Supporting Information

**Between Elemental Match and Mismatch: From $K_{12}Ge_{3.5}Sb_6$ to Salts of $(Ge_2Sb_2)^{2-}$, $(Ge_4Sb_{12})^{4-}$, and $(Ge_4Sb_{14})^{4-}$**

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1. **Synthesis details**

1.1 **General**

All manipulations and reactions were performed in dry argon atmosphere using standard Schlenk or glovebox techniques. Ethane-1,2-diamine (en) was distilled from CaH₂ and stored over 3 Å molecular sieves. Toluene (Acros Organics, 99 %) was distilled from sodium-potassium alloy and stored over 3 Å molecular sieves. 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (crypt-222,[¹] Merck) was dried *in vacuo* for at least 18 hours. [AuMePPh₃] was commercially available from Aldrich.

1.2 **Synthesis of compounds**

1.2.1 **Synthesis of K₁₂Ge₃.₅Sb₆ (1)**

K₁₂Ge₃.₅Sb₆ was prepared by fusion of the elements (ratio: 2:1:1) at 950 °C for 48 hours in a niobium tube, sealed within an evacuated silica ampoule. The single-crystalline solid formed alongside some elemental Ge.

1.2.2 **Synthesis of [K(crypt-222)]₂(Ge₂Sb₂·en (2) and [K(crypt-222)]₄(Ge₄Sb₁₂)·2en (3)**

50 mg (0.183 mmol) of 1 and 139.49 mg (0.371 mmol) of crypt-222 were combined in a Schlenk tube and dissolved in en (5 mL). The reaction mixture was allowed to stir for 24 hours. The resulting intense orange solution was filtered through a standard glass frit. Because carefully layering with toluene (15 mL) and storing for crystallization was not successful, the solvent was evaporated until first crystals were visible. The Schlenk tube was then stored for further crystallization at 5 °C. After 1 day, crystals of compound 2 (orange sticks; >85 % of the crystals) and 3 (dark brown ellipsoids; >5 % of the crystals) formed in the Schlenk tube in approx. 70 % yield overall.

1.2.3 **Synthesis of [K(crypt-222)]₄(Ge₄Sb₁₄) (4)**

80 mg (0.293 mmol) of 1, 221 mg (0.578 mmol) of crypt-222 and 37 mg (0.077 mmol) of [AuMePPh₃] were combined in a Schlenk tube and dissolved in en (3 mL). The reaction mixture was allowed to stir for 3 hours. The resulting dark brown solution was filtered through a standard glass frit, carefully layered with toluene (3 mL), and stored for crystallization at 5 °C. After 40 days, block-like metallic black crystals of compound 4 formed at the wall of the Schlenk tube in approx. 20 % yield.
2. Powder X-ray diffraction (PXRD) of $\text{K}_{12}\text{Ge}_{3.5}\text{Sb}_6$ (1)

Powder X-ray diffraction (PXRD) data were collected on a Stoe StadiMP diffractometer system equipped with a Mythen 1 K silicon strip detector and Cu-K\text{α}-radiation ($\lambda = 1.54056$ Å). The sample of 1 was filled into a glass capillary (0.3 mm diameter), which was sealed air-tightly with soft wax. The tube was then mounted onto the goniometer head using wax (horizontal setup) and rotated throughout the measurement. The diffraction pattern is shown in Figure S1.

![PXRD Pattern](image)

**Figure S1.** PXRD pattern of 1 for comparison as measured (green line) and calculated (black line) from the single-crystal CIF deposited as CCDC 2171370. The slight shift of the reflection positions is due to texture effects. With the aim to explain some additional (weak) reflections (e.g., at 16, 17.5 and 25.5, 29, 29.5, 38.5, 39.5, and 45.5°) we compared the PXRD pattern with all known diffraction patterns of solids comprising K, Nb, Ge, or Sb, or any combination of these elements (~170 compounds in the Pearson data base). However, there is no match; we thus assume that the additional reflections stem from at least one so far unidentified minor binary or ternary by-product that seems to be tightly attached to the single crystals we investigated.
3. Single crystal X-ray crystallography (SCXRD)

3.1 General considerations

The data for the X-ray structural analyses were collected at T = 100.0 K with Mo-Kα-radiation (λ = 0.71073 Å) on area detector systems Stoe IPDS/2T for 1, 2 and 4, Cu-Kα-radiation (λ = 1.54186 Å) on an area detector system Stoe StadiVari and T = 150.0 K with Ga-Kα-radiation (λ = 1.34143 Å) on a Stoe StadiVari diffractometer for 3. The structures were solved by dual space methods of SHELXT from SHELXL-2018/136,[2] and refined by full matrix least-squares methods against $F^2$ with the SHELXL program.[3] All hydrogen atoms were kept riding on calculated positions with isotropic displacement parameters $U = 1.2 U_{eq}$ of the bonding partners. The crystal quality of compound 4 was comparably poor. Zintl compounds, especially ones with highly symmetric clusters in them, tend to suffer from some inherent rotational disorder of the clusters, which can result in diffraction data such as the ones observed here. As we could not reproduce this compound so far, we could not collect a better data set. However, we were able to unambiguously determine the crystal structure from it. Crystallographic data for the structures of 1 – 4 (Table S1 – S6) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2171370 – CCDC-2171373. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) + 44 1223/336-033; e-mail: deposit@ccdc.cam.ac.uk]. Supplementary structural figures (Figures S3 – S7) were created with Diamond 4.[4]
Table S1. Crystal data and details of the structure determinations of compound 1 and 2.

