

Ternary Mn/Ge/Se anions from reactions of $[\text{Ba}_2(\text{H}_2\text{O})_9][\text{GeSe}_4]$: Synthesis and characterization of compounds containing discrete or polymeric $[\text{Mn}_6\text{Ge}_4\text{Se}_{17}]^{6-}$ units†

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$[\text{Ba}_2(\text{H}_2\text{O})_9][\text{GeSe}_4]$ is suitable for the formation of novel M/14/16 anions $[\text{Mn}_6\text{Ge}_4\text{Se}_{17}]^{6-}$ —discrete or linked in an as yet unprecedented porous network—with antiferromagnetically coupled Mn^{II} centers and relatively small electronic excitation energies.

Recently, we reported on the successful coordination chemical approach towards compounds with ternary M/Sn/E anions (M = transition metal, E = S, Se, Te) by reacting *ortho*-chalcogenostannate anions $[\text{SnE}_4]^{4-}$ with transition metal ions.^{1–3} The heterobimetallic character of the anionic substructures in these compounds is reflected by the electronic properties, *e.g.* smaller electronic excitation energies with respect to related binary species. As for a number of similar systems with discrete or extended M/E'/E aggregates (E' = Group 13–16 element),⁴ *e.g.* $[\text{Cd}_{16}\text{In}_{64}\text{S}_{134}]^{44-}$,⁵ $[\text{MGe}_4\text{Se}_{10}]^{2-}$ (M = Mn, Ag₂),⁶ $[\text{M}_4\text{Sn}_3\text{Se}_{13}]^{6-}$ (M = Cd,^{7a} Hg^{2d}) or $[\text{Cu}_2\text{SbS}_3]^-$,⁸ the structures are always based on tetrahedrally coordinated metal atoms, resembling non-oxidic fragments or analogs of zeolite networks.

Our latest investigations were undertaken to clarify the following questions: (1) are *ortho*-chalcogenogermanate anions $[\text{GeE}_4]^{4-}$ also suitable for the preparation of such compounds? (2) do the desired M/Ge/E systems equally combine structural or electronic properties of the formally underlying binary phases M_nE_m or GeE_2 ? (3) is it possible to generate previously unprecedented molecular or polymeric structural features by the employment of doubly charged cations as counterions?

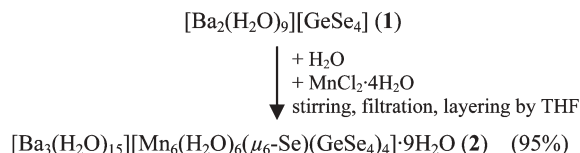
Herein, we start to answer these questions by presenting the first reactions of the water solvate of $\text{Ba}_2[\text{GeSe}_4]$,⁹ $[\text{Ba}_2(\text{H}_2\text{O})_9][\text{GeSe}_4]$ (**1**)¹⁰ with $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ to give $[\text{Ba}_3(\text{H}_2\text{O})_{15}][\text{Mn}_6(\text{H}_2\text{O})_6(\mu_6\text{-Se})(\text{GeSe}_4)_4] \cdot 9\text{H}_2\text{O}$ (**2**) and $[\text{Ba}_3(\text{H}_2\text{O})_{16}][\text{Mn}_6(\text{H}_2\text{O})_3(\mu_6\text{-Se})(\text{GeSe}_4)_4]$ (**3**) (Scheme 1 and Scheme 2). Compounds **1–3** were structurally characterized by means of single crystal X-ray diffraction.^{11,12}

2 and **3** are ionic compounds with three Ba^{2+} ions per formula unit compensating for the six-fold negative charge of the ternary anionic units. The latter have the same Mn/Ge/Se composition and topology in both compounds, but appear either as discrete units

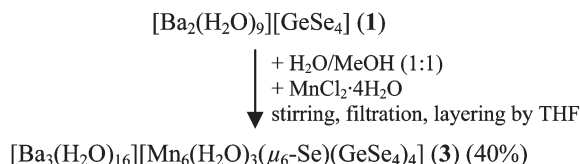
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Scheme 1 Synthesis of compound **2** in water.



Scheme 2 Synthesis of compound **3** in a water/methanol mixture.

(**2**) or are linked to give 2D-layers (**3**). The molecular structure of the anion in **2** is given in Fig. 1.

