Atom Exchange Versus Reconstruction: \((\text{Ge}_x\text{As}_{4-x})^{x^-}(x = 2, 3)\) as Building Blocks for the Supertetrahedral Zintl Cluster \([\text{Au}_6(\text{Ge}_3\text{As})(\text{Ge}_2\text{As}_2)_3]^{3^-}\)

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1. **Synthesis Details**

1.1 **General**

All manipulations and reactions were performed under dry Ar atmosphere using standard Schlenk or glovebox techniques. All solvents were dried and freshly distilled prior to use, crypt-222 (Merck) was dried in vacuo for at least 18 hours. \([\text{K(crypt-222)}]_2(\text{Ge}_2\text{As}_2)\cdot \text{en}\) \((\text{Ge}/\text{As}, \text{Sn}/\text{Bi}, \text{Sn}/\text{Sb} \text{and} \text{Pb}/\text{Sb})\) were prepared according to literatures, respectively. \(\text{[(PPh}_3\text{)AuMe]}\) was commercially available from Aldrich. Samples were shielded from ambient light throughout cluster syntheses.

1.2 **Syntheses**

1.2.1. **Synthesis of** \([\text{K(crypt-222)}]_2[\text{Au}(\text{Ge}_3\text{As})(\text{Ge}_2\text{As}_2)]_3\cdot \text{en}\cdot 2\text{tol} (1)\)

80 mg (0.067 mmol) of \([\text{K(crypt-222)}]_2(\text{Ge}_2\text{As}_2)\cdot \text{en}\) and 48 mg (0.10 mmol) of \(\text{[(PPh}_3\text{)AuMe]}\) were combined in a Schlenk tube and dissolved in en (3 mL). The initially red solution slowly changed to dark brown. 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 15 days, block-like crystals of compound 1 formed at the wall of the Schlenk tube in appr. 6 % yield (Figure S1).

![Crystal photograph of 1](image)

Figure S1. Crystal photograph of 1.

1.2.2. **Synthesis of** \([\text{K(crypt-222)}]_4[[\text{AuSn}_3\text{Bi}_3]]_2\cdot 2\text{py} (2)\)

80 mg (0.052 mmol) of \([\text{K(crypt-222)}]_2(\text{Sn}_2\text{Bi}_2)\cdot \text{en}\) and 25 mg (0.052 mmol) of \(\text{[(PPh}_3\text{)AuMe]}\) were combined in a Schlenk tube and dissolved in pyridine (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 15 days, plate-like crystals of compound 2 formed at the wall of the Schlenk tube in appr. 15 % yield (Figure S2).
1.2.3. Synthesis of [K(crypt-222)]₄[[AuSnSb₃]₂]·2py (3)

80 mg (0.058 mmol) of [K(crypt-222)]₂(Sn₂Sb₂)-en and 28 mg (0.058 mmol) of [(PPh₃)AuMe] were combined in a Schlenk tube and dissolved in pyridine (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 15 days, plate-like crystals of compound 3 formed at the wall of the Schlenk tube in appr. 25 % yield (Figure S3).

1.2.4. Synthesis of [K(crypt-222)]₄[[AuPbSb₃]₂]·3en (4)

80 mg (0.052 mmol) of [K(crypt-222)]₂(Sn₂Sb₂)-en and 24 mg (0.052 mmol) of [(PPh₃)AuMe] 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 15 days, needle-like crystals of compound 4 formed at the wall of the Schlenk tube in appr. 31 % yield (Figure S4).
Figure S4. Crystal photograph of 4.
2. Single crystal X-ray crystallography (SCXRD)

2.1. Single Crystal X-ray Diffraction

The data for the X-ray structural analyses were collected at T = 100.0 K with Mo-Kα-radiation (λ = 0.71073 Å) on a Bruker D8Quest with a CMOS detector for 1 and 3, and on an area detector systems Stoe IPDS/2T for 4, and at T = 100(2) K with Cu Kα-radiation (λ = 1.5418 Å) on a STOE STADIVARI with an image plate detector for 2. The structure was solved by methods of SHELXT from SHELXL-2018/136 and refined by full matrix least-squares methods against \( F^2 \) with the SHELXL program. All hydrogen atoms were kept riding on calculated positions with isotropic displacement parameters \( U = 1.2 U_{eq} \) of the bonding partners. In the refinement of compounds 1 and 5, atoms Ge/As or Sn/Sb were assigned according to the result of the perturbation theory results based on the DFT investigations. The relatively large tendency for disorder of the crypt-222 molecules in compounds 2 and 3 required the application of restraints to this large number of atoms (the alternative application of the back-Fourier-transform method did not produce more reliable results). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-2008055 – CCDC-2008058. 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]. The crystal data and experimental parameters of the structure determinations are collected in Table S1, structural parameters are given in Tables S2-S5. Structure Figures (Figures S5-S8) were created with Diamond 4.

