



Review

Covalently bonded compounds of heavy group 15/16 elements – Synthesis, structure and potential application in material sciences

Stephan Schulz^{a,b,*}^a Institute of Inorganic Chemistry, University of Duisburg-Essen, 45117 Essen, Germany^b Center for Nanointegration Duisburg-Essen (CENIDE), Germany

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ABSTRACT

Our understanding on the nature of weak intermolecular metal–metal interactions as well as of multiple bonding in group 15/16 chemistry, in particular of compounds containing the heaviest elements of both groups – Sb, Bi, Se, and Te – is still scarce. These types of interactions are particularly important for the chemical and physical properties of such main group element compounds. For instance, the formation and disruption of weak intermolecular metal–metal interactions are the origin of the so-called thermochromism. The structural characterization of compounds containing sterically less demanding organic

Abbreviations: AACVD, aerosol-assisted chemical vapor deposition; AFM, atomic force microscopy; Bbt, 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl; DIPP, 2,6-diisopropyl phenyl; DSC, differential scanning calorimetry; EDX, energy-dispersive X-ray spectroscopy; HDA, hexadecylamine; PVP*, poly(1-vinylpyrrolidone)-graft-(1-triacontene); SAED, selected area electron diffraction; SEM, scanning electron microscopy; TEM, transmission electron microscopy; TOPO, tri-n-octylphosphane oxide; Trip, 2,4,6-tri-isopropyl-phenyl, 2,4,6-*i*-Pr₃-C₆H₂; XRD, X-ray diffraction; 8-Seq, tris(quinoline-8-selenolato)-stibine.

* Correspondence to: Institute of Inorganic Chemistry, University of Duisburg-Essen, 45117 Essen, Germany. Tel.: +49 0201 1834635; fax: +49 0201 1833830.

E-mail address: stephan.schulz@uni-due.de

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substituents is therefore of particular interest, since the capability of small substituents to kinetically stabilize the respective metal centers – and hence to suppress intermolecular interactions – is expected to be rather less pronounced.

We will herein summarize the most recent results reported for the synthesis and structural characterization of group 15/16 compounds containing a direct (polar-covalent) element–element bond including compounds containing a terminal, formally double bond. In addition, the capability of selected compounds to serve as *single-source precursor* for the synthesis of the corresponding nanomaterials, in particular Sb_2Te_3 and Bi_2Te_3 , by using wet chemical methods as well as gas phase approaches such as metal organic chemical vapor deposition (MOCVD) processes will be demonstrated.

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1. Introduction

Heteronuclear metal organic compounds with a direct bond between group 15 and group 16 elements, in particular those containing the heaviest homologues of both groups – Sb, Bi, Se, and Te – have received a steadily growing interest over the last decades. This interest is mainly based on their potential to form weak intermolecular metal–metal contacts in the solid state, as is also typical for homonuclear compounds such as distibines (Sb_2R_4) and dibismuthines (Bi_2R_4) as well as in ditellanes ($\text{Te}_2\text{R}'_2$), respectively. The strength of the intermolecular interactions in these types of compounds is known to depend on the size of the organic substituents and their electronic properties. Sterically less demanding substituents force the formation of one- or two-dimensional polymeric networks, whereas sterically demanding substituents hamper the formation of intermolecular contacts (*kinetic stabilization*). Moreover, electron withdrawing substituents rather suppress the formation of intermolecular contacts, i.e. dimethylditellurane Te_2Me_2 forms a chain-like structure in the solid state [1], whereas the shortest intermolecular distance in bis(trifluoromethyl)ditellurane $\text{Te}_2(\text{CF}_3)_2$ exceeds the sum of the van-der-Waals radii of the metal atoms [2]. Comparable findings were observed in tetraalkyldistibines and dibismuthines, which often show chain-like structures in the solid state with weak intermolecular metal–metal interactions [3–5]. The metal–metal interactions are typically interrupted upon melting, resulting in a bathochromic shift between fluid and solid phases, the so-called “thermochromic” effect [6].

