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syntheses, structures, and their interconversion

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Smallest molecular chalcogenidometalate anions of the heaviest metals: syntheses, structures, and their interconversion†

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The syntheses of the first molecular *meta*-selenidomercurate(II), *ortho*-telluridothallate(III) and a hydrate of an *ortho*-selenidoplumbate(IV) are presented alongside an improved and facile synthesis of the selenidobismuthate(III) with almost quantitative yields. By means of quantum chemical calculations, the energetics of the interconversions of small metalate anions is discussed and the existence of the heaviest homologues of $[\text{NO}_2]^-$, $[\text{NO}_3]^-$, $[\text{PO}_4]^{2-}$ and $[\text{CO}_3]^{2-}$ are predicted.

1. Introduction

Chalcogenides of the heavy metals possess intriguing optoelectronic¹ and thermo-electric² properties and have therefore been used in numerous applications.³ Those properties can be fine-tuned and adjusted *via* dimensional reduction,⁴ the choice of elemental combination,⁵ or further incorporation of additional metal species towards multinary compounds.⁶ Conventional solid state syntheses, solvothermal reaction pathways and solution-based methods have been shown to facilitate the generation of a large variety of such compounds, including chalcogenidometalate salts.⁷

Whereas the class of oxidometalates has extensively been studied – regarding both their fundamental properties and their potential applications – only a few reports have been dealing with the elemental combination of atoms of the heaviest metals with heavier chalcogen ligands. Here, we will concentrate on salts of the smallest of the heaviest chalcogenidometalate anions, hence with the general formulae $[\text{M}_x\text{Ch}_y]^{z-}$ (M = Hg, Tl, Pb, Bi; $x = 1$ or 2 ; Ch = Se or Te, $y = 2-4$), of which only the following are known to date. Besides the mononuclear *ortho*-chalcogenidomercurate anion $[\text{HgCh}_4]^{6-}$, received from solid state reactions,⁸ only the linear $[\text{HgCh}_2]^{2-}$ anion, synthesized in solution,⁹ has been reported thus far. Molecular chalcogenidothallates and chalcogenidoplumbates have only been obtained from solution. Molecular chalcogenidothallates have so far been restricted to Schrobil-

gen's dinuclear $[\text{Tl}_2\text{Te}_2]^{2-}$.¹⁰ The largest number of small anions is currently found among the chalcogenidoplumbates. Here, one knows the *ortho*-selenidoplumbate anion $[\text{PbSe}_4]^{4-}$,¹¹ the dinuclear, trigonal bipyramidal $[\text{Pb}_2\text{Ch}_3]^{2-}$ anion,¹² and the mononuclear trigonal pyramidal species $[\text{PbTe}_3]^{4-}$.¹³ For bismuthates, only the trigonal pyramidal $[\text{BiCh}_3]^{3-}$ is known from solid state¹⁴ and solution-based approaches.¹⁵

Based on a broad experience in chalcogenidogermanate and chalcogenidostannate chemistry,¹⁶ we are currently about to extend the investigations on the heaviest tetrel congener as well as related anions of the neighbouring heavy metal elements. For this, we are addressing the synthesis of new small and soluble metalate anions, besides the exploration of their physical properties as well as their reactivity in solution or under solvothermal conditions. During the course of our investigations, we were able to synthesize a number of according compounds comprising new such anions with unprecedented elemental combinations, and were thus interested in general tendencies of the energetics of such species and their hypothetical interconversion. Here we report about our findings for the first time.

2. Experimental and computational details

2.1 General remarks and synthesis details

All manipulations and reactions were performed in an argon atmosphere using standard Schlenk or glovebox techniques under strict exclusion of air and external moisture. Multinary solid mixtures of the nominal parent composition “ $\text{A}_m\text{A}'_n\text{M}_o\text{M}'_p\text{Ch}_q$ ” (A, K; A' = Na; M = Hg, Tl, Bi; M' = Pb; Ch = Se, Te) were prepared by fusion of the elements and K_2Ch ,

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redox active, due to the relatively poor stabilization of formal Pb(IV) by selenide and furthermore supposed to be highly oxophilic. Its relative stability in the presence of H₂O, instead of spontaneous formation of [PbO₄]⁴⁻ or even spontaneous reduction, was thus unexpected. Counterintuitively again, the yield was dramatically increased from a few crystals of the ammoniate, to approx. 20% of the hydrate **9**, although separation of the crystals by hand from the reaction mixture remained necessary.

