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Atom Assignment in Solid-State Structures on the Basis of X-ray Crystallography and DFT Calculations – A Case Study on a Molecular Cu–Sb Alloy

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Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 65th birthday

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The structure determination of the molecular Cu-Sb alloy $[Cu_{28}Sb_{12}(PEt_3)_{12}\{Sb(SiMe_3)_2\}_2]$ was performed by DFT-assisted X-ray crystallography, a powerful combination of methods, widely applicable.

Introduction

Recently, some of our interests have been focused on the synthesis of Cu–Sb clusters and their structural analysis.[1,2] For the synthesis of conventional Cu^I–Sb complexes, Cu^I salts are treated with tertiary stibane ligands to produce coordination compounds analogous to thoroughly investigated $[Cu^IX{\cdot}PR_3]$ (R = organic group, X = anion) complexes.[3] A remarkable achievement in the area of Cu–Sb compounds represents the synthesis of the thermally unstable first copper(I) antimonide complex $[Mes_2SbCu(PMe_3)_2]_2$ (Mes = 2,4,6-trimethylphenyl) by the metathesis reaction of Mes_2SbLi with CuCl.[4] A different approach to the syntheses of copper(I) antimonides involves the reaction of $Sb(SiMe_3)_3$ with Cu^I salts in the presence of tertiary phosphanes. As results from these studies, a series of Cu–Sb cluster complexes {e.g., $[Cu_{10}(Sb_3)_2(SbSiMe_3)_2(dppm)_6]$, $[Cu_{17}Sb_8(dppm)_7]$, and $[Cu_{20}Sb_{10}(PCy_3)_8]$ [dppm = 1,2-bis(diphenylphosphanyl)methane, Cy = cyclohexyl]} was obtained and structurally characterised.[1,2] A common feature of the majority of clusters produced in these reactions are the unexpected ratios of Cu/Sb. This is illustrated by $[Cu_{20}Sb_{10}(PCy_3)_8]$, where physical measurements showed that the concept of oxidation numbers can no longer be applied and that they are instead best described as molecular sections of Cu–Sb alloys.[1] Investigations in this field so far showed a preference for copper–antimony compounds with Cu/Sb = 2:1, a ratio which is observed in the η-phase of the rather complex Cu–Sb phase diagram.[5,6] The structural analysis of these complexes has proven to be impossible by X-ray crystallography alone, but the solid-state structure of $[Cu_{45}Sb_{16}(PEt_2Me)_{16}]$, the largest representative of molecular Cu–Sb alloys, was possible by a combined approach of DFT calculations and X-ray crystallography.[2]

Results and Discussion

Here we describe the so far best example of DFT-assisted X-ray crystallography in the Cu–Sb alloy system, which is, due to the structural diversity, predestined for future discoveries in this field. The reaction of CuOAc and $Sb(SiMe_3)_3$ (ratio 1:1) in the presence of PEt_3 produces the Cu–Sb cluster $[Cu_{28}Sb_{12}(PEt_3)_{12}\{Sb(SiMe_3)_2\}_2]$ (**1**) (Scheme 1).

$$CuOAc + Sb(SiMe_3)_3 \xrightarrow[Et_2O]{PEt_3} [Cu_{28}Sb_{12}(PEt_3)_{12}\{Sb(SiMe_3)_2\}_2]\cdot 2Et_2O\ (\mathbf{1})$$

Scheme 1. Synthesis of **1**.

The initial X-ray structural analysis of black crystals of **1** led to problems with the atom assignment of Cu(5,10,17) and Sb(6,8,10) and their symmetry equivalents, indicated by unusual thermal parameters. All other atoms could be unequivocally identified. Figure 1 represents the refined structural model of **1** based on results obtained from DFT calculations.

