Ternary Mn/Ge/Se Anions from Reactions of [Ba₂(H₂O)₉][GeSe₄]:
Synthesis and Characterization of Compounds Containing
Discrete or Polymeric [Mn₆Ge₄Se₁₇]⁶⁻ Units

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SUPPLEMENTARY INFORMATION
Experimental Details:

General procedures: All synthesis steps were performed with strong exclusion of air and external moisture (N₂ atmosphere at a high-vacuum, double-manifold Schlenk line or Ar atmosphere in a glove box). Methanol and THF were dried and freshly distilled prior to use; water was degassed by applying dynamic vacuum (10⁻³ Torr) for several hours. Ba₂[GeSe₄] was prepared as a light yellow, microcrystalline powder in 95% yield by fusing stoichiometric amounts of BaSe, Ge and Se in a sealed quartz ampoule at 900°C.

Synthesis of [Ba₂(H₂O)₉][GeSe₄] (1): 1.000 g (1.5·10⁻³ mol) of crude Ba₂[GeSe₄] are suspended in 50 mL of water and heated to 100°C. A light orange solution is formed besides some gray powder which turned out to be excess Ge. The solution is filtered from the powder and layered by 50 mL of THF, yielding pale yellow crystals of 1. Yield: 1.145 g (1.4·10⁻³ mol, 92% with respect to originally used Ge).

Synthesis of [Ba₃(H₂O)₁₅][Mn₆(H₂O)₆(µ₆-Se)(GeSe₄)₄]·9H₂O (2): 0.083 g (0.1·10⁻³ mol) of 1 are solved in 5 mL of H₂O producing a yellow solution. A colorless solution of 0.019 g (0.1·10⁻³ mol) of MnCl₂·4H₂O in 5 mL of H₂O is added, whereupon the reaction mixture turns intensely orange and traces of orange powder precipitate. After filtration of the precipitate, 10 mL of THF are allowed to slowly diffuse onto the reaction solution. During several days, orange-red rhombic dodecahedra of 2 crystallize. Yield: 0.046 g (0.016·10⁻³ mol, 95% w.r.t. Mn).

Synthesis of [Ba₃(H₂O)₁₆][Mn₆(H₂O)₃(µ₆-Se)(GeSe₄)₄] (3): 0.083 g (0.1·10⁻³ mol) of 1 are solved in 5 mL of H₂O producing a yellow solution. A colorless solution of 0.019 g (0.1·10⁻³ mol) of MnCl₂·4H₂O in 5 mL of methanol is added, whereupon the reaction mixture turns intensely orange and some orange powder precipitates that can be re-dissolved in water and layered by THF to yield 2. After filtration of the precipitate, the solution is layered by 10 mL of THF. Crystallization of red parallelepipeds of 3 is observed after two weeks. Yield: 0.019 g (0.007·10⁻³ mol, 42% w.r.t Mn).

Magnetic susceptibility measurements:
Data were obtained by the use of a Quantum Design SQUID magnetometer (MPMS-XL) on a sample of finely ground single crystals of 2 (m = 14.50 mg). Experimental data were corrected for the sample holder and for the diamagnetic contribution of the samples calculated from Pascal constants.¹
Details of the X-ray structural analyses:

$T = 203 \text{ K, } \text{AgK} \alpha \text{ radiation (1, 3; } \lambda = 0.56087 \text{ Å) or MoK} \alpha \text{ radiation (2; } \lambda = 0.71073 \text{ Å), graphite monochromator, imaging plate detector STOE IPDS. Structure solution by direct methods, full-matrix-least-squares refinement against } F^2; \text{ software used: SHELXS-96 and SHELXL-97.}[2]

$[H_{18}Ba_2GeO_9Se_4]$ (1, $M = 825.275 \text{ g·mol}^{-1}, \text{ light yellow platelet, 0.20×0.16×0.06 mm}^3$): orthorhombic, space group $Pbca$, $Z = 8$, $a = 1391.6(3) \text{ pm, } b = 1509.7(3) \text{ pm, } c = 1611.6(3) \text{ pm, } V = 3385.9(12)\cdot10^6 \text{ pm}^3, \rho(\text{calc.}) = 3.238 \text{ g·cm}^{-3}, 2\theta = 3 – 46^\circ; 11556 \text{ reflections collected, 4530 independent reflections } [R_{\text{int}} = 0.1392], 2380 \text{ with } I > 2\sigma(I); \mu(\text{MoK} \alpha) = 7.926 \text{ mm}^{-1}; \text{ semicemirical absorption correction, } T_{\text{min}}/T_{\text{max}}: 0.24665/0.27764; 147 \text{ parameters (refinement of Ba, Ge, Se and O atomic sites employing anisotropic displacement parameters; H atoms not calculated). Highest/deepest differential peak/hole: 0.476/–0.456 e·10^{-6} \text{ pm}^{-3}. GOF: 1.003. } R \text{ values: } R_1 = 0.0670 \text{ (for } I > 2\sigma(I), \text{ based on } F), wR_2 = 0.1173 \text{ (all data, based on } F^2).$