Finally, we attempted solvothermal treatment of phases of the nominal composition K_xBi_ySe_z. Due to its thermodynamic preference, K₃[BiSe₃] (**10**) was obtained from all batches. The structure was reported in the literature, however upon a rather cumbersome experimental procedure: Bi₂O₃ was reduced with K₂[CO₃] in a selenium-charged hydrogen stream at 850 °C.¹⁵ **10** can alternatively be obtained from simple fusion of the elements and successive work up *via* excessive washing with en until the filtrate turns colorless. **10** is then obtained as micro-crystalline powder in almost quantitative yields. Single crystals suitable for X-ray analysis were obtained *via* recrystallization by solvothermal treatment in en.

3.1 Crystal structure description

Crystal structure of K₄[HgSe₃]-H₂O (1). **1** crystallizes in the monoclinic space group *P*2₁ with four formula units in the unit cell. The crystal features orthorhombic geometry, but monoclinic symmetry upon pseudo-merohedral twinning pretending orthorhombic symmetry. In the [HgSe₃]⁴⁻ anions in **1**, the Hg²⁺ ions are coordinated by three Se atoms in a distorted trigonal planar manner (deviation from ideal Se–Hg–Se 120° angles by up to 10°; sum of angles around central Hg atom 359.97°). Within the crystal structure, the anions are stabilized by K⁺ and [K(μ-H₂O)K]²⁺ counter ions and thus well separated from each other (see Fig. 1).

Each K⁺ ion is situated in a distorted octahedral environment of five Se atoms and one O atom, with the exception of K4 with coordination number (c.n.) 7 (see ESI†).

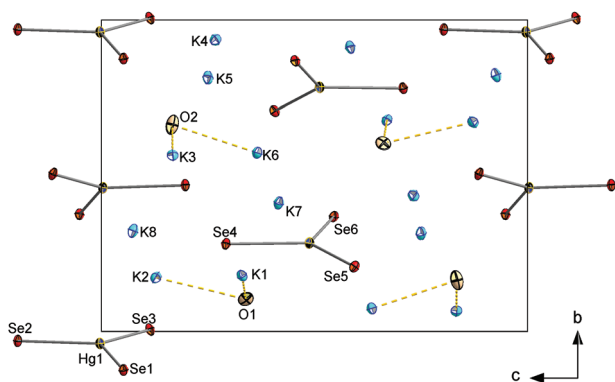


Fig. 1 Fragment of the crystal structure of **1**. Ellipsoids are drawn at 50% probability. Selected structural parameters [Å, °]: Hg–Se: 2.552(2)–2.621(2), K⁺–Se: 3.233(5)–3.620(5), K⁺–O: 2.78(2)–3.19(2), Se–Hg–Se 114.02(6)–129.76(7).

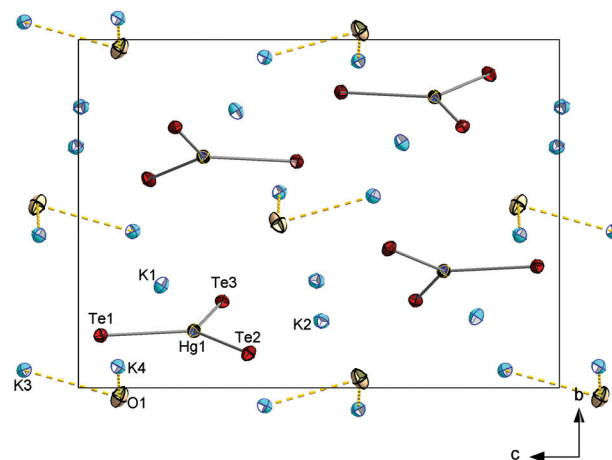


Fig. 2 Fragment of the crystal structure of **2**. Ellipsoids are drawn at 50% probability. Selected structural parameters [Å, °]: Hg–Te: 2.7256(6)–2.7775(6), K⁺–Te: 3.468(2)–3.774(2), K⁺–O: 2.800(7)–3.258(7), Te–Hg–Te 114.427(18)–126.824(18).

Crystal structure of K₄[HgTe₃]-H₂O (2). **2** crystallizes in the orthorhombic space group *P*2₁2₁2₁, a minimal non-isomorphic supergroup to that in **1**, with four formula units in the unit cell. The [HgTe₃]⁴⁻ anions also adopt a distorted trigonal planar shape (deviation from ideal angles by approx. 6°, sum of angles around central Hg atom 359.94°, see Fig. 2).

K⁺ and [K(μ-H₂O)K]²⁺ ions separate the anions from each other, again with distorted octahedral coordination environments of K⁺ ions (see ESI†).