2.2. Details of Structures

Table S1. Crystal data and details of the structure determinations of 4 compounds.

| Compound | 1 | 2 | 3 | 4 |
|----------|---|---|---|---|
| Empirical formula | \( \text{Cs}_4\text{H}_{12}\text{As} \cdot \text{Au} \cdot \text{Ge} \cdot \text{K} \cdot \text{Na}_2 \cdot \text{O}_7 \cdot \text{S}_2 \) | \( \text{Cs}_6\text{H}_{14}\text{Au} \cdot \text{Ba} \cdot \text{K} \cdot \text{Na}_2 \cdot \text{O}_7 \cdot \text{S}_2 \cdot \text{Sn}_2 \) | \( \text{Cs}_4\text{H}_{12}\text{Au} \cdot \text{K} \cdot \text{Na}_2 \cdot \text{O}_7 \cdot \text{S}_2 \cdot \text{Sn}_2 \) | \( \text{Cs}_5\text{H}_{17}\text{Au} \cdot \text{K} \cdot \text{Na}_2 \cdot \text{O}_7 \cdot \text{P}_2 \cdot \text{Sb}_2 \) |
| Formula weight /g mol\(^{-1}\) | 3880.72 | 4789.26 | 4269.95 | 5043.02 |
| Temperature /K | 100 | 100 | 100 | 100 |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | C2/c | P2\(1/2\)/n | P2\(1/2\)/n | P2\(1/2\)/c |
| a /Å | 42.051(19) | 19.480(4) | 19.4134(11) | 15.610(3) |
| b /Å | 23.7223(11) | 15.790(3) | 15.690(9) | 26.030(5) |
| c /Å | 26.8265(12) | 21.809(4) | 21.9347(12) | 17.170(3) |
| \( \beta \) | 90 | 90 | 90 | 90 |
| \( \beta \) | 90 | 90 | 90 | 90 |
| Volume /Å\(^3\) | 23841.0(18) | 6662(2) | 6614.7(6) | 6371(3) |
| Z | 8 | 2 | 2 | 2 |
| \( \rho_{\text{calc}} \) g/cm\(^3\) | 2.237 | 2.388 | 2.144 | 2.629 |
| \( \mu \) /mm\(^{-1}\) | 12.368 | 12.107 | 5.448 | 16.888 |
| \( F(000) \) | 14520 | 4400 | 4028 | 4580 |
| Radiation | MoKα (\( \lambda = 0.71073 \)) | MoKα (\( \lambda = 0.71073 \)) | MoKα (\( \lambda = 0.71073 \)) | MoKα (\( \lambda = 0.71073 \)) |
| 2\( \theta \) range for data collection/° | 4.606 to 56.768 | 3.334 to 53.246 | 4.562 to 49.656 | 5.05 to 53.552 |
| Index ranges | \( -56 \leq h \leq 56, -31 \leq k \leq 31, -35 \leq l \leq 35 \) | \( -24 \leq h \leq 10, -19 \leq k \leq 19, -22 \leq l \leq 22, -18 \leq k \leq 18, -19 \leq h \leq 19, -32 \leq k \leq 32, -21 \leq l \leq 21 \) |
| Refinements collected | 353257 | 41523 | 195355 | 47750 |
| Independent reflections | 288377 [\( R_w = 0.0699, R_{\text{factor}} \) = 0.0308] | 13272 [\( R_w = 0.0888, R_{\text{factor}} \) = 0.1592] | 11375 [\( R_w = 0.0781, R_{\text{factor}} \) = 0.0285] | 13488 [\( R_w = 0.0997, R_{\text{factor}} \) = 0.0836] |
| Data/restraints/parameters | 288370/1904 | 13272/1270/676 | 11375/546/694 | 13488/6/625 |
| Goodness-of-fit on \( F^2 \) | 1.012 | 0.73 | 1.12 | 0.95 |
| Final R indexes \( [F \geq 2 \sigma (F)] \) | \( R_1 = 0.0298, wR_2 = 0.0583 \) | \( R_1 = 0.0509, wR_2 = 0.1122 \) | \( R_1 = 0.0474, wR_2 = 0.1147 \) | \( R_1 = 0.0351, wR_2 = 0.0735 \) |
| Final R indexes \( [\text{all data}] \) | \( R_1 = 0.0511, wR_2 = 0.0650 \) | \( R_1 = 0.1337, wR_2 = 0.1374 \) | \( R_1 = 0.0667, wR_2 = 0.1287 \) | \( R_1 = 0.0603, wR_2 = 0.0780 \) |
| Largest diff. peak/hole \( \sigma / \AA \) | 1.39/1.13 | 1.41/1.74 | 2.03/1.42 | 2.37/1.90 |
| CCDC deposition number | 2008058 | 2008055 | 2008057 | 2008056 |
Figure S5. Unit cell of compound 1.