A central $\mu_6\text{-Se}$ ligand is octahedrally surrounded by six Mn^{II} ions (Fig. 1b) which likewise possess an octahedral coordination geometry by bonding to the central Se atom, four μ_3 -bridging Se ligands and one H_2O molecule. This $[\text{Mn}_6\text{Se}_{13}\text{O}_6]$ core represents a super-octahedron of six face-sharing $[\text{MnSe}_5\text{O}]$ octahedra (Fig. 1c). The twelve μ_3 -bridging Se ligands in this moiety, forming an Se_{12} cubo-octahedron (Fig. 1d), are part of the four tetrahedral $[\text{GeSe}_4]^{4-}$ groups. These are linked with the large octahedron by sharing four of the eight Se_3 -faces in the center of the large octahedral faces (Fig. 1e), producing an overall (idealized) T_d symmetry of the cluster ion.

At ambient conditions, the thermodynamically stable MnSe modification is $\alpha\text{-MnSe}^{13}$ (halite structure type), the smallest part of which is found in the inner $[(\mu_6\text{-Se})\text{Mn}_6(\mu\text{-Se})_{12}]$ cluster fragment of **2**. Therefore, it is surprising that this atomic arrangement, combining both octahedral MnSe coordination and tetrahedral GeSe units, has not been observed with any anionic Mn/E'/Se aggregate so far.¹⁴ The spatial demands and charge of the doubly charged Ba^{2+} cations—that were not present in such phases before—are probably responsible for the formation of this novel M/14/16 anionic structure. The structure-directing role of counterions at the synthesis of compounds containing multinary ions is well known, *e.g.* for zeolitic materials.¹⁵

The magnetic behavior of compounds with Se bridged Mn atoms is largely unknown. For the case of octahedrally surrounded Mn atoms in ternary systems, it was only investigated at $\text{Mn}_2\text{E}'\text{Se}_4$ with $\text{E}' = \text{Si}, \text{Ge}$.¹⁶ To the best of our knowledge, the anionic cluster in **2** is the first molecular complex with a μ_6 -bridging Se

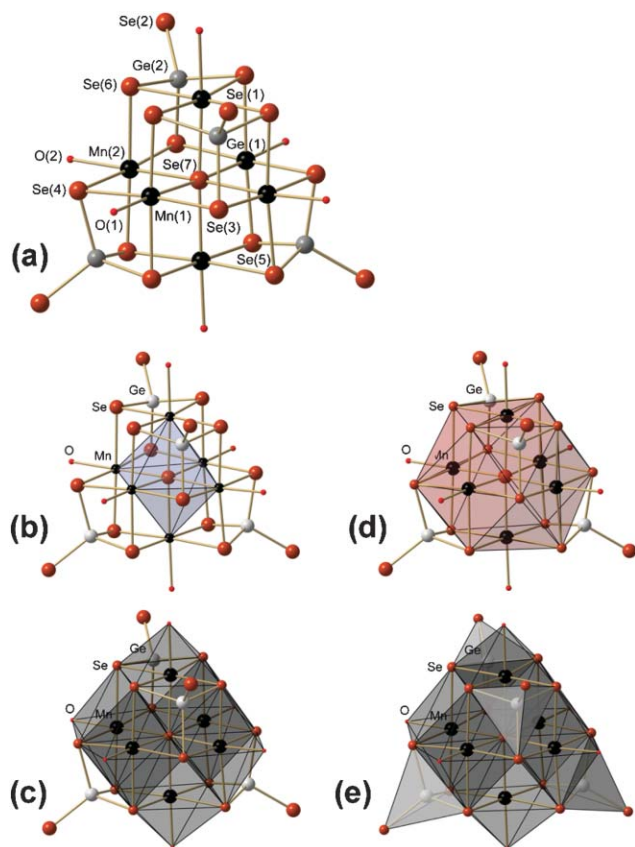


Fig. 1 Molecular structure of the H₂O-ligated, ternary Mn/Ge/Se anion in **2** (a) and illustration of the various coordination polyhedra observed in the cluster ion: central [(μ_6 -Se)M₆] octahedron (b), super-octahedron of six face-sharing [Mn(μ -Se)₅(OH₂)] octahedra (c), non-bonded [(μ -Se)₁₂] cubo-octahedron (d), face-sharing of four [GeSe₄] tetrahedra with the [(μ_6 -Se)Mn₆(μ -Se)₁₂(OH₂)₆] super-octahedron (e).

ligand linking octahedrally coordinated Mn centers. The magnetic properties of **2** were investigated on a sample of finely ground single crystals (Fig. 2).