Crystal structure of K₁₀Na₂[HgTe₃]₂(HCO₂)₃ (3). **3** crystallizes in the monoclinic space group *C*2/*m* with 2 formula units in the unit cell. Maximum deviation from the ideal Te–Hg–Te angle within the [HgTe₃]⁴⁻ anions amounts to 2°, the sum of angles around the central Hg atom is 359.98°. Formiate anions are linked to adjacent formiate anions in two different modes: first *via* one K⁺ ion to form a nearly linear O⁺–K⁺–O⁺ connection (K⁺–O: 2.756(3) Å), and second *via* two slightly bent O⁺–Na⁺–O⁺ bridges (Na⁺–O: 2.898(4)–3.058(5) Å; O⁺–Na⁺–O⁺ 45.66(14)°, 77.19(11)°) and one additional O⁺–K⁺–O⁺ linkage (2.701(3)–2.854(4) Å), see Fig. 3. This way, a complicated 3D cationic network is formed to embed well-separated [HgTe₃]²⁻ anions (see ESI†).

Crystal structure of K₂[HgSe₂]-H₂O (4). **4** crystallizes in the monoclinic space group *P*2₁/*c* with four formula units in the unit cell. Hg²⁺ ions are coordinated by three Se atoms, of which two are μ-bridging to adjacent Hg²⁺ ions, while one is a terminal ligand. This way, {[HgSe₂]²⁻}_n 1D anion strands are formed that extend along [001] (see Fig. 4). One of the two crystallographic independent K⁺ ions (K4) is situated in close vicinity to its symmetry equivalent, forming a trapezoidal [K₂(μ-H₂O)]²⁺ cation *via* bridging by two μ-H₂O. Further saturation of the coordination sphere is achieved by three Se atoms. The second K⁺ ion is coordinated by six Se atoms (K2, see ESI†).



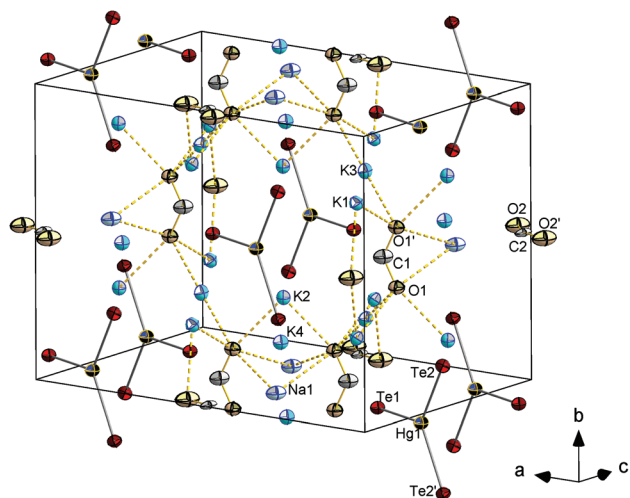


Fig. 3 Fragment of the crystal structure of 3. Ellipsoids are drawn at 50% probability. Selected structural parameters [Å, °]: Hg–Te: 2.7397(4)–2.7795(5), K–Te 3.5028(10)–3.7766(10), K...O 2.701(4)–2.854(4), Na...Te 3.5342(13), Na...O 2.898(4), Te–Hg–Te 119.246(8)–121.482(16).

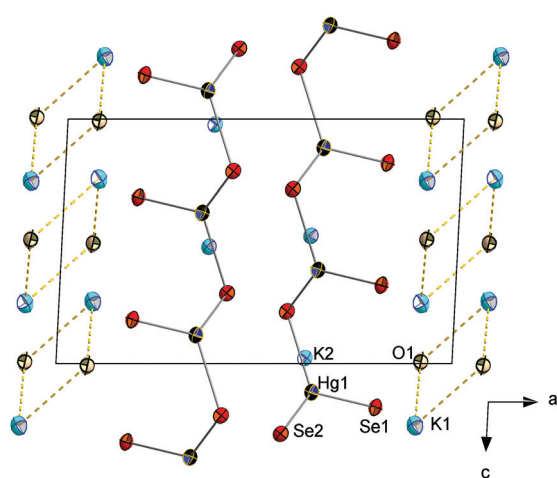


Fig. 4 Fragment of the crystal structure of 4. Ellipsoids are drawn at 50% probability. Selected structural parameters [Å, °]: Hg–Se1 2.5097(10), Hg–Se2 2.5908(10)–2.6090(11), K...Se 3.193(2)–3.497(2), K...O 2.789(9)–3.426(9), Se–Hg–Se 107.19(3)–132.38(3).

Crystal structure of $K_6[Tl_2Se_6] \cdot 2H_2O$ (5). 5 crystallizes in the triclinic space group $P\bar{1}$ with one formula unit in the unit cell. Each (formal) Tl^{3+} ion is coordinated by two terminal Se atoms and two μ -bridging Se atoms, thus forming a molecular, dinuclear $[Tl_2Se_6]^{6-}$ anion. The anions are separated by K^+ ions and $[K(\mu-H_2O)]^{2+}$ units (see Fig. 5). K^+ ions are each coordinated by five Se atoms and one O atom in a distorted octahedral fashion (see ESI†).