Table S2. Selected interatomic distances (in Å) of the experimental and optimized structures of the anion in 1.

| Bond type          | Measured bond length | Calculated bond length | Au6-Ge/As9   | As/Ge1-Ge/As1 |
|--------------------|----------------------|-------------------------|--------------|---------------|
| Au1-As/Ge3        | 2.5497(6)            | 2.594                   | 2.5616(5)    | 2.4581(8)     |
| Au1-Ge/As1        | 2.5662(6)            | 2.573                   | 2.4467(8)    | 2.473         |
| Au1-Ge/As2        | 2.5540(6)            | 2.558                   | 2.4500(7)    | 2.480         |
| Au1-Ge/As5        | 2.5629(6)            | 2.607                   | 2.4572(8)    | 2.440         |
| Au2-As/Ge5        | 2.5546(5)            | 2.599                   | 2.4361(8)    | 2.484         |
| Au2-Ge/As2        | 2.5548(5)            | 2.562                   | 2.4523(8)    | 2.509         |
| Au2-Ge/As3        | 2.5629(5)            | 2.577                   | 2.8053(7)    | 2.797         |
| Au2-Ge/As7        | 2.5644(5)            | 2.612                   | 2.8036(8)    | 2.757         |
| Au3-As/Ge7        | 2.5589(5)            | 2.595                   | 2.4470(7)    | 2.448         |
| Au3-Ge/As1        | 2.5493(5)            | 2.574                   | 2.4561(7)    | 2.485         |
| Au3-Ge/As3        | 2.5535(5)            | 2.560                   | 2.4453(7)    | 2.503         |
| Au3-Ge/As9        | 2.5438(5)            | 2.611                   | 2.8020(7)    | 2.768         |
| Au4-As/Ge3        | 2.5582(6)            | 2.582                   | 2.8071(7)    | 2.755         |
| Au4-As/Ge7        | 2.5474(5)            | 2.578                   | 2.4559(7)    | 2.443         |
| Au4-Ge/As4        | 2.5465(6)            | 2.570                   | 2.4514(7)    | 2.483         |
| Au4-Ge/As8        | 2.5615(6)            | 2.573                   | 2.4396(7)    | 2.503         |
| Au5-Ge/As4        | 2.5513(5)            | 2.580                   | 2.8170(7)    | 2.801         |
| Au5-Ge/As5        | 2.5533(6)            | 2.585                   | 2.8052(7)    | 2.751         |
| Au5-Ge/As6        | 2.5584(5)            | 2.582                   | Ge/As1-Ge/As2| 2.7954(7)    |
| Au5-Ge/As7        | 2.5369(5)            | 2.583                   | Ge/As1-Ge/As3| 2.8099(7)    |
| Au6-As/Ge5        | 2.5609(6)            | 2.594                   | Ge/As2-Ge/As3| 2.8016(7)    |
| Au6-Ge/As6        | 2.5474(5)            | 2.604                   | Ge/As4-Ge/As5| 2.7879(8)    |
| Au6-Ge/As8        | 2.5599(6)            | 2.554                   | Ge/As6-Ge/As7| 2.8279(7)    |
Figure S6. Unit cell of compound 2.