The χT product decreases in the whole temperature range from 15.8 cm³ K mol⁻¹ at 300 K down to 0.7 cm³ K mol⁻¹ at 1.8 K.

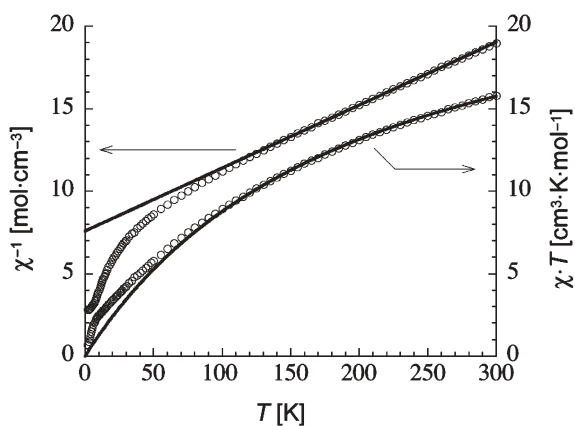


Fig. 2 $1/\chi$ and χT vs. T plot measured at 1000 Oe between 1.8 and 300 K on a polycrystalline sample of **2**. The solid lines represent the best fits obtained with a Curie-Weiss law above 125 K.

This overall behavior indicates dominating antiferromagnetic interactions. A linear extrapolation of χT at 0 K suggests that the [Mn₆O₆Se₁₃] cluster possesses a singlet ground state ($S = 0$). Above 125 K, the $1/\chi$ and χT vs. T plots have been fitted to a Curie-Weiss law. The obtained Curie constant is 26.2 cm³ K mol⁻¹ in good agreement with the presence of $6 \times S = 5/2$ Mn(II). The Weiss constant θ reaches -199 K confirming strong antiferromagnetic interactions between the Mn^{II} centers. Similar interactions through Se bridges have been observed in related materials as shown by their large θ : -217 K in α -MnSe,¹⁷ -550 K in MnSe₂¹⁷ and -240 K in Mn₂GeSe₄.^{16a} While these three-dimensional compounds exhibit long-range magnetic orders, **2** stays paramagnetic down to 1.8 K as expected for a discrete species. It is worth noting that estimation of the local J_i interactions using a numerical approach in the frame of an isotropic Heisenberg model failed to reproduce the magnetic susceptibility in the approximation where only one Mn-(Se)₂-Mn interaction and one Mn-Se-Mn interaction are considered.

By slight variation of the reaction conditions, using a MeOH/water (1 : 1) mixture instead of pure water as solvent (see Scheme 2), one obtains compound **3**. Its anionic substructure is related to that observed in **2**: three of the six water molecules that coordinate to the Mn centers in **2** are replaced by terminal Se ligands of three adjacent, identical anions. *Vice versa*, three of the terminal Se ligands of the central cluster unit coordinate to respective coordination sites of these three neighboring anions. This way, the Mn/Ge/Se units form corrugated layers in **3** which is illustrated in Fig. 3.

The layers are stacked parallel to [010] (nearest inter-layer distances: O \cdots O: 2.920(17) Å, Se \cdots O: 4.523(16) Å, Se \cdots Se: 4.566(14) Å), and embed the nine-fold coordinated Ba²⁺ cations (Ba \cdots O₇Se₂ or Ba \cdots O₆Se₃) within six-membered rings of cluster anions (maximum diameters of the oval holes considering the ionic radii around nearest atoms: 7.4 and 14.6 Å). The packing of the corrugated layers is unprecedentedly similar to that in gray arsenic; the accordingly staggered packing of the layers still allows open channels to run through the crystal parallel to the b axis (θ_{\max} : 3.5 Å, Fig. 3d) that might enable ion exchange.