Crystal structure of $K_6[Tl_2Se_6] \cdot 2K_2CO_3$ (6). 6 crystallizes in the triclinic space group $P\bar{1}$ with one formula unit in the unit cell. The constitution of $[Tl_2Se_6]^{6-}$ anions is the same as found in 5. Carbonate ions are coordinating to eight K^+ ions,

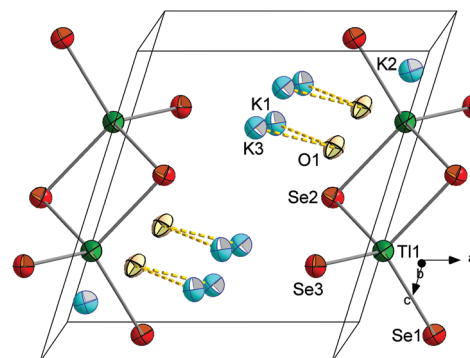


Fig. 5 Fragment of the crystal structure of 5. Ellipsoids are drawn at 50% probability. Selected structural parameters [Å, °]: Tl–Se(1,3) 2.5905(15)–2.5918(15), Tl–Se(2) 2.6876(15)–2.7132(15), K...Se 3.223(4)–3.908(4), K...O 2.766(11)–2.901(12), Se(1)–Tl–Se(3) 114.53(5), Se(1,3)–Tl–Se(2) 106.85(5)–116.66(5), Se(2)–Tl–Se(2′) 96.17(4), K...O...K 96.5(3).

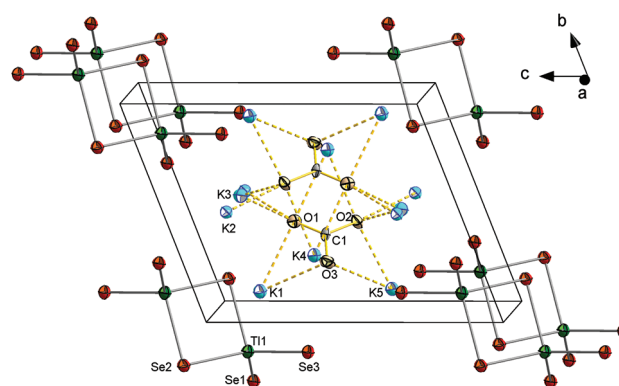


Fig. 6 Fragment of the crystal structure of 6. Ellipsoids are drawn at 50% probability. Selected structural parameters [Å, °]: Tl–Se(1,3) 2.5824(11)–2.5828(12), Tl–Se(2) 2.6629(10)–2.7273(11), K...Se 3.246(2)–3.919(3), K...O 2.681(9)–3.366(9), C–O 1.270(13)–1.327(12), Se(1)–Tl–Se(3) 115.80(3), Se(1,3)–Tl–Se(2) 103.64(4)–116.71(4), Se(2)–Tl–Se(2′) 93.17(3).

three of which are chelated by the same one carbonate ion. Five further terminal K^+ ions, in turn, are situated between two adjacent carbonate ions to form a complicated 2D $[K_{10}(CO_3)_2]^{6+}$ sheet extending between layers of the anions parallel to the ab plane by interconnecting strands of $[K_5(CO_3)]^{3+}$ along the crystallographic a direction (see Fig. 6 and ESI†).

Crystal structure of $K_{0.94}Tl_{0.06}[TlSe_2]$ (7). 7 crystallizes in the tetragonal space group $I4/mcm$ with four formula units in the unit cell, being isostructural with $Tl[TlSe_2]$.³⁰ Hence, $[TlSe_4]$ tetrahedra form 1D strands $\{[TlSe_2]_n\}$ along c by edge sharing (see Fig. 7). The voids between the strands accommodate the counterions, which in 7 represent a statistical mixture of K^+ and Tl^+ ions. Refinement with free second variables results in a 94 : 6 ratio for K : Tl on the positions.