Table S3. Selected interatomic distances (in Å) of the experimental and optimized structures of the anion in 2.

| Bond type       | Measured bond length | Calculated bond length |
|-----------------|----------------------|------------------------|
| Sn1–Sn2         | 3.1558(18)           | 3.157                  |
| Sn3–Sn4         | 2.9553(19)           | 2.986                  |
| Sn3–Sn5         | 3.0627(19)           | 3.128                  |
| Sn4–Sn5         | 3.0606(17)           | 3.129                  |
| Bi1–Sn1         | 3.0481(15)           | 3.067                  |
| Bi1–Sn2         | 3.0485(16)           | 3.069                  |
| Bi1–Sn3         | 3.0080(18)           | 3.048                  |
| Bi1–Sn4         | 3.0405(15)           | 3.044                  |
| Bi2–Sn1         | 2.9913(16)           | 3.004                  |
| Bi2–Sn3         | 2.9909(16)           | 3.025                  |
| Bi2–Sn5         | 3.0350(16)           | 3.045                  |
| Bi3–Sn2         | 2.9673(15)           | 3.004                  |
| Bi3–Sn4         | 2.9827(16)           | 3.023                  |
| Bi3–Sn5         | 3.0115(18)           | 3.043                  |
| Au1–Sn1         | 3.1665(15)           | 3.135                  |
| Au1–Sn1'        | 2.7609(16)           | 2.816                  |
| Au1–Sn2         | 3.2123(14)           | 3.132                  |
| Au1–Sn2'        | 2.7766(14)           | 2.818                  |
| Au1–Bi2         | 2.8448(14)           | 2.846                  |
| Au1–Bi3         | 2.8507(11)           | 2.845                  |
| Au1–Au1'        | 2.8833(16)           | 2.898                  |
| Au1–Sn5         | 2.9584(15)           | 2.904                  |
Figure S7. Unit cell of compound 3.

Table S4. Selected interatomic distances (in Å) of the experimental and optimized structures of the anion in 3.

| Bond type                  | Measured bond length | Calculated bond length |
|----------------------------|----------------------|------------------------|
| Sn/Sb1–Sn/Sb2             | 3.169(3)             | 3.190                  |
| Sn/Sb3–Sn/Sb4             | 2.9864(10)           | 3.011                  |
| Sn/Sb3–Sn/Sb5             | 3.0832(11)           | 3.138                  |
| Sn/Sb4–Sn/Sb5             | 3.0685(10)           | 3.137                  |
| Sb/Sn1–Sn/Sb1             | 2.949(5)             | 2.987                  |
| Sb/Sn1–Sn/Sb2             | 2.911(2)             | 2.986                  |
| Sb/Sn1–Sn/Sb3             | 2.952(3)             | 2.968                  |
| Sb/Sn1–Sn/Sb4             | 2.942(3)             | 2.971                  |
| Sb/Sn2–Sn/Sb1             | 2.942(4)             | 2.924                  |
| Sb/Sn2–Sn/Sb3             | 2.8983(10)           | 2.938                  |
| Sb/Sn2–Sn/Sb5             | 2.9516(11)           | 2.972                  |
| Sb/Sn3–Sn/Sb2             | 2.8953(10)           | 2.924                  |
| Sb/Sn3–Sn/Sb4             | 2.9044(10)           | 2.939                  |
| Sb/Sn3–Sn/Sb5             | 2.9408(11)           | 2.972                  |
| Au1--Sn/Sb1               | 3.183(3)             | 3.182                  |
| Au1--Sn/Sb1\(^{i}\)       | 2.767(2)             | 2.808                  |
| Au1--Sn/Sb2               | 3.2248(8)            | 3.183                  |
| Au1--Sn/Sb2\(^{i}\)      | 2.7884(8)            | 2.809                  |
| Au1--Sn/Sb3               | 2.7607(8)            | 2.769                  |
| Au1--Sn/Sb3\(^{i}\)      | 2.7664(8)            | 2.771                  |
| Au1--Au1\(^{i}\)         | 2.8907(8)            | 2.886                  |
| Au1--Sn/Sb5               | 2.9407(8)            | 2.901                  |
Figure S8. Unit cell of compound 4.

Table S5. Selected interatomic distances (in Å) of the experimental and optimized structures of the anion in 4.

