure Corporation, 1985) of crystallographic programs. Unit weights were used. The orientation of the ethyl group attached to S(7) was found to be disordered between two positions. The orientation of the terminal carbon atom of the ethyl group attached to S(12)was also found to be disordered over two positions. The Ph_4P^+ cation features the expected structural characteristics and calls for no further comment. There are no close cation–anion contacts. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

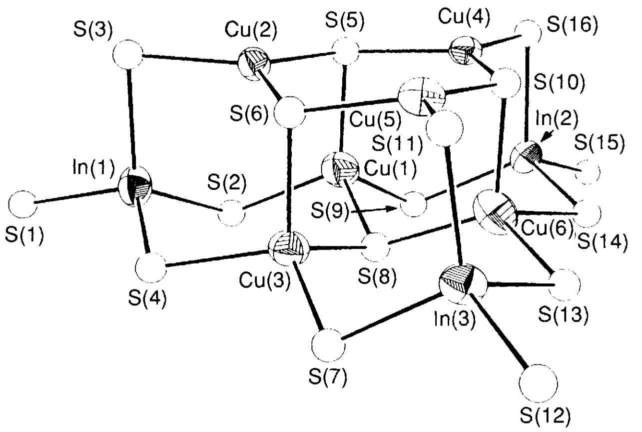
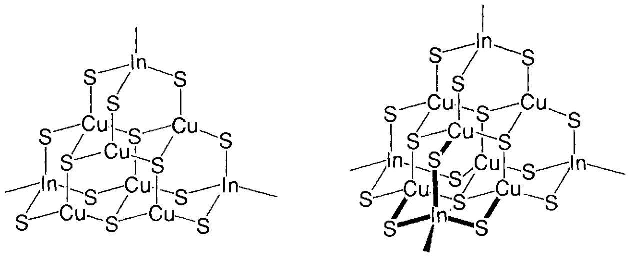


Fig. 2 View of the $[Cu_6In_3(SEt)_{16}]^-$ with labelling scheme showing the flat face associated with the trigonal planar Cu atoms. The Cu_3S_3 six-membered ring is essentially planar.



$[Cu_6In_3S_{16}]$ core $[Cu_6In_4S_{20}]$ core

Fig. 3 Structural relationship of the nona-nuclear cluster $[Cu_6In_3(SEt)_{16}]^-$ and the idealized hypothetical deca-nuclear cluster $[Cu_6In_4(SEt)_{20}]^{2-}$. The trigonal-planar copper atoms must become tetrahedral in the latter. The ethyl groups are not shown. The added $[In(SEt)_4]^-$ fragment is shown in bold.

this molecule lies elsewhere. We note that the overall structure of $[Cu_6In_3(Set)_{16}]^-$ is reminiscent of the chalcopyrite structure of $CuInS_2$,[18] which is also constructed of fused adamantane units. However, in the idealized chalcopyrite structure of $CuInS_2$ the Cu and In atoms are arranged in alternate positions throughout the lattice. The observed 'clustering' of Cu atoms in **I** to form a central $[Cu_6S_4]$ core may have important implications on the observed lower photovoltaic performance of $CuInS_2$-based solar cells. Such clustering of Cu atoms may also be occurring in $CuInS_2$ to form metallic Cu_xS 'islands' (defects) in the material which can act as dark-conducting paths, thus shorting the photovoltaic device. This is not unreasonable since the mobility of Cu atoms is known to be high in many of its compounds. In fact, it is the high mobility of this atom which is responsible for the formation of metallic islands of CuS in semiconducting Cu_2S which causes the relatively rapid degradation of the Cu_2S/CdS based solar cells.[19] A similar Cu clustering may not be as extensive in the selenium analogue $CuInSe_2$ owing to the greater distance between Cu atoms (*ca.* 4.1 *vs.* 3.9 Å in $CuInS_2$).[20]

In summary, a novel nona-nuclear mixed-Cu-In thiolato cluster has been stabilized with an overall truncated tetrahedral structure based on adamantane building units. By virtue of its structural analogy to $CuInS_2$, $[Cu_6In_3(SEt)_{16}]^-$ is an important compound in helping us gain further insight, at the molecular level, of the properties of this photovoltaic material.

Financial support from the National Science Foundation for a Presidential Young Investigator Award, CHE-8958451 is gratefully acknowledged. The X-ray instrumentation used in this work was purchased in part with funds from NSF grant CHE-8908088. We also thank the Center for Electron Optics at Michigan State University for use of the electron microscopy facilities. Partial support was provided by NASA. Dr Aloysius Hepp of NASA Lewis Research Center, Cleveland OH, is acknowledged for fruitful discussions.

Received, 11th November 1991; Com. 1/05709J

References

1 $[Cu_{6-x}Au_x(SCH_2CH_2S)_4]^{2-}$, $[Ag_{6-x}Au_x(SCH_2CH_2S)_4]^{2-}$ were the first examples of heterometallic thiolate clusters involving elements in the same periodic group; G. Henkel, B. Krebs, P. Betz, H. Fietz and K. Saatkamp, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1326.