Crystal structure of $\{K_5[TlTe_4] \cdot 2KOH\}_3 \cdot 10H_2O$ (8). 8 crystallizes in the trigonal space group $R\bar{3}c$ with six formula units in



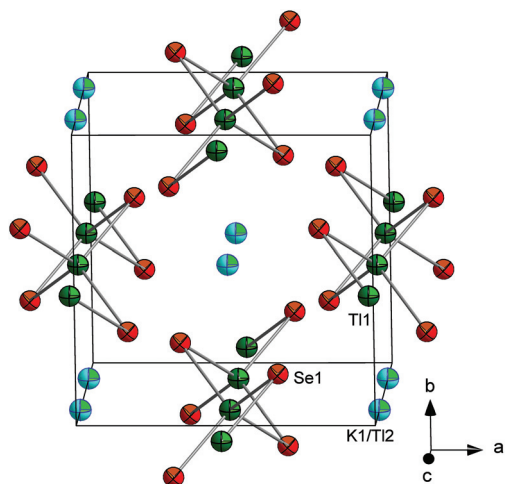


Fig. 7 Fragment of the crystal structure of 7. Ellipsoids are drawn at 50% probability. Two-colored K1/Tl2 ellipsoids indicate statistical disorder on the respective positions. Selected structural parameters [\AA , $^\circ$]: Tl–Se 2.6653(7), K...Se 3.4299(4), Tl–Tl 3.5052(5), Se–Tl–Se 97.77(3), 115.619(14).

the unit cell. The (formal) Tl^{3+} ions are surrounded by Te atoms in a tetrahedral mode, thus forming molecular $[\text{TlTe}_4]^{3-}$ anions that are embedded in and separated by a complex 3D $\{\text{K}\cdots(\text{OH})\cdots\text{K}\cdots(\text{H}_2\text{O})\}_n$ substructure (see Fig. 8). Most of the K^+ ions are hexacoordinate in an octahedral manner ($\text{K5}\cdots\text{Te}_6$), a distorted octahedral manner ($\text{K3}\cdots\text{Te}_4\text{O}_2$), a distorted tetrahedral ($\text{K2}\cdots\text{Te}_3\text{O}$) or a trigonal prismatic manner ($\text{K1}\cdots\text{Te}_3\text{O}_3$). One of the cations is nonacoordinate ($\text{K4}\cdots\text{Te}_2\text{O}_7$). O atoms in turn are either surrounded by 6 K^+ ions in a distorted octahedral fashion (O1, O4) or possess a tetragonal pyramidal environment by 5 K^+ ions (O2, O3) (see ESI †). As illustrated in Fig. 8, the crystal structure of this first *ortho*-chalcogenidothalate salt is extreme complex, with a *c* axis of 39.226(6) \AA and a unit cell volume of 9718(2) \AA^3 , which is very large for an *ortho*-chalcogenidometalate salt. Maybe the steric requirements or even the electrostatic properties of the $[\text{TlCh}_4]^{5-}$ anion impede a suitable and efficient packing of alkali(ne earth) metal cations along with the anions; hence, co-crystallization with two formula units of KOH might be essential, however leading to the shown structural complexity.

Crystal structure of $\text{K}_4[\text{PbSe}_4]\cdot n\text{-H}_2\text{O}$ (9). 9 crystallizes in triclinic space group $P\bar{1}$ with two formula units in the unit cell. Compound 9 is isostructural with $\text{K}_4[\text{PbSe}_4]\cdot n\text{-NH}_3$.¹¹ The presence of water instead of ammonia was unambiguously confirmed by structure solution and refinement using a very precise data set: the refinement of nitrogen atoms on the respective positions led to not positive-defined displacement parameters; furthermore, the two hydrogen atoms per water molecule were localized on the difference Fourier map and refined freely. Thus, 9 indeed represents the second known *ortho*-chalcogenidoplumbate(IV) salt (see Fig. 9). Bond lengths and angles are in good agreement with the reported structure parameters of the ammoniate.