| Bond type   | Measured bond length | Calculated bond length |
|-------------|----------------------|------------------------|
| Pb1–Pb2    | 3.3114(7)            | 3.318                  |
| Pb3–Pb4    | 3.1444(7)            | 3.194                  |
| Pb3–Pb5    | 3.2285(7)            | 3.306                  |
| Pb4–Pb5    | 3.2268(7)            | 3.305                  |
| Sb1–Pb1    | 3.0573(8)            | 3.098                  |
| Sb1–Pb2    | 3.0703(13)           | 3.098                  |
| Sb1–Pb3    | 3.0101(9)            | 3.041                  |
| Sb1–Pb4    | 3.0213(8)            | 3.043                  |
| Sb2–Pb1    | 2.9571(9)            | 3.025                  |
| Sb2–Pb3    | 2.9912(9)            | 3.016                  |
| Sb2–Pb5    | 3.0028(9)            | 3.044                  |
| Sb3–Pb2    | 2.9817(8)            | 3.024                  |
| Sb3–Pb4    | 2.9811(12)           | 3.017                  |
| Sb3–Pb5    | 3.0035(10)           | 3.043                  |
| Au1···Pb1  | 3.2236(6)            | 3.178                  |
| Au1···Pb1¹  | 2.8951(12)           | 2.926                  |
| Au1···Pb2  | 3.2418(8)            | 3.181                  |
| Au1···Pb2¹  | 2.8671(7)            | 2.926                  |
| Au1···Sb2  | 2.7475(10)           | 2.769                  |
| Au1···Sb3  | 2.7293(8)            | 2.772                  |
| Au1···Au1  | 2.8957(8)            | 2.870                  |
| Au1···Pb5  | 3.0528(10)           | 2.984                  |
3. Energy Dispersive X-ray Spectroscopy (EDS) Analysis and Micro-X-ray Fluorescence Spectroscopy (µ-XFS) Analysis

3.1. Energy Dispersive X-ray Spectroscopy (EDS) of 1

EDS analysis of 1 was carried out using an EDS-device Voyager 4.0 of Noran Instruments coupled with an electron microscope CamScan CS 4DV. Data acquisition was performed with an acceleration voltage of 25 kV and 100 s accumulation time. Results are summarized in Table S6 and illustrated in Figure S9. Note that the deviation of the K content is observed very frequently in EDS analyses of these very air-sensitive Zintl cluster compounds.

Table S6. EDS analysis of 1 (K, Au, Ge, As).

| Element | Element wt % | Weight % err. (1 sigma) | Atom % | Element ratio observed | Element ratio calc |
|---------|--------------|-------------------------|--------|------------------------|-------------------|
| K-K     | 2.57         | 1.78                    | 6.82   | 1.55                   | 3.00              |
| Au-L    | 49.97        | 1.38                    | 26.32  | 6.00                   | 6.00              |
| Ge-K    | 25.82        | 1.09                    | 36.89  | 8.41                   | 9.00              |
| As-K    | 21.64        | 0.10                    | 29.97  | 6.83                   | 7.00              |
| Total   | 100.00       | 0.10                    | 100.00 | 100.00                 |                   |

Figure S9. EDS analysis of 1.

3.2. Micro-X-ray Fluorescence Spectroscopy (µ-XFS) Analysis

All µ-XFS measurements were performed with a Bruker M4 Tornado, equipped with an Rh-target X-ray tube and a Si drift detector. The emitted fluorescence photons are detected with an acquisition time of 100 s. Quantification of the elements is achieved through deconvolution of the spectra. Results are summarized in Table S7. Figures S10-S12 present the spectra for 2–4 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 $\text{Au}_{2.00}\text{Sn}_{10.00}\text{Pn}_{6.00}$ in 2–4. We assume that accumulation of K at the crystal surface upon exposure to air is responsible for the anomalous results. This is observed commonly for very these very air-sensitive compounds.

Table S7. µ-XFS analysis of 2 - 4 (K, Au, Sn, Pb, Sb, Bi).

| Element | Element wt % | Weight % err. (1 sigma) | Atom % | Element ratio observed | Element ratio calc |
|---------|--------------|-------------------------|--------|------------------------|-------------------|
| 2       |              |                         |        |                        |                   |
| K-K     | 15.11        | 0.00                    | 41.36  | 14.11                  | 4.00              |
| Au-L    | 10.78        | 0.00                    | 5.86   | 2.00                   | 2.00              |
| Sn-L    | 38.01        | 0.00                    | 34.28  | 11.70                  | 10.00             |
| Bi-L    | 36.11        | 0.00                    | 18.50  | 6.31                   | 6.00              |
| Total   | 100.00       |                         | 100.00 |                        |                   |
| 3       |              |                         |        |                        |                   |
| K-K     | 11.55        | 0.00                    | 30.01  | 7.80                   | 4.00              |
| Au-L    | 14.90        | 0.00                    | 7.69   | 2.00                   | 2.00              |
| Sn-L    | 41.96        | 0.00                    | 35.93  | 9.34                   | 10.00             |
| Sb-L    | 31.59        | 0.00                    | 26.37  | 6.86                   | 6.00              |
| Total   | 100.00       |                         | 100.00 |                        |                   |
| 4       |              |                         |        |                        |                   |
| K-K     | 4.10         | 0.00                    | 16.22  | 3.32                   | 4.00              |
| Au-L    | 12.44        | 0.00                    | 9.77   | 2.00                   | 2.00              |
| Pb-L    | 61.20        | 0.00                    | 45.71  | 9.36                   | 10.00             |
| Sb-L    | 22.27        | 0.00                    | 28.30  | 5.79                   | 6.00              |
| Total   | 100.00       |                         | 100.00 |                        |                   |