| Compound | 1                      | 2                      |
|----------|------------------------|------------------------|
| Empirical formula          | Ge$_{0.29}$K$_{0.5}$Sb$_{0.5}$ | C$_{38}$H$_{40}$Ge$_2$K$_2$Na$_{12}$O$_{12}$Sb$_2$ |
| Formula weight [g mol$^{-1}$] | 121.15                  | 1279.96                |
| Temperature [K]              | 100                     | 100                    |
| Crystal system               | hexagonal               | monoclinic             |
| Space group                  | P$_6_3$/m               | P$_2_1$                |
| a [Å]                        | 13.3366(19)             | 11.9235(5)             |
| b [Å]                        | 13.3366(19)             | 20.4010(6)             |
| c [Å]                        | 5.3594(11)              | 12.4643(5)             |
| α [°]                        | 90                      | 90                     |
| β [°]                        | 90                      | 118.271(3)             |
| γ [°]                        | 120                     | 90                     |
| Volume [Å$^3$]               | 825.5(3)                | 2670.30(19)            |
| Z                             | 12                      | 2                      |
| ρ$_{\text{calc}}$ [g cm$^{-3}$] | 2.924                   | 1.592                  |
| μ [mm$^{-1}$]                | 9.467                   | 2.329                  |
| F(000)                       | 662                     | 1300                   |
| Radiation                    | Mo–Kα ($\lambda = 0.71073$ Å) | Mo–Kα ($\lambda = 0.71073$ Å) |
| 2Θ range for data collection [°] | 3.526 to 53.406          | 3.71 to 58.44          |
| Index ranges                 | –16 ≤ h ≤ 16, –16 ≤ k ≤ 15, | –15 ≤ h ≤ 16, –27 ≤ k ≤ 28, |
|                             | –6 ≤ l ≤ 6             | –17 ≤ l ≤ 17           |
| Reflections collected        | 7288                    | 47254                  |
| Independent reflections      | 650                     | 14393                  |
|                             | [R$_{\text{int}}$ = 0.1336, R$_{\text{sigma}}$ = 0.0458] | [R$_{\text{int}}$ = 0.1151, R$_{\text{sigma}}$ = 0.1067] |
| Data/restraints/parameters   | 650/0/25                | 14393/1/559            |
| Goodness–of–fit on F$^2$    | 1.073                   | 0.885                  |
| Final R indexes [I ≥ 2σ(I)] | R$_1$ = 0.0355, wR$_2$ = 0.0738 | R$_1$ = 0.0440, wR$_2$ = 0.0959 |
| Final R indexes [all data]  | R$_1$ = 0.0464, wR$_2$ = 0.0767 | R$_1$ = 0.0757, wR$_2$ = 0.1030 |
| Largest diff. peak/hole [e Å$^{-3}$] | 1.4/-1.4               | 1.17/-0.93             |
| Flack parameter [5]         | –                       | 0.012(14)              |
| CCDC number                  | 2171370                 | 2171371                |
Table S2. Crystal data and details of the structure determinations of compound 3 and 4.