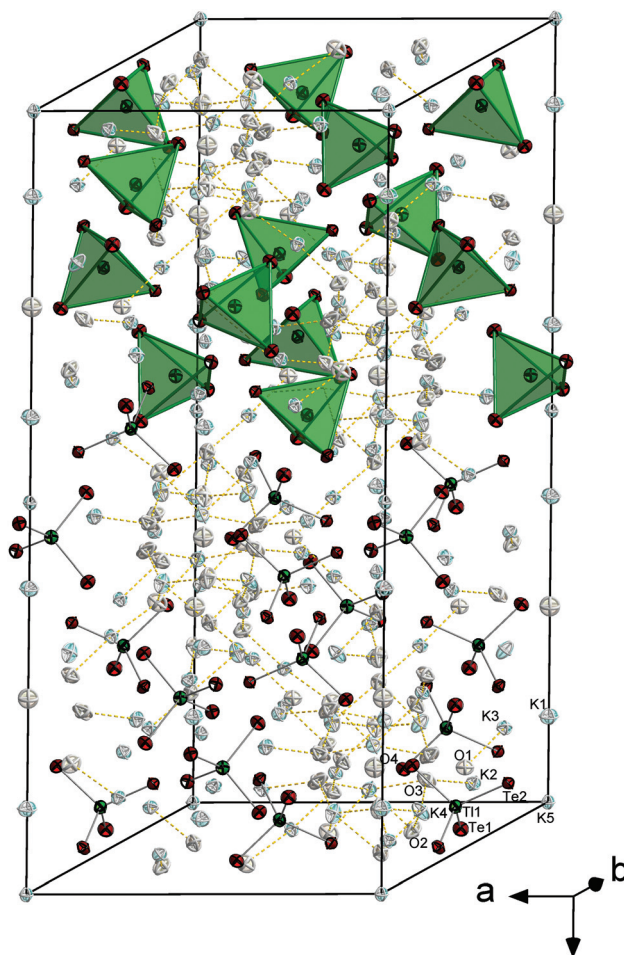


Fig. 8 Fragment of the crystal structure of 8. Ellipsoids are drawn at 50% probability. K and O atoms are drawn in opaque mode, and some of the tetrahedral anions are shown as polyhedra for clarity. Selected structural parameters [\AA , $^\circ$]: Tl–Te 2.8386(12)–2.8458(13), K...Te 3.537(4)–3.916(5), K...O 2.753(15)–3.053(6), Te–Tl–Te 107.26(3)–122.43(3).

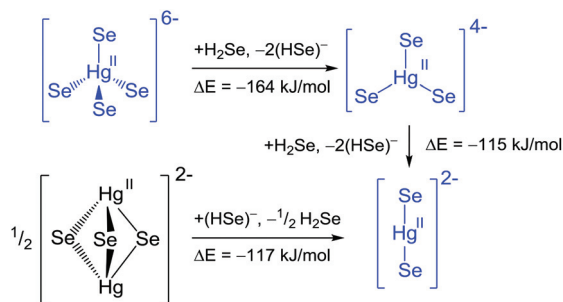
3.2 Quantum chemical calculations

The compounds presented above served to fill some of the existing gaps in the spectrum of known mononuclear or dinuclear chalcogenidometalate anions of the heaviest metals (see Table 1 below). However, many combinations have still not been observed experimentally. We were thus interested, whether according, yet missing species are (a) local minima on the respective energy hypersurfaces, and whether they are (b) accessible *via* chemical reactions in principle.

This might then allow for recommendations for future synthetic approaches: in the case of endoenergetic reactions, classical solid state reaction would more likely be successful, while in the case of an exoenergetic reaction, a reaction in solution should in principle be also possible or even preferred.

In a first step, we simultaneously optimized electronic and geometric structures of all mononuclear anions (*meta* and *ortho* type) and the pseudo-dimeric ones by means of DFT calculations, followed by the determination of second derivatives





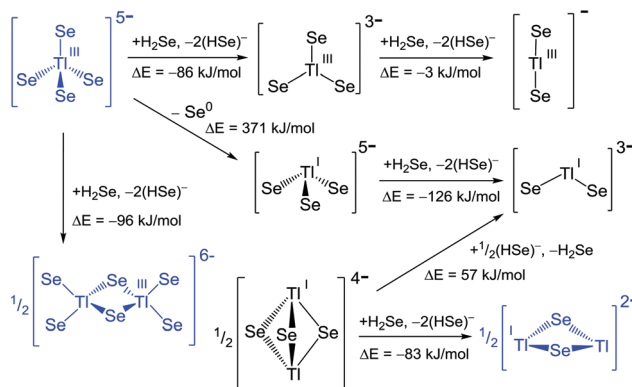
Scheme 1 Reaction pathways and energies for the transformation of chalcogenidomercurates. Blue colour indicates experimentally observed anions.

Thus, although $[\text{Hg}_2\text{Se}_3]^{2-}$ is a minimum on the energy hypersurface, it becomes obvious, why no such species has been reported so far: in solution the transformation towards $[\text{HgSe}_2]^{2-}$ is expected, while a solid state reaction employing the respective 2 : 2 : 3 stoichiometric ratio rather produces an extended mercurate framework structure, such as $\text{K}_2\text{Hg}_2\text{Se}_3$.²⁵ Obviously, this structure type is not available for the 6 : 1 : 4 ratio, hence solid state reactions allow for the isolation of the tetrahedral $[\text{HgSe}_4]^{6-}$ subunit. A comparison of the Hg–Se bond lengths for the planar $[\text{HgSe}_3]^{4-}$ (2.64 Å) versus $[\text{HgSe}_3]^{5-}$ (3.01 Å) is in agreement with the formal +II oxidation state at the Hg atoms in 1–3.

