Molecular Alloys: Syntheses and Structures of the Copper−Antimony Clusters $[Cu_{17}Sb_8(dppm)_6(Ph_2PCHPPh_2)]$ and $[Cu_{20}Sb_{10}(PCy_3)_8]$

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The syntheses, structures and theoretical investigations of the copper-antimony clusters $[Cu_{17}Sb_8(dppm)_6(Ph_2PCHPPh_2)]$ [**1**, dppm = bis(diphenylphosphanyl)methane] and $[Sb_{10}Cu_{20}(PCy_3)_8]$ (**2**, Cy = Cyclohexyl) are reported.

Introduction

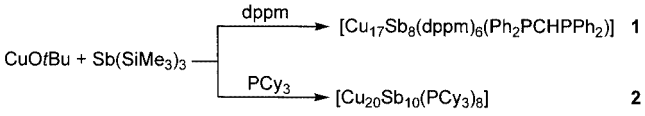
Over the last decade our major field of interest has been the synthesis and structural analysis of metal clusters in which metal atoms are bridged by main-group elements. Special focus was placed on Group 15 and Group 16 bridged metal arrangements, and examples for both cluster classes are numerous.[1] Examples of copper clusters bridged by higher homologues of Group 15 are scarce. Yamada et al. have studied cluster cations of the type $Cu_nSb_m^+$ produced by a gas aggregation source and found that the magic numbers [n, m = (4, 1), (5, 6), (6, 7)] reflect the stability of jellium-shell closings.[2] However, only recently were we able to synthesise and structurally characterise the first Cu−Sb cluster $[Cu_{10}(Sb_3)_2(SbSiMe_3)_2(dppm)_6]$ using Schlenk techniques.[3] All these Cu−Sb cluster species contain Sb−Sb bonds as a common structural motif.

Our approach to Group 15/coinage metal clusters generally involves the reaction of a metal salt MX (M = transition metal; X = halide, carboxylate, alkoxide) with a trimethylsilyl derivative of a main-group element in the presence of a tertiary phosphane. A second route is the metathesis reaction of a transition-metal salt with alkali-metallated Group 15 trimethylsilyl compounds.

Results and Discussion

During the course of the investigations into the syntheses of copper−antimony clusters we explored the potential of both routes. The compounds presented in this communication have all been prepared using the first route.

The reactions of dppm and PCy_3 with one equivalent of CuO*t*Bu and subsequent reaction with $Sb(SiMe_3)_3$ produced the copper−antimony clusters $[Cu_{17}Sb_8(dppm)_6(Ph_2PCHPPh_2)]$ **1** and $[Cu_{20}Sb_{10}(PCy_3)_8]$ **2** (Scheme 1).



Scheme 1. Syntheses of the Cu−Sb clusters in a THF/hexane solution

Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the unit cell and nine lattice-bound THF molecules (Figure 1). The copper atoms are located on faces and edges of a central trigonal antiprismatic arrangement of Sb(2−7). The trigonal faces Sb(2,3,4) and Sb(5,6,7) are capped by Sb(1) and Sb(8). Cu(13) is located in the centre of a Sb(5,6,7) triangle. Cu(17) is the only copper atom in **1** that is coordinated to a carbon atom [Cu(17)−C(138) 2.08(2) Å] and does not bridge at least two Sb centres.[4] Observed Sb−Cu bond lengths and Cu···Cu distances of **1** are in the ranges 2.561(4)−3.086(4) and 2.515(4)−3.041(5) Å, respectively, and are similar to those observed in the cluster $[Cu_{10}(Sb_3)_2(SbSiMe_3)_2(dppm)_6]$ [Cu−Sb av. 2.60 Å, Cu···Cu 2.583(2)−2.675(2) Å].[3] It is noteworthy in this context that the short Cu···Cu distances of **1** (ca. 2.5 Å) are predominantly between tetrahedral and trigonal Cu centres, and are more likely to be the result of geometric requirements than of Cu−Cu bonding. During the course of the reaction partial deprotonation of dppm by CuO*t*Bu occurred, and the structure of **1** is composed