Figure S10. Micro X-ray fluorescence spectrum of 2 with the results of the deconvolution algorithm. Colors are used as follows: K (pink), Au (red), Sn (light blue), Bi (green).
Figure S11. Micro X-ray fluorescence spectrum of compound 3 with the results of the deconvolution algorithm. Colors are used as follows: K (light blue), Au (red), Sn (green), Sb (yellow).

Figure S12. Micro X-ray fluorescence spectrum of compound 4 with the results of the deconvolution algorithm. Colors are used as follows: K (green), Au (red), Pb (blue), Sb (light blue).
4. Electrospray ionization mass spectrometry (ESI-MS) Investigations

4.1. Methods

All mass spectra were recorded with a Thermo Fisher Scientific Finnigan LTQ-FT spectrometer in negative ion mode. We prepared a fresh reaction solution of the reaction leading to compound 1 in DMF, and solutions of single crystals of the compounds 2–4 in freshly distilled DMF inside a glovebox. 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 DMF for 2 hours before and at least 10 minutes 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, Tube lens Voltage: −121.75, Sheath Gas: 45, Sweep Gas: 0, Auxiliary Gas: 40. Assignable high-resolution mass peaks are shown in Figures S13-S31.

4.2. Mass spectra of the reaction solution yielding 1

ESI-MS measurements on single crystals of 1 failed, which we attribute to its larger molar mass in combination with a rather coordination-type bonding. Yet, we were able to identify important species in the reaction solution, which indicate the co-existence of (Ge₂As₂)²⁻ (in protonated, monoanionic form), (Ge₃As)³⁻, and also (GeAs)⁻. The latter is not part of the cluster anion, yet must form alongside of (Ge₃As)³⁻, according to equation (1) provided in the main document. Hence, we can take the spectra as further indication of the correctness of our findings. The high resolution images of the said species are provided in Figures S13-S17. Note that ESI mass spectra of Zintl anions always show monoanions, even though the original charge was higher.

Figure S13. Overview of ESI(−) mass spectrum recorded immediately upon injection of a fresh reaction solution of 1 in DMF.
Figure S14. High-resolution ESI mass spectrum in negative ion mode recorded immediately upon injection of a fresh reaction solution of 1 in DMF, indicating the coexistence of (Ge$_3$As)$^-$ and (GeAs$_3$)$^-$ . Topmost: measured, below: simulated.

Figure S15. High-resolution ESI mass spectrum in negative ion mode recorded immediately upon injection of a fresh reaction solution of 1 in DMF, indicating the coexistence of (Ge$_3$As)$^-$ and (Ge$_2$As$_2$H)$^-$. Topmost: measured, below: simulated.
Figure S16. High-resolution ESI mass spectrum in negative ion mode recorded immediately upon injection of a fresh reaction solution of 1 in DMF, indicating the coexistence of (Ge$_3$As)$^-$ and (Ge$_2$As$_2$H)$^-$, and (GeAs)$_3^−$. Topmost: measured, below: simulated.

Figure S17. High-resolution ESI mass spectrum in negative ion mode recorded immediately upon injection of a fresh reaction solution of 1 in DMF, indicating the occurrence of (Ge$_2$As$_2$H)$^−$. Top: measured, bottom: simulated.
4.3. Mass spectra of 2

Figure S18. Overview of ESI(−) mass spectrum recorded immediately upon injection of a fresh solution of 2 in DMF.

Figure S19. High-resolution ESI mass spectrum in negative ion mode of \((\text{SnBi}_3)^-\), recorded immediately upon injection of a fresh solution of 2 in DMF. Top: measured, bottom: simulated.
Figure S20. High-resolution ESI mass spectrum in negative ion mode of \((\text{SnBi}_3)^-\), recorded immediately upon injection of a fresh solution of 2 in DMF. Top: measured, bottom: simulated.