| Compound | 3              | 4              |
|----------|----------------|----------------|
| Empirical formula | C_{76}H_{160}Ge_{4}K_{4}N_{12}O_{24}Sb_{12} | C_{72}H_{144}Ge_{4}K_{4}N_{8}O_{24}Sb_{14} |
| Formula weight [g mol\(^{-1}\)] | 3533.91 | 3657.2 |
| Temperature [K] | 293(2) | 100 |
| Crystal system | monoclinic | orthorhombic |
| Space group | C2/c | Pbca |
| \(a\) [Å] | 26.4406(6) | 25.2845(6) |
| \(b\) [Å] | 16.3553(5) | 17.6555(6) |
| \(c\) [Å] | 30.4115(7) | 28.4760(7) |
| \(\alpha\) ['\(^\circ\)] | 90 | 90 |
| \(\beta\) ['\(^\circ\)] | 114.632(2) | 90 |
| \(\gamma\) ['\(^\circ\)] | 90 | 90 |
| Volume [Å\(^3\)] | 11954.5(6) | 12712.0(6) |
| \(Z\) | 4 | 4 |
| \(\rho_{\text{calc}}\) [g cm\(^{-3}\)] | 1.964 | 1.911 |
| \(\mu\) [mm\(^{-1}\)] | 16.185 | 4.036 |
| \(F(000)\) | 6832 | 6968 |
| Radiation | Ga–Ka–K\(\alpha\) (\(\lambda = 1.34143\) Å) | Mo–K\(\alpha\) (\(\lambda = 0.71073\) Å) |
| 2\(\Theta\) range for data collection ['\(^\circ\)] | 5.562 to 124.994 | 2.86 to 49.998 |
| Index ranges | \(-31 \leq h \leq 16, -21 \leq k \leq 19, -31 \leq l \leq 40\) | \(-29 \leq h \leq 30, -20 \leq k \leq 20, -33 \leq l \leq 31\) |
| Reflections collected | 36521 | 72060 |
| Independent reflections | 13877 | 11165 |
| \([R_{\text{int}} = 0.0409, R_{\text{sigma}} = 0.0495]\) | \([R_{\text{int}} = 0.1165, R_{\text{sigma}} = 0.0734]\) |
| Data/restraints/parameters | 13877/0/609 | 11165/1188/568 |
| Goodness–of–fit on \(F^2\) | 1.048 | 0.944 |
| Final \(R\) indexes \([I \geq 2\sigma(I)]\) | \(R_1 = 0.0600, wR_2 = 0.1793\) | \(R_1 = 0.0933, wR_2 = 0.2668\) |
| Final \(R\) indexes \([\text{all data}]\) | \(R_1 = 0.0868, wR_2 = 0.1892\) | \(R_1 = 0.1598, wR_2 = 0.2978\) |
| Largest diff. peak/hole [e Å\(^{-3}\)] | 1.4/-1.4 | 1.17/-0.93 |
| CCDC number | 2171372 | 2171373 |
3.2 Structure details

3.2.1 Structure details of $K_{12}Ge_4Sb_6$ (1)

Table S3. Selected interatomic distances (in Å) and bond angles (in degrees) of the experimental and optimized structures of the anion in 1. Geometry optimization of the anion in 1 was performed in point group $D_{3h}$.

| Atom1 | Atom2 | Distance (exp) | Distance (calc) |
|-------|-------|----------------|-----------------|
| Sb1   | Ge1   | 2.5676(6)      | 2.56            |

| Atom1 | Atom2 | Atom3 | Angles (exp) | Angles (calc) |
|-------|-------|-------|--------------|---------------|
| Sb1   | Ge1   | Sb1'  | 120.0        | 120.0         |
| Sb1   | Ge1   | Sb1'' | 120.0        | 120.0         |
| Sb1'  | Ge1   | Sb1'' | 120.0        | 120.0         |

$^{1}$-X,1-Y,1-Z; $^{*}$+X,+Y,1+Z

Figure S2. Fourier-Map of the Ge–Ge unit of compound 1.
3.2.2 Structure details of \([\text{K(crypt-222)}]_2(\text{Ge}_2\text{Sb}_2)\cdot\text{en}\) (2)

![Unit cell of compound 2 viewed along the crystallographic a axis. H atoms have been omitted for clarity.](image)

**Figure S3.** Unit cell of compound 2 viewed along the crystallographic a axis. H atoms have been omitted for clarity.

**Table S4.** Selected interatomic distances (in Å) and bond angles (in degrees) of the experimental and optimized structures of the anion in 2. Geometry optimization of the anion in 2 was performed in point group \(C_{2v}\).

| Atom1 | Atom2 | Distance (exp) | Distance (calc) |
|-------|-------|----------------|-----------------|
| Sb1   | Sb2   | 2.7889(8)      | 2.83            |
| Sb1   | Ge1   | 2.7057(10)     | 2.73            |
| Sb1   | Ge2   | 2.7013(12)     | 2.73            |
| Sb2   | Ge1   | 2.6945(9)      | 2.73            |
| Sb2   | Ge2   | 2.6943(9)      | 2.73            |
| Ge1   | Ge2   | 2.5317(11)     | 2.55            |

| Atom1 | Atom2 | Atom3 | Angles (exp) | Angles (calc) |
|-------|-------|-------|--------------|---------------|
| Ge1   | Sb1   | Sb2   | 58.71(2)     | 58.82         |
| Ge2   | Sb1   | Sb2   | 58.75(3)     | 58.82         |
| Ge2   | Sb1   | Ge1   | 55.84(3)     | 55.56         |
| Ge1   | Sb2   | Sb1   | 59.10(2)     | 58.82         |
| Ge2   | Sb2   | Ge1   | 56.04(3)     | 55.56         |
| Sb2   | Ge1   | Sb1   | 62.19(2)     | 62.36         |
| Ge2   | Ge1   | Sb1   | 61.99(3)     | 62.22         |
| Ge2   | Ge1   | Sb2   | 61.97(3)     | 62.22         |
| Sb2   | Ge2   | Sb1   | 62.25(2)     | 62.36         |
| Ge1   | Ge2   | Sb1   | 62.17(3)     | 62.22         |
| Ge1   | Ge2   | Sb2   | 61.98(3)     | 62.22         |
3.2.4 Structure details of \([K(\text{crypt}-222)]_4(\text{Ge}_4\text{Sb}_{12})\cdot2\text{en}\) (3)