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of a $[Cu_{16}Sb_8(dppm)_6]$ unit and metallated dppm [Cu(dppm)]. The structure of the $[Cu_{16}Sb_8(dppm)_6]$ unit in **1** is similar to the structure found for the Group 16 bridged copper cluster $[Cu_{16}Te_8(P^nPr_2Ph)_{10}]$, thus raising questions about the oxidation state of the metal atoms in **1**.[5] In the neutral copper cluster $[Cu_{16}Te_8(P^nPr_2Ph)_{10}]$ the situation is clear with eight formally Te^{2-} centres coordinated to 16 Cu^I centres.[5] The core of **1**, however, consists of eight Sb centres and sixteen Cu centres arranged in the subunit $[Cu_{16}Sb_8(dppm)_6]$. Additional [Cu(dppm)] gives the neutral complex $[Cu_{17}Sb_8(dppm)_6(Ph_2PCHPPh_2)]$ (**1**). The presence of both Cu^I and Cu^{II} centres in the structure cannot be detected. The UV spectra of brown crystals of **1** (200−900 nm) do not show charge-transfer bands similar to those observed in Cu−Te clusters or absorption maxima characteristic for Cu^{II} centres.[5] A similar situation was found for $[Cu_{20}Sb_{10}(PCy_3)_8]$ (**2**), which crystallizes in the monoclinic space group $P2_1/n$ with four molecules of THF as lattice-bound solvent (Figure 2).

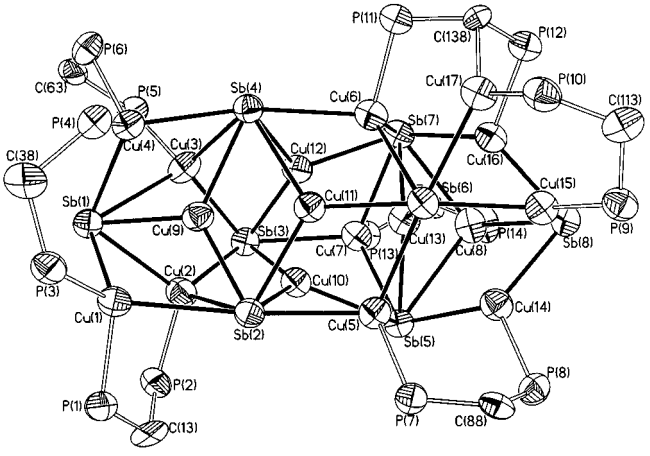

Figure 1. Molecular structure of $[Cu_{17}Sb_8(dppm)_6(Ph_2PCHPPh_2)]$ (**1**); phenyl groups have been omitted; ellipsoids at 50% probability level; selected bond lengths (Å): Cu−Sb 2.561(4) [Sb(2)−Cu(9)] to 3.086(4) [Sb(2)−Cu(2)], shortest Cu−Cu distance 2.515(4) [Cu(2)−Cu(9)], Cu(17)−C(138) 2.08(2), av. Cu−P 2.25

The solid-state structure of **2** consists of two distorted edge-sharing Sb_6 octahedra [Sb(2,3,3a,1,5a,4a) and Sb(4,5,1a,3a,3,2a)] in which the trigonal faces are capped by μ_3-Cu(1,5,6). In the centrosymmetric cluster **2**, the shared edge of the Sb_6 octahedra is bridged by Cu(3) [Cu(3)−Sb(3) 2.7009(19) Å]. The peripheral Cu(2,4,8,10) are coordinated by phosphane ligands. The cyclohexyl substituents of the phoshine ligands form an organic shell preventing the central $Cu_{20}Sb_{10}$ core from further aggregation. Cu(9) exhibits a distorted linear coordination environment [Sb(1A)−Cu(9)−Sb(5): 164.86(7)°] and would perhaps show a similar coordination environment to Cu(3) in a more extended solid-state structure than that of **2**. To elucidate the electronic structure and in particular the oxidation state of the copper atoms involved in the formation of **2**, further experiments (measurement of the temperature dependence of the magnetic susceptibility and of the field dependence of the magnetization between 1.83 K and 100 K) were carried out on polycrystalline samples of **2** (crystals of **1** are contaminated with an amorphous precipitate, so we focused on samples of **2**). As a result, we found that **2** has a diamagnetic ground state with an average susceptibility of −0.003 emu/mol (value in agreement with that expected for a diamagnetic material).