Figure S21. High-resolution ESI mass spectrum in negative ion mode of \((\text{AuSn}_4\text{Bi}_4)^-\), recorded immediately upon injection of a fresh solution of 2 in DMF. Top: measured, bottom: simulated.
Figure S22. High-resolution ESI mass spectrum in negative ion mode of (AuSn₄Bi₂)⁻, recorded immediately upon injection of a fresh solution of 2 in DMF. Top: measured, bottom: simulated.

4.4. Mass spectra of 3

Figure S23. Overview of ESI(−) mass spectrum recorded immediately upon injection of a fresh solution of 3 in DMF.
Figure S24. High-resolution ESI mass spectrum in negative ion mode of (Sn₆Sb₃)⁻, recorded immediately upon injection of a fresh solution of 3 in DMF. Top: measured, bottom: simulated.

Figure S25. High-resolution ESI mass spectrum in negative ion mode of (AuSn₄Sb₄)⁻, recorded immediately upon injection of a fresh solution of 3 in DMF. Top: measured, bottom: simulated.
Figure S26. High-resolution ESI mass spectrum in negative ion mode of \((\text{AuSn}_5\text{Sb}_6)^-\), recorded immediately upon injection of a fresh solution of 3 in DMF. Top: measured, bottom: simulated.

4.5. Mass spectra of 4

Figure S27. Overview of ESI(−) mass spectrum recorded immediately upon injection of a fresh solution of 4 in DMF.
Figure S28. High-resolution ESI mass spectrum in negative ion mode of \((\text{PbSb}_3)^-\), recorded immediately upon injection of a fresh solution of 3 in DMF. Top: measured, bottom: simulated.

Figure S29. High-resolution ESI mass spectrum in negative ion mode of \((\text{PbSb}_3)^-\), recorded immediately upon injection of a fresh solution of 3 in DMF. Top: measured, bottom: simulated.
Figure S30. High-resolution ESI mass spectrum in negative ion mode of \((\text{AuPb}_4\text{Sb}_4)^-\), recorded immediately upon injection of a fresh solution of 3 in DMF. Top: measured, bottom: simulated.

Figure S31. High-resolution ESI mass spectrum in negative ion mode of \((\text{AuPb}_6\text{Sb}_2)^-\), recorded immediately upon injection of a fresh solution of 3 in DMF. Top: measured, bottom: simulated.
5. Quantum Chemical Investigations

5.1. Methods

All calculations were undertaken by employing density functional theory (DFT) methods as implemented in the program system TURBOMOLE V7.1.1.6,7 We applied the TPSS functional.8 The used basis sets were of the quality def2-TZVP (for the exchange reactions) and dhf-TZVP (for the study of the four dimeric anions [(AuPbBi₃)₂]⁻ and 2–4).9 We additionally used the corresponding auxiliary basis sets10 and effective core potentials at Sn, Pb, Sb, Bi, and Au atoms.11

The bonding situation – in particular that of the Au atoms – was examined by means of population analyses based on occupation numbers (Paboon)12 and upon inspection of localized molecular orbitals (LMOs).13 The pictures of the LMOs were created with gOpenMol.14

5.2 Reaction Energies for the Exchange Reactions

Table S8. Reaction energies for the exchange reactions, $E_{XR}$, corresponding to the first step of equation (1) in the main document.\textsuperscript{a} Tt indicates the involved tetrel atom, Pn indicates the involved pnictogen atom.

| Tt   | Pn | $E_{XR}$ / kJ mol\textsuperscript{−1} |
|------|----|----------------------------------|
| Si   | P  | −66.16                           |
|      | As | −61.03                           |
|      | Sb | −51.92                           |
|      | Bi | −34.99                           |
| Ge   | P  | −111.43                          |
|      | As | −110.23                          |
|      | Sb | −107.17                          |
|      | Bi | −91.00                           |
| Sn   | P  | −40.90                           |
|      | As | −50.20                           |
|      | Sb | −59.44                           |
|      | Bi | −49.24                           |
| Pn   | P  | −30.26                           |
|      | As | −41.62                           |
|      | Ab | −57.38                           |
|      | Bi | −49.27                           |

\textsuperscript{a} 2 (Tt₂Pn₂)²⁻ $\iff$ (Tt₃Pn)³⁻ + (TtPn₃)⁻
Table S9. Geometrical consideration of pseudo-tetrahedral anions (Tt₅Pn₄ₓ)²⁻. A denotes the atomic radii (in Å)¹⁵ of the Tt atoms: 1.11 (Si), 1.20 (Ge), 1.39 (Sn), 1.46 (Pb). B denotes the atomic radii (in Å)¹⁵ of the Pn atoms: 1.07 (P), 1.19 (As), 1.39 (Sb), 1.48 (Bi).