**Figure S4.** Molecular structure of the \((\text{Ge}_4\text{Sb}_{12})^{-4}\) anion in 3 with full labelling scheme and indication of the 50%:50% positional disorder of Sb7, Sb8, and Ge3/Sb9 (semi-transparent atoms and bonds). Thermal ellipsoids are shown at 30% probability.

**Figure S5.** Unit cell of compound 3 viewed along the crystallographic \(b\) axis. H atoms have been omitted for clarity.
Table S5. Selected interatomic distances (in Å) and bond angles (in degrees) of the experimental and optimized structures of the anion in 3. The calculated bond lengths and angles are given for the energetically favored isomer I. Geometry optimization of the anion in 3 was performed without any symmetry restrictions.

| Atom1 | Atom2 | Distance (exp) | Distance (calc) |
|-------|-------|----------------|-----------------|
| Ge1   | Ge1\(^1\) | 2.4538(17)     | 2.47            |
| Ge1   | Sb2\(^1\) | 2.5827(11)     | 2.64            |
| Ge1   | Ge2/Sb1 | 2.5822(11)     | 2.47            |
| Ge1   | Sb8    | 2.5214(14)     | 2.65            |
| Ge1\(^1\) | Ge3/Sb9 | 2.6682(16)     | 2.50            |
| Sb5   | Sb4'/Ge4' | 2.7613(8)     | 2.79            |
| Sb5   | Sb4/Ge4 | 2.7612(8)      | 2.79            |
| Sb2   | Sb3    | 2.7908(7)      | 2.88            |
| Sb2   | Sb4'/Ge4' | 2.7952(7)     | 2.88            |
| Sb3   | Sb4/Ge4 | 2.7874(8)      | 2.84            |
| Sb3   | Ge2/Sb1 | 2.8103(8)      | 2.73            |
| Ge2/Sb1 | Sb6/Ge5 | 2.7872(9)      | 2.75            |
| Sb6/Ge5 | Sb7   | 2.5758(17)     | 2.88            |
| Sb6/Ge5 | Ge3/Sb9 | 2.6789(14)    | 2.73            |
| Sb7   | Sb8    | 2.8732(18)     | 2.89            |
| Sb7   | Ge3/Sb9 | 2.7613(17)     | 2.73            |

| Atom1  | Atom2  | Atom3  | Angles (exp) | Angles (calc) |
|--------|--------|--------|--------------|---------------|
| Ge1\(^1\) | Ge1    | Sb2\(^1\) | 109.29(3)     | 109.5         |
| Ge1\(^1\) | Ge1    | Ge2/Sb1 | 101.72(6)     | 107.0         |
| Ge1\(^1\) | Ge1    | Sb8    | 98.79(4)      | 97.1          |
| Ge1    | Ge1\(^1\) | Ge3/Sb9 | 108.85(5)     | 109.9         |
| Sb2    | Ge1\(^1\) | Ge3/Sb9 | 101.57(5)     | 107.2         |
| Ge2/Sb1 | Ge1    | Sb2\(^1\) | 111.59(4)     | 114.9         |
| Sb1'/Ge2' | Ge1\(^1\) | Ge3/Sb9 | 123.50(5)     | 121.5         |
| Sb8    | Ge1    | Sb2\(^1\) | 122.87(5)     | 110.4         |
| Sb8    | Ge1    | Ge2/Sb1 | 109.75(5)     | 114.9         |
| Sb4/Ge4 | Sb5    | Sb4'/Ge4' | 95.89(3)      | 96.9          |
| Ge1\(^1\) | Sb2    | Sb3    | 94.56(3)      | 92.5          |
| Ge1\(^1\) | Sb2    | Sb4'/Ge4' | 96.63(3)      | 100.7         |
| Sb3    | Sb2    | Sb4'/Ge4' | 105.86(2)     | 104.5         |
| Sb2    | Sb3    | Ge2/Sb1 | 107.92(2)     | 110.3         |
| Sb4/Ge4 | Sb3    | Sb2    | 100.25(2)     | 100.2         |
| Sb4/Ge4 | Sb3    | Ge2/Sb1 | 94.04(2)      | 93.3          |
| Atom1  | Atom2     | Atom3    | Angles (exp) | Angles (calc) |
|--------|-----------|----------|-------------|---------------|
| Sb5    | Sb4/Ge4   | Sb2'     | 102.42(2)   | 102.9         |
| Sb5    | Sb4/Ge4   | Sb3      | 100.88(2)   | 101.8         |
| Sb3    | Sb4/Ge4   | Sb2'     | 103.49(2)   | 102.3         |
| Ge1    | Ge2/Sb1   | Sb3      | 89.60(3)    | 88.7          |
| Ge1    | Ge2/Sb1   | Sb6/Ge5  | 95.35(3)    | 90.9          |
| Sb6/Ge5| Ge2/Sb1   | Sb3      | 106.73(3)   | 101.9         |
| Sb1'/Ge2'| Sb6'/Ge5'| Sb8      | 103.43(3)   | 104.5         |
| Sb7    | Sb6/Ge5   | Ge2/Sb1  | 105.76(4)   | 105.0         |
| Sb7    | Sb6/Ge5   | Ge3/Sb9  | 63.37(5)    | 58.3          |
| Ge3/Sb9| Sb6/Ge5   | Ge2/Sb1  | 108.36(4)   | 114.5         |
| Sb6/Ge5| Sb7       | Sb8      | 106.90(5)   | 104.6         |
| Sb6/Ge5| Sb7       | Ge3/Sb9  | 60.14(4)    | 58.2          |
| Ge3/Sb9| Sb7       | Sb8      | 105.36(5)   | 106.9         |
| Ge1    | Sb8       | Sb6'/Ge5'| 95.37(4)    | 98.8          |
| Ge1    | Sb8       | Sb7      | 94.64(5)    | 89.5          |
| Sb7    | Sb8       | Sb6'/Ge5'| 108.22(5)   | 104.8         |
| Ge1'   | Ge3/Sb9   | Sb6/Ge5  | 97.22(4)    | 92.3          |
| Ge1'   | Ge3/Sb9   | Sb7      | 95.25(5)    | 95.6          |
| Sb6/Ge5| Ge3/Sb9   | Sb7      | 56.50(4)    | 63.6          |

