



Dalton Transactions

Supporting Information

Smallest Molecular Chalcogenidometalate Anions of the Heaviest Metals: Syntheses, Structures, and their Interconversion

G. Thiele,^a C. Donsbach,^a R. Riedel,^a M. Marsch,^a K. Harms,^a and S. Dehnen^{*a}

^aFachbereich Chemie, Wissenschaftliches Zentrum für Materialwissenschaften, Philipps-Universität Marburg, Hans-Meerwein-Straße, D-35043 Marburg, Germany, email: dehnen@chemie.uni-marburg.de

SUPPLEMENTARY INFORMATION

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Supplementary details on single crystal X-ray crystallography

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Supplementary details on single crystal X-ray diffraction

X-ray diffraction experiments. K_3BiSe_3 has been reported before, data for completeness only.^[1] Data of the X-ray structure analysis: T = 100 K (**1-7**, **9**, K_3BiSe_3) or 293 K (**8**), graphite monochromator (mirror optics for **9**), imaging plate detector Stoe IPDS2T (**1**, **4-6**), IPDS2 (**2**, **3**, **7**, K_3BiSe_3), IPDS (**8**) or Bruker Quest (**9**). All structures were solved by direct methods in WinGX^[2] and OLEX2^[3] refined by full-matrix least-squares refinement against F^2 in SHELXL-2014/7.^[4] Absorption correction were performed numerically including shape optimization with STOE X-Area^[5] (**1-8**, K_3BiSe_3) or semi-empirically with Bruker SADABS (multi-scan, **9**).^[6] Tables S1 – S4 summarize the crystallographic data of all crystalline compounds. CCDC 1430781 (**1**), 1430782 (**2**), 1430783 (**3**), 1430784 (**4**), 1430785 (**5**), 1430786 (**6**), 1430787 (**7**), 1430788 (**8**), 1430789 (**9**), and 1430790 (K_3BiSe_3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Refinement details and crystallographic information for compounds **1-10** are listed in Table S1-S3. Supplementary structure figures are provided in Figures S1-S13.

Table S1. Crystallographic and refinement details for Compounds **1 – 3**.

Compound	$\text{K}_4[\text{HgSe}_3]\cdot\text{H}_2\text{O}$ (1)	$\text{K}_4[\text{HgTe}_3]\cdot\text{H}_2\text{O}$ (2)	$\text{K}_{10}\text{Na}_2[\text{HgTe}_3]_2(\text{HCO}_2)_3$ (3)
Empirical formula	HgK_4OSe_3	HgK_4OTe_3	$\text{C}_3\text{Hg}_2\text{K}_{10}\text{Na}_2\text{O}_6\text{Te}_6$
Formula weight /g·mol ⁻¹	609.87	755.79	1735.79
Crystal color and shape	Clear yellow block	Metallic black block	Red stick
Crystal size /mm	0.09·0.13·0.15	0.03·0.05·0.07	0.07·0.08·0.26
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1$	$P2_12_12_1$	$C2/m$
a /Å	8.4929(4)	9.0201(4)	14.4612(11)
b /Å	9.6479(3)	10.1697(4)	11.0898(11)
c /Å	13.1996(6)	14.0216(7)	9.9243(8)
β /°	90.066(4)		93.367(10)
V /Å ³	1081.56(8)	1286.23(10)	1588.8(2)
Z	4	4	2
$\rho_{\text{calc}}/\text{g}\cdot\text{cm}^{-3}$	3.745	3.903	3.628
$\mu(\text{MoK}\alpha)/\text{mm}^{-1}$	25.801	19.876	16.405
2θ range/°	4.22–63.86	4.94–58.25	4.11–53.29
Abs. corr. $T_{\text{min}}/T_{\text{max}}$	0.2342 / 0.6341	0.2743 / 0.6320	0.0980 / 0.4974
Reflections measured	25771	25063	10793
Independent reflections	7227	3449	1777
$R(\text{int})$	0.0955	0.0620	0.0455
Independent reflections ($I > 3\sigma(I)$)	6656	3363	1712
Parameters	165	84	81
$R_1(I > 3\sigma(I))$	0.0498	0.0220	0.0215
wR_2 (all data)	0.1174	0.0480	0.0496
Goof (all data)	1.006	1.055	1.081
Max. peak / hole /e ⁻ ·10 ⁻⁶ ·pm ⁻³	2.775 / -6.997	1.064 / -0.935	0.155 / -1.249
CCDC number	1430781	1430782	1430783

Table S2. Crystallographic and refinement details for Compounds 4 – 6.