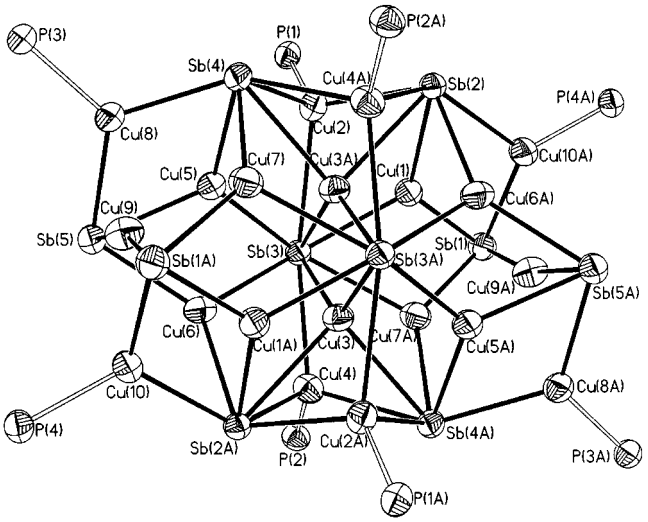

Figure 2. Molecular structure of $[Cu_{20}Sb_{10}(PCy_3)_8]$ (**2**); cyclohexyl groups have been omitted; ellipsoids at 50% probability level; selected bond lengths (Å): Cu−Sb 2.457(2) [Cu(9)−Sb(5)] to 3.106(2) [Cu(2)−Sb(3)], shortest Cu···Cu distance 2.517(2) [Cu(5)−Cu(6)], av. Cu−P 2.24

Independently, a DFT study was carried out to probe these findings.[6] To analyse the properties of the Cu−Sb bond we started with a set of small clusters Cu_nSb_m, n = 1−3; m = 1, 2 summarized in Table 1. Such clusters can provide information about the nature of the Cu−Sb bond with increasing cluster size and different compositions in the absence of ligand effects. Since the electronegativities of Cu and Sb are identical (Pauling scale), no significant charge transfer is expected upon formation of the Cu−Sb bond.[7] This is reflected by the results of Mulliken population analyses (Table 1), which predicts only negligible charge transfer in all small clusters. This confirms the covalent, alloy-like nature of the cores of the Cu−Sb compounds **1** and **2**.

Table 1. Calculated properties of small Cu−Sb clusters: spin state and molecular symmetry, Cu−Sb and Cu−Cu bond lengths (Å) and Mulliken atomic charges

	CuSb	Cu_2Sb	Cu_3Sb	Cu_3Sb_2
State (symmetry)	$^3\Sigma^-$	$^2B_2$ (C_{2v})	$^1A_1$ (C_{3v})	$^2B_2$ (C_{2v})
Cu−Sb	2.43	2.45	2.47	2.51; 2.60
Cu−Cu	−	2.49	2.50	2.55
q_{Cu}	0.07	0.03	0.005	0.02−0.03
q_{Sb}	−0.07	−0.06	−0.01	−0.04

To investigate the electronic properties of **2** we performed calculations on the model complex **2a** in which the PCy_3 ligands were replaced by PMe_3. The experimental structure of **2** shows a C_i molecular symmetry which was also kept during structure optimisations of **2a**. The calculated ground state of **2a** is ^1A_g with close-lying triplet ^3A_g (0.2 eV higher). Since the BP86 functional is known to stabilise lower spin states, this result just indicates singlet and triplet states that are similar in energy. However, the magnetic measurements indicate a diamagnetic nature of **2** and confirm the singlet ground state. The calculated structural parameters (Table 2) of **2a** are generally in good agreement with the experimental results for **2**.