\[1\] ^{1-X,+Y,3/2-Z}
3.2.5 Structure details of \([K(\text{crypt-222})_4(Ge_4Sb_{14})]\) (4)

**Figure S6.** Molecular structure of the \((Ge_4Sb_{14})^4^-\) anion in 4 with full labelling scheme. Thermal ellipsoids are shown at 30% probability.

**Figure S7.** Unit cell of compound 4 viewed along the crystallographic \(b\) axis. H atoms have been omitted for clarity.
Table S6. Selected interatomic distances (in Å) and bond angles (in degrees) of the experimental and optimized structures of the anion in 4. Geometry optimization of the anion in 4 was performed in point group $C_{2h}$.

| Atom1  | Atom2   | Distance (exp) | Distance (calc) |
|--------|---------|----------------|-----------------|
| Sb1/Ge3 | Sb3/Ge5 | 2.7785(19)     | 2.89            |
| Sb1/Ge3 | Sb6/Ge8 | 2.778(2)       | 2.86            |
| Sb1/Ge3 | Ge1'    | 2.582(2)       | 2.65            |
| Sb3/Ge5 | Sb4/Ge6 | 2.8129(19)     | 2.88            |
| Sb3/Ge5 | Ge2/Sb8 | 2.777(2)       | 2.71            |
| Sb2/Ge4 | Sb4/Ge6 | 2.8012(19)     | 2.86            |
| Sb2/Ge4 | Sb7/Ge9 | 2.761(2)       | 2.89            |
| Sb2/Ge4 | Ge1     | 2.563(2)       | 2.65            |
| Sb4/Ge6 | Sb5     | 2.758(2)       | 2.79            |
| Sb5    | Sb6/Ge8 | 2.784(2)       | 2.79            |
| Ge2/Sb8 | Sb7'/Ge9' | 2.748(2)    | 2.71            |
| Ge2/Sb8 | Ge1     | 2.534(3)       | 2.46            |
| Sb6/Ge8 | Sb7/Ge9 | 2.795(2)       | 2.88            |
| Ge1    | Ge1'    | 2.425(4)       | 2.54            |