The different arrangement of cluster anions in compounds **2** and **3** is reflected by different electronic excitation energies. The onset of absorption, *i.e.* the smallest possible electronic excitation energy due to charge transfer from Se-p (and Mn-d) orbitals into empty Mn (and Ge) based orbitals,¹⁸ is red-shifted from 2.2 eV (**2**) to 2.0 eV (**3**). This can be explained by the higher proximity of the cluster units in the layers with respect to the discrete positions (average distances between central μ_6 -bridging Se atoms of adjacent anions are 13.4 Å in **2**, 12.7 Å in **3**), and by weakening of the coordination environment from MnSe₅O to MnSe_{5.5}O_{0.5} on average. Both absorption energies are slightly smaller than the optical gaps in the binary solids MnSe¹⁹ and GeSe₂²⁰ (2.5 eV both), although only very small sections of the respective solids are formally represented in **2** or **3**. Thus, the relative decrease of the optical absorption energies of compounds with ternary M/14/16 anions in comparison to the M/16 or 14/16 binary solids is even more distinct than for related phases with anionic M/Sn/Se² or M/Sn/S^{7b,c} subunits.

Future investigation will focus on reactions of further chalcogenogermanates and chalcogenostannates containing cations of double or higher charge to provoke the formation of

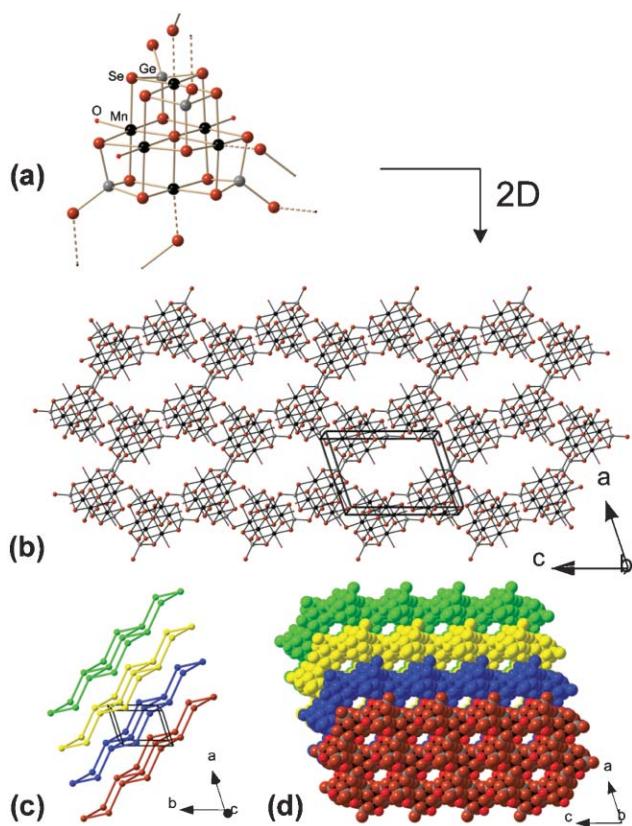


Fig. 3 Structure of one monomeric unit (a) of the ternary anion in **3** (broken bonds represent bonds to adjacent cluster units) and its formal condensation into a layered coordination polymer (b); different representations of the packing of the 2D layers: linkage of cluster centers within four layers viewing down the *c* axis to illustrate the topological relationship to the structure of gray arsenic (c); space-filling representation of four stacked layers viewing down the *b* axis (d).

further types of ternary anions and to study the influence of compositions and structures on opto-electronic or magnetic properties.

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- 11 X-Ray data (203 K, STOE IPDS diffractometer, Ag-K α radiation (**1**, **3**), Mo-K α radiation (**2**), graphite monochromator). **1**: orthorhombic, *Pbca*, *Z*: 8, *a*: 13.916(3) Å, *b*: 15.097(3) Å, *c*: 16.116(3) Å, *V*: 3385.9(12) Å³, *R*: 0.0670, *wR*: 0.1173, *GoF*: 1.003; **2**: rhombohedral, *R3c* (Flack: 0.01(2)), *Z*: 6, *a*: 20.463(3) Å, *c*: 25.119(5) Å, *V*: 9109(3) Å³, *R*: 0.0369, *wR*: 0.0845, *GoF*: 1.051; **3**: triclinic, *P-1*, *Z*: 2, *a*: 12.184(2) Å, *b*: 15.089(3) Å, *c*: 15.868(3) Å, α : 88.732(9)°, β : 73.68(3)°, γ : 71.06(3)°, *V*: 2640.4(9) Å³, *R*: 0.0387, *wR*: 0.1258, *GoF*: 0.822. CCDC 279906, 284719 and 284720. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513305j.
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