2 K. Zweibel and R. Mitchell, *CuInSe$_2$ and CdTe: Scale-up for Manufacturing*, Solar Energy Research Institute, Dec. 1989 and references cited therein; R. A. Mickelsen and W. S. Chen, in *Ternary and Multinary Compounds*, ed. S. K. Deb and Z. Zunger, Proceedings of the 7th Conference, Materials Research Society, 1987, pp. 39–47; J. M. Steward, W. S. Chen, W. E. Devaney and R. A. Mickelsen, in *Ternary and Multinary Compounds*, Proceedings of the 7th Conference, Materials Research Society, 1987, pp. 59–64; K. W. Mitchell, G. A. Pollock and A. V. Mason, *20th IEEE Photovoltaic Specialists Conference*, 1988, 1542.

3 L. L. Kazmerski, M. S. Ayyagari, G. A. Sanborn and F. R. White, *J. Vac. Sci. Technol.* 1976, **13**, 139; H. Neumann, E. Nowak, B. Schumann and G. Kuhn, *Thin Solid Films*, 1980, **74**, 197; A. F. Fray and P. Lloyd, *Thin Solid Films*, 1979, **58**, 29; R. D. Tomlinson, D. Omezi, J. Parkes and M. J. Hampshire, *Thin Solid Films*, 1979, **64**, L3.

4 E. R. Don, S. R. Barber and R. Hill, *Proc. 3rd European Communities Photovoltaic Energy Conference*, Cannes, 1980, pp. 897–901.

5 R. A. Mickelsen and W. S. Chen, *Appl. Phys. Lett.*, 1980, **36**, 371.

6 J. Piekoszweski, J. J. Loferski, R. Beaulieu, J. Beall, B. Roesller and J. Schewchun, *Proc. 14th IEEE Photovoltaic Specialists Conference*, 1980, 980–985.

7 S. P. Grindle, A. H. Clark, S. Rezaie-Serej, E. Falconer, J. McNeily and L. Kazmerski, *J. Appl. Phys.*, 1980, **51**, 5464.

8 L. L. Kazmerski, *Thin Solid Films* 1979, **57**, 99; J. B. Mooney, R. H. Lamoreaux and C. W. Bates, *Low-Cost Process for p-n Junction-Type Solar Cell: Final Report*, SRI International SERI Subcontract No. 8104-04, 1981.

9 R. Nomura, S. Fujji, K. Kanaya and H. Matsuda, *Polyhedron*, 1990, **9**, 361.

10 (*a*) G. J. Kubas, *Inorg. Synth.*, 1970, **19**, 90; (*b*) E. Heckel, *Chem. Abst.*, 1967, **66**, 46487e.

11 I. G. Dance, M. L. Scudder and L. J. Fitzpatrick, *Inorg. Chem.*, 1985, **24**, 2547; C. D. Garner, J. R. Nicholson and W. Clegg, *Inorg. Chem.*, 1984, **23**, 2148.

12 R. K. Chada, P. C. Hayes, H. E. Mabrouk and D. Tuck, *Can. J. Chem.*, 1987, **65**, 804; W. Hirpo, S. Dhingra and M. G. Kanatzidis, to be published.

13 B. Krebs, D. Voelker and K.-O. Stiller, *Inorg. Chim. Acta*, 1982, **65**, L101.

14 (*a*) G. S. H. Lee, D. C. Craig, Ida Ma, M. L. Scudder, T. D. Bailey and I. G. Dance, *J. Am. Chem. Soc.*, 1988, **110**, 4863; (*b*) I. G. Dance, *Polyhedron*, 1986, **5**, 1037; (*c*) A. Choy, D. Craig, I. G. Dance and M. L. Scudder, *J. Chem. Soc., Chem. Commun.*, 1982, 1246; (*d*) I. G. Dance, A. Choy and M. L. Scudder, *J. Am. Chem. Soc.*, 1984, **106**, 6285; (*e*) K. S. Hagen and R. H. Holm, *Inorg. Chem.*, 1983, **22**, 3171; (*f*) K. S. Hagen, D. W. Stephan and R. H. Holm, *Inorg. Chem.*, 1982, **21**, 3928; (*g*) I. G. Dance and J. C. Calabrese, *J. Chem. Soc., Chem. Commun.*, 1975, 762; (*h*) I. G. Dance, *J. Am. Chem. Soc.*, 1979, **101**, 6264.

15 D. Coucouvanis, C. N. Murphy and S. K. Kanodia, *Inorg. Chem.*, 1980, **19**, 2993.

16 D. Craig, I. G. Dance and R. Garbutt, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 165.

17 B. Krebs and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 769.

18 L. L. Kazmerski, M. S. Ayyagari and G. A. Sanborn, *J. Appl. Phys.*, 1975, **46**, 4865.

19 K. Zweibel, *Harnessing Solar Power: The Photovoltaics Challenge*, Plenum Press, New York, 1990, pp. 135–140.

20 H. Hahn, G. Frank, W. Klingler, A. Meyer and D. Storger, *Z. Anorg. Allg. Chem.*, 1953, **271**, 153; B. Tell, J. L. Shay and H. M. Kasper, *Phys. Rev.*, 1971, **B4**, 2463.