| Atom1 | Atom2 | Atom3   | Angles (exp) | Angles (calc) |
|-------|-------|---------|--------------|---------------|
| Ge1   | Ge2/Sb8 | Sb3/Ge5 | 88.58(6)     | 89.4          |
| Ge1   | Ge2/Sb8 | Sb7'/Ge9' | 87.68(6)   | 89.4          |
| Ge1   | Sb2/Ge4 | Sb4/Ge6 | 94.77(5)     | 92.1          |
| Ge1   | Sb1/Ge3 | Sb7/Ge9 | 95.06(6)     | 91.9          |
| Ge1   | Sb1/Ge3 | Sb3/Ge5 | 96.55(5)     | 91.9          |
| Ge1   | Sb1/Ge3 | Sb6/Ge8 | 93.33(6)     | 92.1          |
| Ge1   | Ge1    | Ge2/Sb8 | 105.57(9)    | 108.7         |
| Ge1   | Ge1    | Sb1'/Ge3' | 106.06(9)  | 106.0         |
| Ge1   | Ge1    | Sb2/Ge4 | 106.85(10)   | 106.0         |
| Ge2/Sb8 | Sb3/Ge5 | Sb1/Ge3 | 107.20(5)    | 113.2         |
| Ge2/Sb8 | Sb3/Ge5 | Sb4/Ge6 | 94.93(5)     | 93.7          |
| Ge2'/Sb8' | Sb7/Ge9 | Sb2/Ge4 | 109.25(6)    | 93.7          |
| Ge2''/Sb8'' | Sb7/Ge9 | Sb6/Ge8 | 95.36(6)     | 113.2         |
| Ge2/Sb8 | Ge1    | Sb1'/Ge3' | 116.05(7)  | 114.3         |
| Ge2/Sb8 | Ge1    | Sb2/Ge4 | 115.37(7)    | 114.3         |
| Sb1/Ge3 | Sb3/Ge5 | Sb2/Ge4 | 98.75(5)     | 95.5          |
| Sb1/Ge3 | Sb6/Ge8 | Sb7/Ge9 | 103.89(5)    | 102.7         |
| Sb1/Ge3 | Sb6/Ge8 | Sb5     | 101.85(5)    | 98.9          |
Table S6 (continued)

| Atom1          | Atom2          | Atom3          | Angles (exp) | Angles (calc) |
|----------------|----------------|----------------|--------------|---------------|
| Sb2/Ge4        | Sb4/Ge6        | Sb3/Ge5        | 102.99(5)    | 102.7         |
| Sb2/Ge4        | Sb7/Ge9        | Sb6/Ge8        | 97.92(5)     | 95.5          |
| Sb2/Ge4        | Ge1            | Sb1'/Ge3'      | 106.22(6)    | 106.8         |
| Sb3/Ge5        | Sb1/Ge3        | Sb6/Ge8        | 107.80(5)    | 110.7         |
| Sb4/Ge6        | Sb5            | Sb6/Ge8        | 95.30(5)     | 97.3          |
| Sb5            | Sb4/Ge6        | Sb3/Ge5        | 101.93(5)    | 105.7         |
| Sb5            | Sb4/Ge6        | Sb2/Ge4        | 100.77(5)    | 98.9          |
| Sb5            | Sb6/Ge8        | Sb7/Ge9        | 102.20(6)    | 105.7         |
| Sb7/Ge9        | Ge2'/Sb8'      | Sb3'/Ge5'      | 114.89(6)    | 106.7         |
| Sb7/Ge9        | Sb2/Ge4        | Sb4/Ge6        | 108.83(6)    | 110.7         |

1-X,1-Y,2-Z
4. Micro X-ray fluorescence spectroscopy (µ-XFS) analysis

4.2 Micro-X-ray fluorescence spectroscopy (µ-XFS) analysis of 1, 2 and 3

All µ-XFS measurements were performed on single crystal samples with a Bruker M4 Tornado, equipped with an Rh-target X-ray tube, poly capillary optics and a Si drift detector. The emitted fluorescence photons are detected with an acquisition time of 180 s. Quantification of the elements is achieved through deconvolution of the spectra. Results are summarized in Table S7. Figures S8–S10 show the spectra for 1 – 3 along with the results of the deconvolution algorithm. Several measurements produced unreasonably large values for the % K. Removal of K from the calculations afforded excellent agreement with the expected atomic ratio of close to Ge\textsubscript{2.00}Sb\textsubscript{2.00} in 2, and Ge\textsubscript{4.00}Sb\textsubscript{12.00}, respectively. It is a typical finding though for such compounds, the reasons for which could not be clarified so far. Measurements of compound 4 were not possible owing to the failure to reproduce it to date.

Table S7. µ-XFS analysis of 1, 2 and 3 (K, Ge, Sb).

|     | Element | Element wt % | Atom % | Element ratio observed | Element ratio calc |
|-----|---------|--------------|--------|------------------------|-------------------|
| 1   | K-K     | 33.78        | 56.78  | 13.8                   | 12.00             |
|     | Ge-K    | 20.47        | 18.53  | 4.5                    | 3.50              |
|     | Sb-L    | 45.75        | 24.69  | 6                      | 6.00              |
|     | Total   | 100.00       | 100.00 |                        |                   |
| 2   | K-K     | 24.20        | 44.64  | 3.45                   | 2.00              |
|     | Ge-K    | 26.07        | 25.90  | 2.00                   | 2.00              |
|     | Sb-L    | 49.47        | 29.46  | 2.27                   | 2.00              |
|     | Total   | 100.00       | 100.00 |                        |                   |
| 3   | K-K     | 11.27        | 26.27  | 5.67                   | 4.00              |
|     | Ge-L    | 14.42        | 18.10  | 3.90                   | 4.00              |
|     | Sb-L    | 74.31        | 55.63  | 12.00                  | 12.00             |
|     | Total   | 100.00       | 100.00 |                        |                   |
Figure S8. Micro X-ray fluorescence spectrum of 1 with the results of the deconvolution algorithm.