Compound	K ₂ [HgSe ₂]·H ₂ O (4)	K ₆ [Tl ₂ Se ₆]·2H ₂ O (5)	K ₆ [Tl ₂ Se ₆]·2K ₂ CO ₃ (6)
Empirical formula	HgK ₂ OSe ₂	K ₆ O ₂ Se ₆ Tl ₂	C ₂ K ₁₀ O ₆ Se ₆ Tl ₂
Formula weight /g·mol ⁻¹	452.71	1149.10	1393.52
Crystal color and shape	Orange block	Red plates	Orange block
Crystal size /mm	0.09·0.10·0.11	0.03·0.05·0.27	0.04·0.09·0.12
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	12.0228(7)	7.6343(9)	7.2063(7)
<i>b</i> /Å	7.7956(5)	8.3256(10)	8.6457(8)
<i>c</i> /Å	7.4526(4)	8.4777(10)	10.6249(10)
α /°		94.535(10)	70.120(7)
β /°	92.853(4)	103.250(9)	88.516(8)
γ /°		108.831(9)	79.234(8)
<i>V</i> /Å ³	697.63(7)	489.53(11)	611.06(10)
<i>Z</i>	4	1	1
ρ_{calc} /g·cm ⁻³	4.310	3.898	3.787
$\mu(\text{MoK}\alpha)$ /mm ⁻¹	33.572	28.849	23.824
2 θ range/°	3.39–55.99	5.01–53.42	4.08–53.22
Abs. corr. <i>T</i> _{min} / <i>T</i> _{max}	0.0080 / 0.1879	0.0607 / 0.4403	0.0664 / 0.3569
Reflections measured	4436	3592	5713
Independent reflections	1475	1696	2570
<i>R</i> (int)	0.0864	0.1028	0.1418
Independent reflections (<i>I</i> > 3 σ (<i>I</i>))	1304	1471	2449
Parameters	56	74	119
<i>R</i> ₁ (<i>I</i> > 3 σ (<i>I</i>))	0.0429	0.0600	0.0658
<i>wR</i> ₂ (all data)	0.1084	0.1603	0.1773
Goof (all data)	1.050	1.034	1.094
Max. peak / hole /e ⁻ ·10 ⁻⁶ ·pm ⁻³	4.190 / -2.746	2.872 / -2.399	4.761 / -5.063
CCDC number	1430784	1430785	1430786

Table S3. Crystallographic and refinement details for Compounds **7** – **9**.

Compound	$\text{K}_{0.94}\text{Tl}_{0.06}[\text{TlSe}_2]$ (7)	$\{\text{K}_5[\text{TlTe}_4]\cdot 2\text{KOH}\}_3\cdot 10\text{H}_2\text{O}$ (8)	$\text{K}_4[\text{PbSe}_4]\cdot \text{en}\cdot \text{H}_2\text{O}$ (9)
Empirical formula	$\text{K}_{0.94}\text{Se}_2\text{Tl}_{1.06}$	$\text{K}_{21}\text{O}_{16}\text{Te}_{12}\text{Tl}_3$	$\text{C}_2\text{H}_{10}\text{K}_4\text{N}_2\text{OPbSe}_4$
Formula weight / $\text{g}\cdot\text{mol}^{-1}$	410.89	3221.41	757.55
Crystal color and shape	Black block	Red block	Red block
Crystal size /mm	0.08-0.10-0.12	0.20-0.21-0.30	0.08-0.10-0.13
Crystal system	Tetragonal	Trigonal	Triclinic
Space group	$I4/mcm$	$R\bar{3}c$	$P\bar{1}$
$a/\text{\AA}$	8.0075(12)	16.9135(16)	8.0377(5)
$b/\text{\AA}$			8.1958(5)
$c/\text{\AA}$	7.0104(9)	39.226(6)	12.6944(7)
$\alpha/^\circ$			92.602(2)
$\beta/^\circ$			102.770(2)
$\gamma/^\circ$			93.193(2)
$V/\text{\AA}^3$	449.51(15)	9718(2)	812.87(8)
Z	4	6	2
$\rho_{\text{calc}}/\text{g}\cdot\text{cm}^{-3}$	6.072	3.303	3.095
$\mu(\text{MoK}\alpha)/\text{mm}^{-1}$	54.829	14.126	20.333
2θ range/ $^\circ$	7.19-53.34	4.81-51.01	4.98-54.31
Abs. corr. $T_{\text{min}}/T_{\text{max}}$	0.0091 / 0.1154	0.0125 / 0.0816	0.2086 / 0.7455
Reflections measured	3160	19680	34827
Independent reflections	147	2014	3611
$R(\text{int})$	0.1902	0.2312	0.0560
Independent reflections ($I > 3\sigma(I)$)	145	1330	3462
Parameters	11	81	151
$R_1(I > 3\sigma(I))$	0.0272	0.0583	0.0181
wR_2 (all data)	0.0567	0.1449	0.0405
Goof (all data)	1.232	0.892	1.132
Max. peak / hole / $\text{e}^{-}\cdot 10^{-6}\cdot\text{pm}^{-3}$	1.824 / -1.322	1.667 / -2.212	1.332 / -1.396
CCDC number	1430787	1430788	1430789

Table S4. Crystallographic and refinement details for K_3BiSe_3 (**10**).