Figure 1. Thermal ellipsoids drawing of the unit cell of 1 (50% probability). For clarity, some of the $[\text{GeSe}_4]^4 -$ anions (top) and some of the coordination polyhedra around Ba atoms (bottom) are drawn as polyhedra. Selected interatomic distances [Å]: Ge–Se: 2.330(2) – 2.363(2), Ba…Se: 3.3993(16) – 3.4374(19), Ba…O: 2.740(14) – 2.947(9).
\([H_{60}Ba_{3}Ge_{4}Mn_{6}O_{30}Se_{17}]\) (2, \(M = 2914.82\) g\cdot mol\(^{-1}\), fragment of an orange-red rhombic dodecahedron, 0.16×0.16×0.10 mm\(^3\)): rhombohedral, space group \(R\overline{3}c\) (Flack: 0.01(2)), \(Z = 6\), \(a = 2046.3(3)\) pm, \(c = 2511.9(5)\) pm, \(V = 9109(3)\cdot 10^{6}\) pm\(^3\), \(\rho(\text{calc.}) = 3.188\) g\cdot cm\(^{-3}\), 2\(\theta = 4\) – 51\(^\circ\), 40197 reflections collected, 3786 independent reflections \([R_{\text{int}} = 0.1120]\), 3413 with \(I > 2\sigma(I)\); \(\mu(\text{MoK}\alpha) = 15.313\) mm\(^{-1}\); semicempirical absorption correction, \(T_{\text{min}}/T_{\text{max}}: 0.21290/0.31967\); 184 parameters (refinement of Ba, Mn, Ge, Se and O atomic sites employing anisotropic displacement parameters; H atoms not calculated). Highest/deepest differential peak/hole: 0.360/–0.317 e\(^{-}\cdot 10^{-6}\) pm\(^{-3}\). GOF: 1.051. \(R\) values: \(R_1 = 0.0369\) (for \(I > 2\sigma(I)\), based on \(F\)), \(wR_2 = 0.0845\) (all data, based on \(F^2\)).

\textbf{Figure 2.} Thermal ellipsoids drawing of the anion in 2 (50% probability, left hand side) and view of the crystal packing in 2 (inset at top right hand side). Selected interatomic distances [Å]: Mn–(\(\mu_6\)-Se): 2.713(2), 2.7165(19), Mn–(\(\mu_3\)-Se): 2.744(2) – 2.824(2), Mn–O: 2.251(8), 2.353(8), Ge–(\(\mu_3\)-Se): 2.3623(15) – 2.3734(13), Ge–Se\(_{\text{term}}\): 2.328(3), 2.3284(15), Ba…Se: 3.3268(13) – 3.924(2), Ba…O: 2.730(9) – 2.831(7).
$[H_{38}Ba_3Ge_4Mn_6O_{13}Se_{17}]$ (3, $M = 2716.663$ g·mol$^{-1}$, red parallelepiped, $0.14 \times 0.10 \times 0.06$ mm$^3$): triclinic, space group P–1, $Z = 2$, $a = 1218.4(2)$ pm, $b = 1508.9(3)$ pm, $c = 1586.8(3)$ pm, $\alpha = 88.73(3) ^\circ$, $\beta = 73.68(3) ^\circ$, $\gamma = 71.06(3) ^\circ$, $V = 2640.4(9) \times 10^6$ pm$^3$, $\rho(\text{calc.}) = 3.412$ g·cm$^{-3}$, $2 \theta = 3 - 42^\circ$, 11503 reflections collected, 5403 independent reflections [$R_{\text{int}} = 0.0503$], 4802 with $I > 2 \sigma(I)$; $\mu(\text{MoK} \alpha) = 17.580$ mm$^{-1}$; semicempirical absorption correction, $T_{\text{min}}/T_{\text{max}}$: 0.32511/0.79369; 442 parameters (refinement of Ba, Mn, Ge, Se and non-disordered O atomic sites employing anisotropic displacement parameters; two O atoms of water molecules disordered over two positions (assignment of according split positions); refinement of disordered O atomic sites employing isotropic displacement parameters; H atoms not calculated). Highest/deepest differential peak/hole: 1.321/–0.708 e·10$^{-6}$pm$^{-3}$. GOF: 0.822. $R$ values: $R_1 = 0.0387$ (for $I > 2 \sigma(I)$, based on $F$), $wR_2 = 0.1258$ (all data, based on $F^2$).

**Figure 3.** Thermal ellipsoids drawing (50% probability) of one monomeric unit of the anion in 3. Selected interatomic distances [Å]: Mn–($\mu_6$–Se): 2.699(2) – 2.840(2), Mn–($\mu_3$–Se): 2.689(2) – 2.893(2), Mn–($\mu$–Se): 2.781(2) – 2.840(2), Mn–O: 2.284(8) – 2.328(8), Ge–($\mu_3$–Se): 2.3582(16) – 2.3798(16), Ge–($\mu_6$–Se): 2.3168(18) – 2.3283(16), Ge–Se$_{\text{intra}}$: 2.3145(16), ($\mu_6$–Se)…($\mu_6$–Se) (intra-layer): 10.674(6) – 10.807(6), ($\mu_3$–Se)…($\mu_3$–Se) (inter-layer): 11.616(7) – 15.090(9); selected interatomic distances [Å] within the counterion assembly of (O, Se)-coordinated Ba$^{2+}$ cations (Ba…O$_6$Se$_2$ or Ba…O$_6$Se$_3$; not drawn): Ba…Se: 3.3159(10) – 3.5991(10), Ba…O: 2.733(8) – 3.185(9).
Optical absorption spectroscopy:
The optical absorption behavior of the quarternary phases 2 and 3 was investigated on suspensions of the compounds, using a Perkin Elmer Lambda 900 spectrometer. The suspensions have been generated by grinding single crystals in nujol oil between two quartz plates. Figure 4 shows the UV-visible absorption spectra of 2 and 3.

![Absorption spectra](image)

**Figure 4** UV-vis spectra of 2 (dashed line) and 3 (solid line), recorded as suspensions in nujol oil. Onset of absorption is observed at 2.2 eV (2) or 2.0 eV (3), respectively, in agreement with the visible colors of the compounds.