Table 2. Comparison of selected calculated and experimental structural parameters of **2a** and **2**; bond lengths in Å and bond angles in degrees

Parameter	Calculated (**2a**)	Experimental (**2**)
Cu(3)−Cu(3A)	2.50	2.53
Cu(3A)−Cu(5)	2.61	2.63
Cu(9)−Sb(5)	2.53	2.46
Cu(3)−Sb(3)	2.75	2.70
Sb(1A)−Cu(9)−Sb(5)	171.6	164.9

Conclusion

Based on these results and the UV spectra we suggest that the concept of oxidation numbers and localised Cu^{II} and Cu^{I} centres cannot be applied to the Sb−Cu clusters presented here. Instead, **1** and **2** represent intermediates in the reaction of $Sb(SiMe_3)_3$ and Cu*O*t*Bu* that gives the Cu_2Sb alloy which is still under investigation.[8] The results presented here demonstrate that reactions of $Sb(SiMe_3)_3$ with Cu*O*t*Bu* in the presence of tertiary phosphanes can give rise to a class of Sb−Cu clusters that can be regarded as the first representatives of a possibly larger family of phosphane-stabilised molecular alloys with the metal composition $[Cu_2Sb]_n$.

Experimental Section

General Remarks: All operations were carried out in an atmosphere of purified argon. THF was refluxed over potassium and freshly distilled. Hexane was dried with $LiAlH_4$. $P(Cy)_3$ and dppm were purchased from Aldrich and used without further purification. $Sb(SiMe_3)_3$ was prepared according to a literature procedure.[9] Magnetic susceptibility measurements were performed using a Quantum Design SQUID magnetometer MPMS-XL. The magnetic data were corrected for the sample holder (plastic bag) and the diamagnetic contribution calculated from the Pascal constants.[10]

1: A solution of dppm (0.49 g, 1.27 mmol) in 3 mL THF was added to a solution of Cu*O*t*Bu* (0.27 g, 2.00 mmol) tin 5 mL THF. The brown solution was briefly heated to reflux and then allowed to cool down to room temperature. $Sb(SiMe_3)_3$ (3.85 mL, 0.66 mmol, 0.17 M in hexane) was then added at −78 °C. After storage at −40 °C for two weeks, the mixture was allowed to stand at room temperature for another two weeks to produce dark brown crystals of $[Cu_{17}Sb_8(dppm)_6(Ph_2PCHPPh_2)]$ **1** (nine molecules of THF as lattice-bound solvent) (0.10 g, 16%), decomposition at room temperature. The UV/Vis spectrum of **1** does not show any bands. $C_{211}H_{225}Cu_{17}O_9P_{14}Sb_8$:calcd. C 47.0, H 4.2; found C 44.1, H 3.4.

2: A solution of PCy_3 (0.56 g, 2.00 mmol) in 5 mL THF was added to a solution of Cu*O*t*Bu* (0.27 g, 2.00 mmol) *t*in 10 mL THF_3. The reaction mixture was briefly heated to reflux and then allowed to cool down to room temperature. $Sb(SiMe_3)_3$ (3.85 mL, 0.66 mmol, 0.17 M in hexane) was then added at −78 °C. After storage at −40 °C for two weeks, the mixture was allowed to stand at room temperature for another two weeks to produce dark brown crystals of **2** (0.15 g, 31%). The UV/Vis spectrum of **2** does not show any bands. $C_{304}H_{560}P_{16}Cu_{40}Sb_{20}O_4$: calcd. C 37.4, H 5.8; found C 37.0, H 5.7.

Deviations in the elemental analyses from the calculated values show loss of lattice-bound solvent. Crystals of **1** and **2** were dried under vacuum.

X-ray Crystallographic Study: Data for both compounds were collected on a Stoe IPDS II diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 (all data) using the SHELXTL software package.[11] Hydrogen atoms were placed in calculated positions, non-hydrogen atoms were assigned anisotropic thermal parameters.