Figure S9. Micro X-ray fluorescence spectrum of 2 with the results of the deconvolution algorithm.
Figure S10. Micro X-ray fluorescence spectrum of compound 3 with the results of the deconvolution algorithm.
5. Electrospray ionization mass spectrometry (ESI-MS) investigations of the extraction process of

5.1 Methods

In order to explore the possible formation pathway, we prepared a series of reactive extraction solutions of K₁₂Ge₃.₅Sb₆ (1) in en, like those from which compounds 2 and 3 were crystallized. The reaction solutions were allowed to stir for 5 minutes, 30 minutes, 3 hours, 1 day, 1 week and 2 weeks, before the measurements.

All mass spectra were recorded with a Thermo Fischer Scientific Finnigan LTQ-FT spectrometer in negative ion mode. The solutions were injected into the spectrometer with gastight 250 µL Hamilton syringes by syringe pump infusion. All capillaries within the system were washed with dry en/toluene mixture (1:1) 2 hours before and at least 10 min in between measurements to avoid decomposition reactions and consequent clogging.

The following ESI parameters were used: Spray Voltage: 3.6 kV, Capillary Temp: 290 °C, Capillary Voltage: −20 kV, Tube lens Voltage: −121.75 kV, Sheath Gas: 45, Sweep Gas: 0, Auxiliary Gas: 40. Assignable high-resolution mass peaks are shown in Figures S11–S21.

5.1.1 Mass spectra of the reaction solution yielding 2 and 3 (5 min)

Figure S11. Overview of ESI(−) mass spectrum recorded immediately upon injection of a fresh reaction solution yielding 2 and 3 in en (5 min).
Figure S12. High-resolution ESI mass spectrum in negative ion mode recorded immediately upon injection of a fresh reaction solution yielding 2 and 3 in en (5 min), indicating the existence of (HGe\textsubscript{2}Sb\textsubscript{2})\textsuperscript{−}. Topmost: measured, below: simulated.

Figure S13. High-resolution ESI mass spectrum in negative ion mode recorded immediately upon injection of a fresh reaction solution yielding 2 and 3 in en (5 min), indicating the existence of (GeSb\textsubscript{3})\textsuperscript{−}. Topmost: measured, below: simulated.
5.1.2 Mass spectra of the reaction solution yielding 2 and 3 (30 min)

Figure S14. Overview of ESI(−) mass spectrum recorded immediately upon injection of a fresh reaction solution yielding 2 and 3 in en (30 min).

Figure S15. High-resolution ESI mass spectrum in negative ion mode recorded immediately upon injection of a fresh reaction solution yielding 2 and 3 in en (30 min), indicating the existence of Sb$_5^-$_. Topmost: measured, below: simulated.
Figure S16. High-resolution ESI mass spectrum in negative ion mode recorded immediately upon injection of a fresh reaction solution yielding 2 and 3 in en (30 min), indicating the existence of Sb$_7^-$
Topmost: measured, below: simulated.

5.1.3 Mass spectra of the reaction solution yielding 2 and 3 (3 h)

Figure S17. Overview of ESI(−) mass spectrum recorded immediately upon injection of a fresh reaction solution yielding 2 and 3 in en (3 h).
Figure S18. High-resolution ESI mass spectrum in negative ion mode recorded immediately upon injection of a fresh reaction solution yielding \(2\) and \(3\) in en (30 min), indicating the existence of Sb\(_9^{-}\). Topmost: measured, below: simulated.

5.1.4 Mass spectra of the reaction solution yielding \(2\) and \(3\) (1 d)

Figure S19. Overview of ESI(−) mass spectrum recorded immediately upon injection of a fresh reaction solution yielding \(2\) and \(3\) in en (1 d).
5.1.5 Mass spectra of the reaction solution yielding 2 and 3 (1w and 2w)

Figure S20. Overview of ESI(−) mass spectrum recorded immediately upon injection of a fresh reaction solution yielding 2 and 3 in en (1 w).