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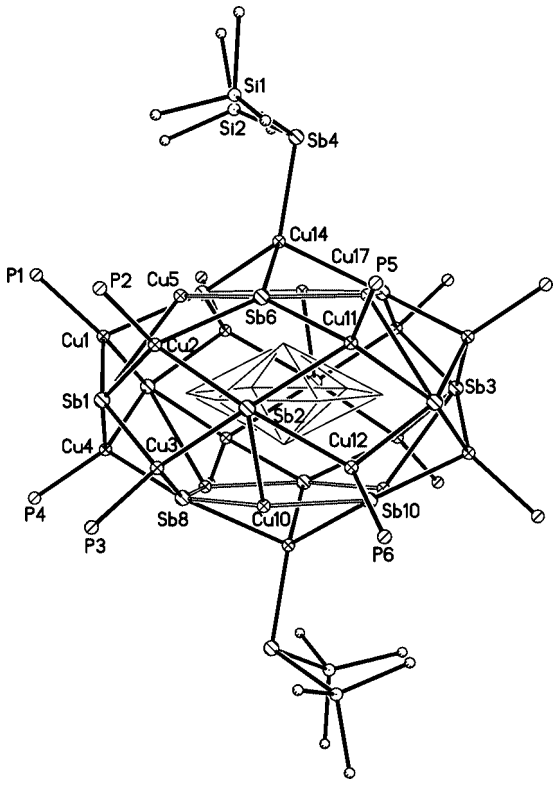
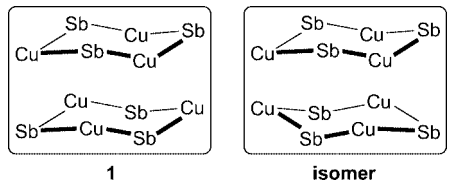


Figure 1. Molecular structure of **1**. Et groups and bonds to the inner $[Cu_8]$ unit and solvent have been omitted for clarity. Selected ranges of bond lengths [Å]: Cu–Sb 2.5322(11)–3.109(11), Cu–P 2.213(2)–2.228(2), Sb(4)–Si(1) 2.542(3), Sb(4)–Si(2) 2.547(3), short Cu–Cu distances observed in the inner $[Cu_8]$ unit 2.410(1), 2.476(1).

The DFT study was carried out to allow reliable assignment of atom types to the positions in question [Cu(5,10,17), Sb(6,8,10) and symmetry equivalents]. All calculations were performed with the TURBOMOLE program package[7] by employing the BP86 functional with the very efficient MARI-J approximation,[8] and recently developed TZVP basis sets.[9] For P–Me and –Et smaller basis sets were used. The number of contracted basis functions is as follows: Sb [6s5p3d2f], Cu [6s4p4d1f], Si [5s5p2d1f], P [5s5p2d1f], C [5s3p1d], and H [2s]. The core electrons 1s to 3d of Sb (28 electrons) were modeled by a small-core ECP (Effective Core Potential), taking into account scalar relativistic effects.[10] The results of these calculations give a clear preference to six-membered $[CuSb]_3$ rings (indicated by open bonds in Figure 1) over Cu_6, Sb_6, Cu_4Sb_2, Cu_2Sb_4, and permutations thereof. $[CuSb]_3$ rings, however, can be in different orientations relative to each other (Scheme 2).

The calculated structures of **1** and a conformer (generated by the exchange of all Cu and Sb positions within slightly puckered six-membered rings) are equally stable (Δ = 4 kJ/mol) and fit with a structure solution of X-ray crystallographic data, based on these DFT suggestions. The calculated structure of the acentric isomer of **1** (Scheme 2, right) is 28 kJ/mol more stable than calculated **1** but shows larger deviations of Cu–Sb bond lengths and would require lower crystallographic symmetry. Although an acentric structure of **1** was initially ruled out when refinement of a



Scheme 2. Relative arrangement of $[CuSb]_3$ rings in **1** and its isomer.

structural model in the space group $P2_1$ did not indicate a preference for Cu or Sb on any site in the highlighted six-membered $[CuSb]_3$ rings (Figure 1; Scheme 2, right), the findings of DFT calculations and X-ray crystallographic results are not contradictory and point towards individual acentric cluster molecules with a 50:50 distribution. This results in a pseudo-centrosymmetric solid-state structure of **1** representing the average composition rather than an individual molecule. Based on these considerations, the structure of **1** and its conformer was solved and refined in the space group $P2_1/n$. Atomic positions within the six-membered rings were refined with 50% occupancy of both Cu and Sb. The solid-state structure of **1** (Figure 1) consists of a central hexagonal-bipyramidal arrangement of Cu atoms surrounded by a distorted icosahedral arrangement of Sb atoms and an additional layer of a capped hexagonal prism of 14 Cu atoms (Figure 2).