| Tt/Pn  | \(\frac{|B-A|}{(B+A)}\) | \(\frac{(B-A)}{(B+A)}\) |
|--------|---------------------|---------------------|
| Si/P   | 0.018               | -0.018              |
| Si/As  | 0.035               | 0.035               |
| Si/Sb  | 0.112               | 0.112               |
| Si/Bi  | 0.143               | 0.143               |
| Ge/P   | 0.057               | -0.057              |
| Ge/As  | 0.004               | -0.004              |
| Ge/Sb  | 0.073               | 0.073               |
| Ge/Bi  | 0.104               | 0.104               |
| Sn/P   | 0.130               | -0.130              |
| Sn/As  | 0.076               | -0.076              |
| Sn/Sb  | 0.000               | 0.000               |
| Sn/Bi  | 0.031               | 0.031               |
| Pb/P   | 0.154               | -0.154              |
| Pb/As  | 0.102               | -0.102              |
| Pb/Sb  | 0.025               | -0.025              |
| Pb/Bi  | 0.007               | 0.007               |

5.3 Calculated Minimum Structure of \{[AuPb₅Bi₃]₂\}⁴⁻

Figure S32 shows the calculated minimum structure of \{[AuPb₅Bi₃]₂\}⁴⁻ and gives the corresponding structural data. The atom labelling corresponds to Figure 5 in the manuscript.

![Figure S32. Calculated minimum structure for \{[AuPb₅Bi₃]₂\}⁴⁻. Selected distances are given in Å: Pb1–Pb2 3.29, Pb3–Pb4 3.15, Pb(3,4)–Pb5 3.28, Bi1–Pb(1,2) 3.18, Bi1–Pb(3,4) 3.11, Bi(2,3)–Pb(1,2) 3.11, Bi(2,3)–Pb(3,4) 3.10, Bi(2,3)–Pb5 3.11, Au1–Au1¹ 2.92, Au1–Pb(1,2) 3.16, Au1–Pb(1¹,2) 2.96, Au1–Bi(2,3) 2.87.](image-url)
5.4 Bonding situation of the Au atoms

The results of the Paboon analysis are provided in Table S10.

Table S10. Calculated shared electron (SEN) numbers for the Au···Au contacts in the anions \([\text{[AuTt}_2\text{Pn}_2]_2]^{2−}\) (Tt: Sn, Pb; Pn: Sb, Bi) and averaged SEN numbers for the Tt–Tt bonds for comparison.

| Anion | Bond          | SEN  |
|-------|---------------|------|
| \([\text{[AuSn}_2\text{Sb}_2]_2]^{2−}\) | Au···Au | 0.1152 |
|       | Ω(Sn–Sn)     | 0.8871 |
| \([\text{[AuSn}_2\text{Bi}_2]_2]^{2−}\) | Au···Au | 0.1246 |
|       | Ω(Sn–Sn)     | 0.9249 |
| \([\text{[AuPb}_2\text{Sb}_2]_2]^{2−}\) | Au···Au | 0.1579 |
|       | Ω(Pb–Pb)     | 0.7661 |
| \([\text{[AuPb}_2\text{Bi}_2]_2]^{2−}\) | Au···Au | 0.1416 |
|       | Ω(Pb–Pb)     | 0.8045 |

Figures S33–S35 show the localized molecular orbitals (LMOs) of \([\text{[AuPb}_5\text{Sb}_2]_2]^{4−}\) with largest contributions from the Au atoms, mainly involved in three-center bonds with two main group atoms. These LMOs look qualitatively the same for all four isostructural anions \([\text{[AuTt}_3\text{Pn}_3]_2]^{4−}\) studied herein. Additional aurophilic interactions between the two Au atoms may be present, but the fact that the two subunits hold together, obviously may be rationalized without them.

Figure S33. Localized molecular orbital of the 3-center interaction between the atoms Pb1, Bi2, and Au1 (Pb: yellow, Pb: blue, Au: purple; contours drawn at ±0.048 a.u.).
Figure S34. Localized molecular orbital of the 3-center interaction between the atoms Pb5′, Bi2′, and Au1′ (Pb: yellow, Pb: blue, Au: purple; contours drawn at ±0.048 a.u.).

Figure S35. Localized molecular orbital of the 3-center interaction between the atoms Pb1′, Pb2′, and Au1 (Pb: yellow, Pb: blue, Au: purple; contours drawn at ±0.048 a.u.).
6. References for the Supporting Information

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