Figure S21. Overview of ESI(−) mass spectrum recorded immediately upon injection of a fresh reaction solution yielding 2 and 3 in en (2 w).
6. Quantum Chemical Investigations

6.1 Methods of the DFT Studies of the Solid State Compound 1

Structural optimization based on the crystallographic data was conducted using the Vienna Ab initio Simulation Package (VASP)\(^5\) with a 1×1×2 supercell to model the unusual distribution of the sub-occupied Ge2 and Ge3 atoms along the c-axis. Subsequent bond analysis was conducted with the help of the Local Orbital Basis Suite Towards Electronic Structure Reconstruction (LOBSTER)\(^6\) package by projecting the PAW-based\(^7\) wavefunctions onto a local orbital basis. This allowed for the calculation of Löwdin charges\(^8\) and bond orders as expressed in the crystal orbital bond index (COBI).\(^9\)

6.2 Methods of the DFT Studies of Molecular Anions

Simultaneous optimization of the geometric and electronic structures of the anions in 1 – 4 were undertaken using the program system Turbomole V7.5.1.\(^10-11\) Density functional theory (DFT)\(^12\) methods were employed throughout these studies. We employed the TPSS functional\(^13\) and basis sets of quality dhf-TZVP\(^14\) with additional use of auxiliary basis sets\(^15\) and effective core potentials\(^16\) at the Sb atoms. Negative charges were compensated with the conductor-like screening model (COSMO).\(^17\) Partial charges were calculated by means of Mulliken\(^18\) and natural population analyses (NPA).\(^19\) Localized molecular orbitals were obtained according to Boys' method.\(^20\)

The anions in 1 – 4 were initially optimized without any symmetry restrictions and later re-optimized with higher symmetry point groups, where appropriate (1: \(D_{3h}\), 2: \(C_{2v}\), 4: \(C_{2h}\)). Calculation of force constants with the module NumForce verified all structures to be minima on the potential energy hypersurface.

6.3 Details of the Quantum Chemical Investigations of Compound 1

The chosen convergence criteria for the VASP structure optimization were \(10^{-8}\) eV for electronic and \(5 \cdot 10^{-3}\) eV Å for ionic iteration steps whereas the kinetic energy cutoff was 500 eV. The VASP-recommended PAW pseudopotentials were chosen for these calculations using a \(k\)-point mesh of 0.02 to 0.04 Å\(^{-1}\) with Blöchl’s tetrahedron integration method\(^21\) and a smearing factor of 0.05 eV. In addition, the solid-state-optimized generalized gradient approximation (GGA)\(^22\) and the Becke-Johnson dampened D3-Method to approximate the van-der-Waals interactions\(^23\) were chosen.
Figure S22. Comparison of the canonical MOs of the anion in 1 with \((\text{CO}_3)^{2-}\). Geometry optimizations were performed in point group \(D_{3h}\). Contour values are drawn at ±0.05 a.u.
6.4 Details of the Quantum Chemical Investigations of Compound 2

Figure S23. Computationally optimized structure and representative localized molecular orbitals (LMOs) of the anion in 2. Contour values are drawn at ±0.05 a.u.

Figure S24. Canonical molecular orbitals of the anion in 2. Contour values are drawn at ±0.05 a.u.
6.5 Details of the Quantum Chemical Investigations of the Anion in 3

**Figure S25.** Overview of the 20 computationally obtained isomers of the anion in 3.
Figure S26. Localized molecular orbitals (LMOs) of the most stable isomer of the anion in 3 (isomer I in Figure S25), representing different two-center (a-v) and one-center (w-ak) interactions: Ge–Ge bonds (a–c), Ge–Sb bonds (d–k), Sb–Sb bonds (l–v), lone-pairs at a Ge atom (w, x) and at Sb atoms (y-ak). Contour values are drawn at ±0.05 a.u.
Figure S27. Canonical molecular orbitals of the most stable isomer of the anion in 3 (isomer I in Figure S25). Contour values are drawn at ±0.03 a.u.
6.6 Details of the Quantum Chemical Investigations of the Anion in 4

Figure S28. Representative localized molecular orbitals (LMOs) of the most stable isomer of the anion in 4, representing different two-center (a-h) and one-center (i, j) interactions: Ge–Ge bonds (a–b), Ge–Sb bonds (c–d), Sb–Sb bonds (e–h), and of the lone-pair at Ge atoms (i) and at μ-bridging Sb atoms (j). Contour values are drawn at ±0.05 a.u.
Figure S29. Canonical molecular orbitals of the most stable isomer of the anion in compound 4. Contour values are drawn at ±0.03 a.u.
Figure S30. Calculated isomers of (Ge₄P₁₄)⁺⁺ and relative energies ΔE with respect to the global minimum structure.
Figure S31. Calculated isomers of (Ge₄As₁₄)⁴⁻ and relative energies ΔE with respect to the global minimum structure.
Figure S32. Calculated isomers of (Ge₄Sb₁₄)⁴⁻ (anion in 4) and relative energies ΔE with respect to the global minimum structure.
Figure S33. Calculated isomers of \((\text{Ge}_2\text{Bi}_{14})^{4-}\) and relative energies \(\Delta E\) with respect to the global minimum structure.
7. References for the Supporting Information

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