Group 15/16 compounds such as bis(dialkylstibanyl)chalcogenanes $\text{R}_2\text{Sb-E-SbR}_2$ (E=S, Se, Te) [7–9] and bis(dialkylbismuthanyl)chalcogenanes $\text{R}_2\text{Bi-E-BiR}_2$ (E=S, Se, Te) [10–13], which are accessible by insertion reactions of elemental chalcogens into the metal–metal bonds of the corresponding distibines and dibismuthines, also exhibit weak intermolecular contacts in the solid state, resulting in thermochromic behavior upon melting [14]. In addition, compounds of the general type $\text{R}_2\text{SbER}'$ (E=S, Se, Te; R=Me, Et, R'=Me, Ph) [15–17], which were synthesized by reactions of distibines and dibismuthines with dichalcogenanes $\text{E}'_2\text{R}_2$ (E'=S, Se, Te) [8,10,18–22], were reported to be thermochromic. Me_2SbTeMe for instance is a red liquid at room temperature that solidifies at -52°C with formation of a red solid, which turns yellow-orange at -80°C . In addition, Et_2SbTeMe is an orange liquid at room temperature that solidifies at -80°C to a green-yellow solid. Unfortunately, even though these types of compounds were well known for years, solid state structures of compounds containing sterically less demanding organic substituents such as methyl or ethyl groups, which are typically liquid at ambient temperature, remained almost unknown.

The second major point of interest in group 15/16 chemistry in the last decades was the synthesis and structural characterization of compounds containing hetero-multiple bonds between the group 15 and group 16 atoms [23,24]. Compounds containing a formal double bond were successfully stabilized by either

the introduction of sterically overcrowded ligands, which typically prevent the molecules from self-condensation and/or polymerization (ring formation), or by use of specific N,C,N-pincer-type ligands, which were successfully applied for the stabilization of monomeric antimony(III) chalcogenides of the general type LSbE (E=S, Se) [25,26]. These compounds contain highly polar, terminal Sb–E bonds ($\text{Sb}^{\delta+}\text{--E}^{\delta-}$) (E=Se, Te) due to the donation of electron density from the N atoms to the Sb atom, while according to theoretical studies, the terminal Sb–E bonds in hypothetical PhSb=E molecules are less polar and exhibit more double bond character due to the lack of extra donor atoms. Surprisingly, solid state structures of organoantimony(V) chalcogenides R_3SbE bearing an unsupported terminal Sb–E bond are almost unknown, even though triethylchalcogenostiboranes Et_3SbS and Et_3SbSe have been initially prepared more than 150 years ago by Carl Jakob Löwig and Eduard Schweizer [27]. Triphenylthiostiborane Ph_3SbS , aside from $p\text{-Tol}_3\text{SbS}$ the only structurally characterized triorganylthiostiborane [28–32], shows a short Sb–S bond (2.244(1) Å), which was described by Pebler et al. as partial double bond due to $d\pi\text{--}p\pi$ interaction, whereas Otera et al. described the Sb–S bond in Me_3SbS as highly polar single bond with some ionic stabilization due to the large electronegativity difference between Sb and S [33]. Therefore, our knowledge on the nature of the bonding in these types of compounds is still rather sparse.

Finally, group 15/16 compounds have received growing interest in recent years as molecular precursors, so-called *single-source precursors*, for the synthesis of the corresponding binary materials of the general type M_2E_3 (M=Sb, Bi; E=S, Se, Te). Sb_2S_3 for instance is of particular interest for technical applications in sensitized solar cells (SSCs) [34–36], in ferroelectric phase transition materials [37] and in battery materials [38–40]. In addition, nanoparticles as well as thin films of Sb_2Te_3 , Bi_2Se_3 as well as Bi_2Te_3 , which belong to the M_2E_3 layered materials (M=Sb, Bi; E=S, Se, Te) with tetradymite structure, are of particular interest for technical applications as thermoelectric materials. Sb_2Te_3 for instance is a narrow band-gap ($E_{\text{gap}} = 0.26\text{ eV}$) semiconductor with good thermoelectric properties near room temperature [41–43]. Although many promising thermoelectric materials have been discovered in recent years, antimony and bismuth chalcogenide-based materials are still the most widely used. In the last decade, the effect of nanostructuring on the enhancement of the thermoelectric figure of merit zT , which is mainly based on the decoupling of thermal and electrical conductivity due to the different lengths scales of the mean free path of electrons and phonons [44], was demonstrated. Moreover, Bi_2Te_3 , Bi_2Se_3 , and Sb_2Te_3 are of particular technological interest since they are prototypical topological insulators – bulk insulators with metallic surfaces. In contrast, Sb_2Se_3 lacks a sufficiently strong spin–orbit interaction to develop the topological surface state [45]. In order to generate technologically important M_2E_3 materials with defined optical and physical properties, bottom-up chemistry approaches are currently investigated. So-called *single-source precursors* are known to have a promising potential for the synthesis of nanostructured M_2E_3 materials [36,46–50].

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