Crystal data for 1: $C_{211}H_{225}Cu_{17}O_9P_{14}Sb_8$; M = 5392.67; triclinic, space group $P\bar{1}$, Z = 2; a = 17.503(2) Å, b = 22.469(3) Å, c = 29.642(4) Å, α = 80.80(1)°, β = 76.70(1)°, γ = 69.20(1)°; V = 10567(2) Å^3; T = 150(2) K; $F(000)$ = 5348; $D_{calcd.}$ = 1.695 g cm^{-3}. Of 38611 reflections measured 26935 were unique (R_{int} = 0.1025). 1655 parameters; final wR_2 = 0.2404 (all data); R_1 = 0.0974 [$I > 2\sigma(I)$]; largest difference peak and hole 1.44 and −1.26 e·Å^{-3}; disordered components were refined with isotropic thermal parameters.

Crystal data for 2: $C_{152}H_{280}Cu_{20}O_2P_8Sb_{10}$; M = 4875.82; monoclinic, space group $P2_1/n$; Z = 2; a = 15.984(3) Å, b = 28.640(6) Å, c = 19.444(4) Å, β = 100.60(3)°; V = 8749(3) Å^3; T = 123(2) K; $F(000)$ = 4836; $D_{calcd.}$ = 1.851 g·cm^{-3}. Of 30565 reflections measured 15110 were unique (R_{int} = 0.0681). 865 parameters; final wR_2 = 0.1472 (all data); R_1 = 0.0631 [$I > 2\sigma(I)$]; largest difference peak and hole 1.855 and −1.335 e·Å^{-3}.

CCDC-216800 and -216801 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (int.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] S. Dehnen, A. Eichhöfer, D. Fenske, *Eur. J. Inorg. Chem.* **2002**, 279−317.
[2] Y. Yamada, H. T. Deng, E. M. Snyder, A. W. Castleman Jr., *Chem. Phys. Lett.* **1993**, *203*, 330−336.

[3] J. Besinger, J. Treptow, D. Fenske, *Z. Anorg. Allg. Chem.* **2002**, *628*, 512−515.
[4] Cu−C distances in the complex [Cu(dppm)] are 1.96(2) and 2.00(2) Å: A. Camus, N. Marsich, G. Nardin, L. Randaccio, *J. Organomet. Chem.* **1973**, *60*, C39−C42.
[5] A. Eichhöfer, J. F. Corrigan, D. Fenske, E. Tröster, *Z. Anorg. Allg. Chem.* **2000**, *626*, 338−348.
[6] All calculations were performed with the TURBOMOLE program package: [6a] R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, *162*, 165−169. [6b] O. Treutler, R. Ahlichs, *J. Chem. Phys.* **1995**, *102*, 346−354. We used the Becke−Perdew (BP86) exchange-correlation functional within the resolution of the identity (*R*I) approximation. [6c] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098−3100. [6d] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200−1211. [6e] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822−8824; erratum: J. P. Perdew, *Phys. Rev. B* **1986**, *34*, 7406. [6f] K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, *242*, 652. The basis and auxiliary basis set used in the DFT calculations was triple-valence basis and auxiliary basis sets with one polarization function (TZVP). [6g] A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571−2577. [6h] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829−5835. [6i] K. Eichkorn, F. Weigend, O. Treutler, R. Ahlrichs, *Theor. Chem. Acc.* **1997**, *97*, 119−124.
[7] [7a] L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, New York, **1960**, pp. 644. [7b] L. Pauling, *General Chemistry*, Freeman, San Francisco, **1970**.
[8] Cu−Sb distances in Cu_2Sb alloy are 2.701(1)−2.834(1) Å, Cu···Cu 2.602(1): [8a] W. B. Pearson, *A Hanbook of Lattice Spacings and Structures of Metals and Alloys*, Pergamon Press, New York, **1967**, vol. 2. [8b] J. Nuss, M. Jansen, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1152−1157 and references cited therein.
[9] G. Becker, A. Münch, C. Witthauer, *Z. Anorg. Allg. Chem.* **1982**, *492*, 15−27.
[10] E. A. Boudreaux, L. N. Mulay (eds.), *Theory and Applications of Molecular Paramagnetism*, John Wiley & Sons, New York, **1976**.
[11] SHELXTL-97, G. M. Sheldrick, University of Göttingen, **1997**.

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