To the best of our knowledge, no chalcogenidomercurate(I) anion has been characterized so far. Nevertheless, we calculated the corresponding anions $[\text{Hg}_2\text{Se}_3]^{4-}$ (trigonal bipyramidal) and $[\text{HgSe}_3]^{5-}$ (trigonal planar or pyramidal). The trigonal bipyramidal anion does not converge into a reasonable structure. The *meta*-mercurate(I) is a minimum on the energy hypersurface in the planar and the pyramidal conformation, with the latter being favoured, but both compounds are open shell systems, which is expected to hamper their isolation.

Thallates. The situation for chalcogenidothallates is somewhat more complex in terms of the availability of different oxidation state. Both, +I and +III, are known within experimentally observed metalate anions, as *ortho*-chalcogenidothallate(III) anion $[\text{TlCh}_4]^{5-}$ (5–8) and the butterfly-like chalcogenidothallate(I) anion $[\text{Tl}_2\text{Ch}_2]^{2-}$. However, as shown in Scheme 2, even more of the small anions turned out to be minima on the energy hypersurface.

Hypothetic reaction cascades starting out from the *ortho*-thallate anion through a molecular *meta*-thallate anion $[\text{TlSe}_3]^{3-}$ and further on to a linear $[\text{TlSe}_2]^{-}$ anion are exoenergetic, but especially the second step is only slightly exoenergetic. Principally, the existence of the respective species under the simulated conditions should hence be possible. However, this pathway is obviously excelled by the shown and observed dimerization, which is even more exoenergetic. A possible redox reaction yielding a pyramidal $[\text{TlSe}_3]^{5-}$ anion is energetically highly disfavoured, such that the exoenergetic step to the bent $[\text{TlSe}_2]^{3-}$ species is not achievable this way. Thus, it

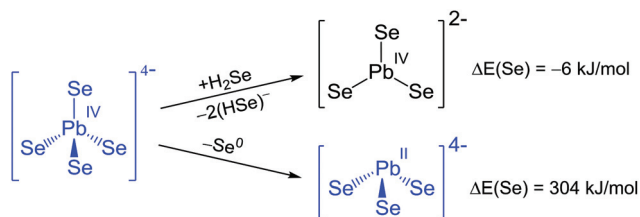


Scheme 2 Reaction pathways and energies for the transformation of selenido-thallates. Blue colour indicates experimentally observed anions.

becomes perspicuous why an interconversion between thallate(III) and thallate(I) anions have not yet been observed. Regarding the possible thallate(I) species, both $[\text{TlSe}_2]^{3-}$ and the butterfly-like $[\text{Tl}_2\text{Se}_2]^{2-}$ anion should be accessible from an energetic point of view starting out from a (hypothetical) $[\text{Tl}_2\text{Se}_3]^{4-}$ bipyramid, but only the second was observed so far. Neither Schrobilgen's comprehensive NMR studies on such systems,¹⁰ nor our own attempts¹⁶ have so far yielded any indication of further thallate(I) anions. However, a related compound, $[\text{TlTe}_3\text{Pb}]^{3-}$,^{12b} was published, hence further extension and variations of the synthetic approached should eventually allow for the synthesis of the other species, maybe even by the use of the quoted ternary anion.

Plumbates. As for the lighter homologues, the only possible mononuclear chalcogenidoplumbates are those given in Scheme 3, besides $[\text{Pb}_2\text{Ch}_3]^{2-}$. Reaction energies for transformations starting from $[\text{Pb}_2\text{Ch}_3]^{2-}$, however, require the elimination of Pb^{2+} or the simulation of PbSe formation, both of which are not feasible with the methods used here (see also above). Bent $[\text{PbCh}_2]^{2-}$, as found in the anionic Tl/Ch system, possess two imaginary vibrational modes, thus does not represent a minimum on the energy hypersurface.

The degradation of *ortho*-selenidoplumbate(IV) anion towards a carbonate homologue under release of a selenide ligand is not associated with a significant energy change,



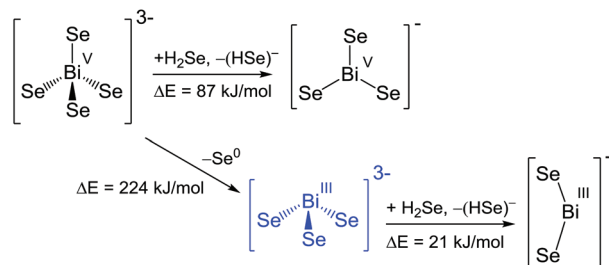
Scheme 3 Reaction pathways and energies for the transformation of selenidoplumbates. Blue colour indicates experimentally observed anions, however, in the case of the $[\text{PbCh}_3]^{2-}$ anion, only the tellurium analogue has been isolated so far.



hence differences either considering a solvent shell or a counterion environment may easily overcompensate it to an overall preference of the tetrahedral anion. An oxidative elimination of selenium to form the pyramidal $[\text{PbSe}_3]^{4-}$ anion is considerably endoenergetic, apparently contradicting the experimental observation of the *meta*-telluridoplumbate(II), but in agreement with a synthesis starting out from a Pb(II) precursor and thus avoiding the disfavoured redox reaction step. Moreover, the distinct energetic preference of the *ortho*-selenidoplumbate(IV) over its dissociation or dechalcogenation is in line with its formation in and crystallization from solution, even as a hydrate like **9**.