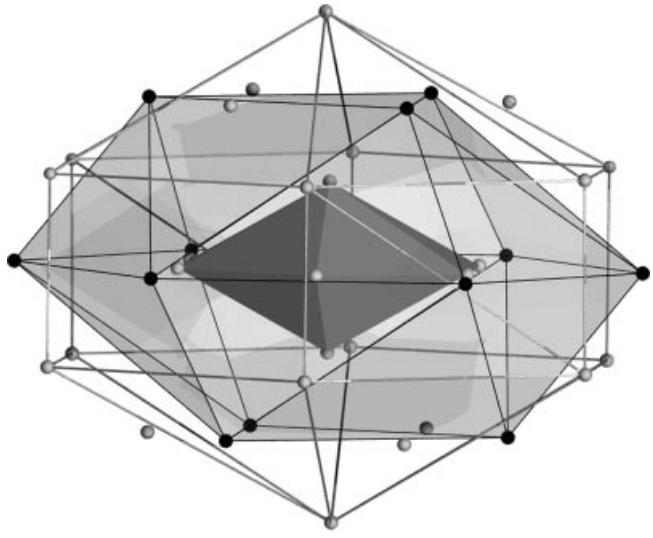


Figure 2. Polyhedral model of the cluster core found in **1** (Sb black, Cu grey).

Over six of the twelve trigonal faces of the hexagonal-prismatic arrangement Cu atoms are located, which form the crucial six-membered $[CuSb]_3$ rings together with two Sb_3 faces of the icosahedral arrangement of the Sb atoms (Figures 1 and 2). Cu atoms in the hexagonal prism are coordinated by P atoms of PEt_3 ligands [Cu–P 2.213(2)–2.228(2) Å], whilst two $[Sb(SiMe_3)_2]$ ligands coordinate the two capping Cu atoms [Cu(14) and its symmetry-equivalent atom].

Conclusion

The exchange of lattice positions in other copper–transition metal compounds is well known.[11] Indications for statistical occupation of atomic positions in a molecular Cu–Sb alloy (resulting here in the cocrystallisation of two conformers), however, are in this case to the best of our knowledge observed for the first time. An increasing number of copper and antimony atoms in metal clusters could lead to even more challenging structural analyses of these species and will propagate the use of DFT methods where conventional X-ray crystallography on its own fails to give convincing results.

Experimental Section

General Remarks: All operations were carried out under purified nitrogen. Hexane and diethyl ether were dried with $LiAlH_4$ and freshly distilled. PEt_3, $Sb(SiMe_3)_3$, and CuOAc were prepared according to published procedures.[12]

Synthesis of 1: CuOAc (0.24 g, 2.00 mmol) was dissolved in Et_2O (8 mL) and PEt_3 (0.56 mL, 4.00 mmol). The yellow solution was cooled to –78 °C and $Sb(SiMe_3)_3$ (2.91 mL, 2.00 mmol, 0.31 M in hexane) was added. The brown reaction mixture was stored at –78 °C for 12 h and was then warmed up to –8 °C and stored for four weeks. Black crystals of **1** were isolated (0.08 g, 21%), but decomposed at room temperature, precluding elemental analysis. **1** is insoluble in ethereal solvents and hydrocarbons.

X-ray Crystallographic Study of 1: Crystallography data for the compound were collected with a Stoe IPDS II diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined by full-matrix least squares on F^2 (all data) using the SHELXTL software package.[13] Hydrogen atoms were placed in calculated positions, non-hydrogen atoms were assigned anisotropic thermal parameters. $C_{92}H_{238}Cu_{28}O_2P_{12}Sb_{14}Si_4$; M = 5342.42; monoclinic, space group $P2_1/n$; Z = 4; a = 19.0392(5) Å, b = 22.0502(6) Å, c = 19.4760(5) Å, β = 97.145(2)°; V = 8112.9(4) Å^3; T = 120(2) K; $F(000)$ = 5132; $D_{calcd.}$ = 2.187 g cm^{-3}; 52524 reflections measured, of which 17705 were unique (R_{int} = 0.0689); 455 parameters; final wR_2 = 0.1572 (all data); R_1 = 0.0588 [$I > 2\sigma(I)$]; largest difference peak/hole = 3.554/–3.273°e·Å^{-3}; disordered components were refined with isotropic thermal parameters. A numerical absorption correction was performed. CCDC-281468 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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