Bismuthates. For chalcogenidobismuthates, the list of experimentally observed anions is the smallest along the elemental combinations investigated in the current study. However, the list of hypothetical anions comprises four minima on the energy hypersurface (see Scheme 4). Further minima on the energy hypersurface with intriguing electronic features are the neutral trigonal bipyramidal Bi_2Ch_3 , which however rather exist as the extended solid state compounds paraganajuatite³² or tellurobismuthite,³³ and two chalcogen-bismuth cations $[\text{Bi}_2\text{Ch}_2]^{2+}$ with butterfly-like geometry and linear $[\text{BiCh}_2]^+$. For the reasons given above, these shall not be discussed in the context of chalcogenidometalate anion chemistry.

All reactions starting from a hypothetical *ortho*-bismuthate(V) anion including stepwise elimination and/or dissociation of $\text{Se}^0/\text{Se}^{2-}$ are endoenergetic. Thus the existence of $[\text{BiSe}_4]^{3-}$ does not seem to be generally unrealistic. However, very obviously, so far only chalcogenidobismuthates of Bi(III) have been produced that seem to be kinetically stable enough not to undergo the hypothetical, exoenergetic oxidation towards the tetrahedral species. $[\text{BiSe}_3]^-$ would be the second heaviest possible homologue of the nitrate $[\text{NO}_3]^-$ anion, yet its formation is not favourable according to energetic considerations. Also a bent $[\text{BiSe}_2]^-$ species represents a minimum on the energy hypersurface, yet its formation from the observed $[\text{BiSe}_3]^{3-}$ anion would require another 21 kJ mol⁻¹. For this, although not isolated yet, the list of potentially observable Bi/Se anions definitely include the homologues of $[\text{NO}_3]^-$, $[\text{PO}_4]^{3-}$ and $[\text{NO}_2]^-$ in addition to the observed $[\text{BiCh}_3]^{3-}$ anions. The



Scheme 4 Reaction pathways and energies for the transformation of selenidobismuthates. Blue colour indicates experimentally observed anions.

Table 2 Overview of previously known (x) or newly synthesized (✓) dinuclear selenidometalates or telluridometalates of Hg, Tl, Pb, or Bi as central atoms. Empty boxes indicate so far unknown species. Circles indicate that the calculated structures of the selenides represent local minima on the energy hypersurfaces. The entry n/a indicates that an according species was not considered as it would be either neutral or cationic. According tellurides have not been calculated in this study

	Lower formal oxidation state of M		Lower formal oxidation state of M		Higher formal oxidation state of M	
	Se	Te	Se	Te	Se	Te
Hg	n/a		○		○	
Tl	○	×	○		○	✓
Pb	n/a		⊗	×	○	
Bi	n/a		n/a		○	

remaining challenge is finding an appropriate synthetic approach, such as described recently and once more herein for salts of $[\text{PbSe}_4]^{4-}$.

4 Conclusions

We presented the synthesis and structure of novel *ortho*- and *meta*-chalcogenidometalates of mercury, thallium and lead, including the first molecular *meta*-chalcogenidomercurate(II), the first *ortho*-chalcogenidothallate(III) and the second *ortho*-selenidoplumbate(IV). The latter emerged for the first time and unexpectedly as its hydrate salt. In addition, we reported a new and facile synthetic pathway for the generation of the *meta*-selenidobismuthate in almost quantitative yield. The existence of all those anions inspired quantum chemical investigations of structures and energetics of the diverse species with different elemental combinations. We discussed hypothetical reaction energies, which helped to rationalize the observations and to predict further species to be isolated in future work. In the case of the chalcogenidoplumbates, the heaviest $[\text{CO}_3]^{2-}$ homologues are generally stable, however most likely not accessible *via* solution based techniques. The same is valid for the chalcogenidobismuthate homologues of $[\text{NO}_3]^-$. Tables 1 and 2 summarize the experimental and theoretical findings for all smallest molecular chalcogenidometalate anions of the heaviest metals, including the new ones.

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