Compound	K_3BiSe_3 (10)
Empirical formula	BiK_3Se_3
Formula weight / $g \cdot mol^{-1}$	563.16
Crystal color and shape	Orange block
Crystal size /mm	0.03·0.04·0.05
Crystal system	Cubic
Space group	$P2_13$
$a / \text{\AA}$	9.7193(3)
$V / \text{\AA}^3$	918.13(9)
Z	4
$\rho_{calc} / g \cdot cm^{-3}$	4.074
$\mu(MoK\alpha) / mm^{-1}$	32.361
2θ range/ $^\circ$	5.92–53.30
Abs. corr. T_{min}/T_{max}	0.2349 / 0.4811
Reflections measured	5430
Independent reflections	660
$R(int)$	0.0878
Independent reflections ($I > 3\sigma(I)$)	611
Parameters	22
$R_1(I > 3\sigma(I))$	0.0231
wR_2 (all data)	0.0403
Goof (all data)	0.925
Max. peak / hole $/e^- \cdot 10^{-6} \cdot pm^{-3}$	0.669 / -0.584
CCDC number	1430790

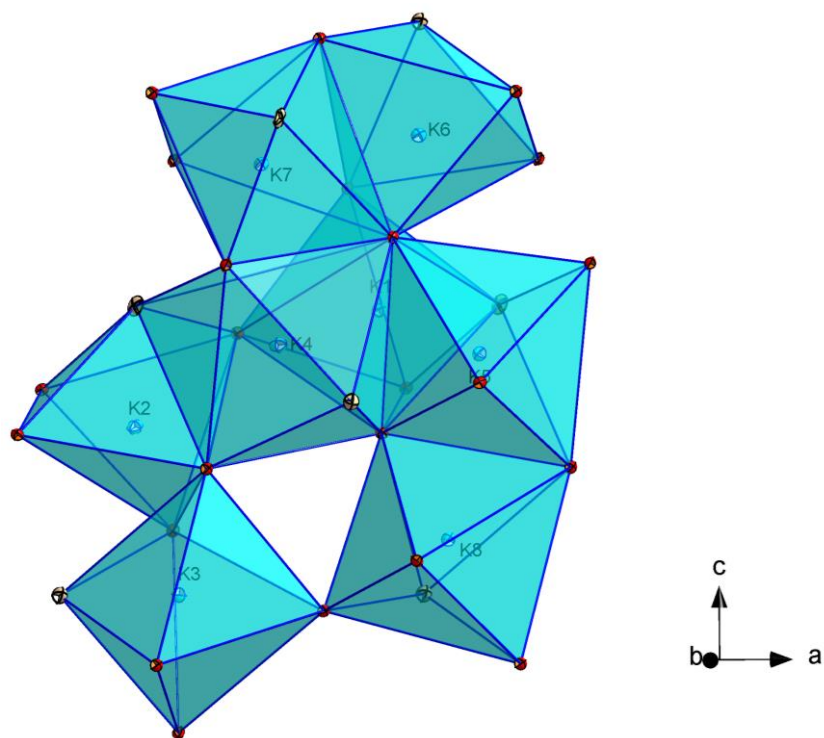


Figure S1. Representation of the K^+ environment in the crystal structure of **1**. Ellipsoids are drawn at 50% probability.

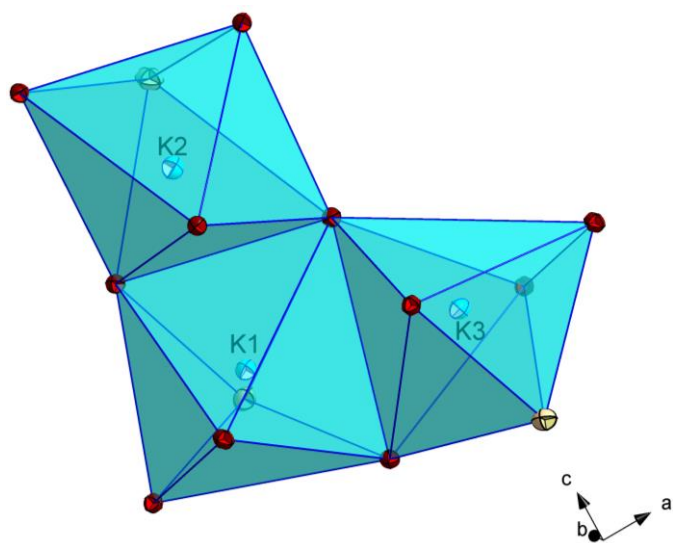


Figure S2. Representation of the K^+ environment in the crystal structure of **2**. Ellipsoids are drawn at 50% probability.

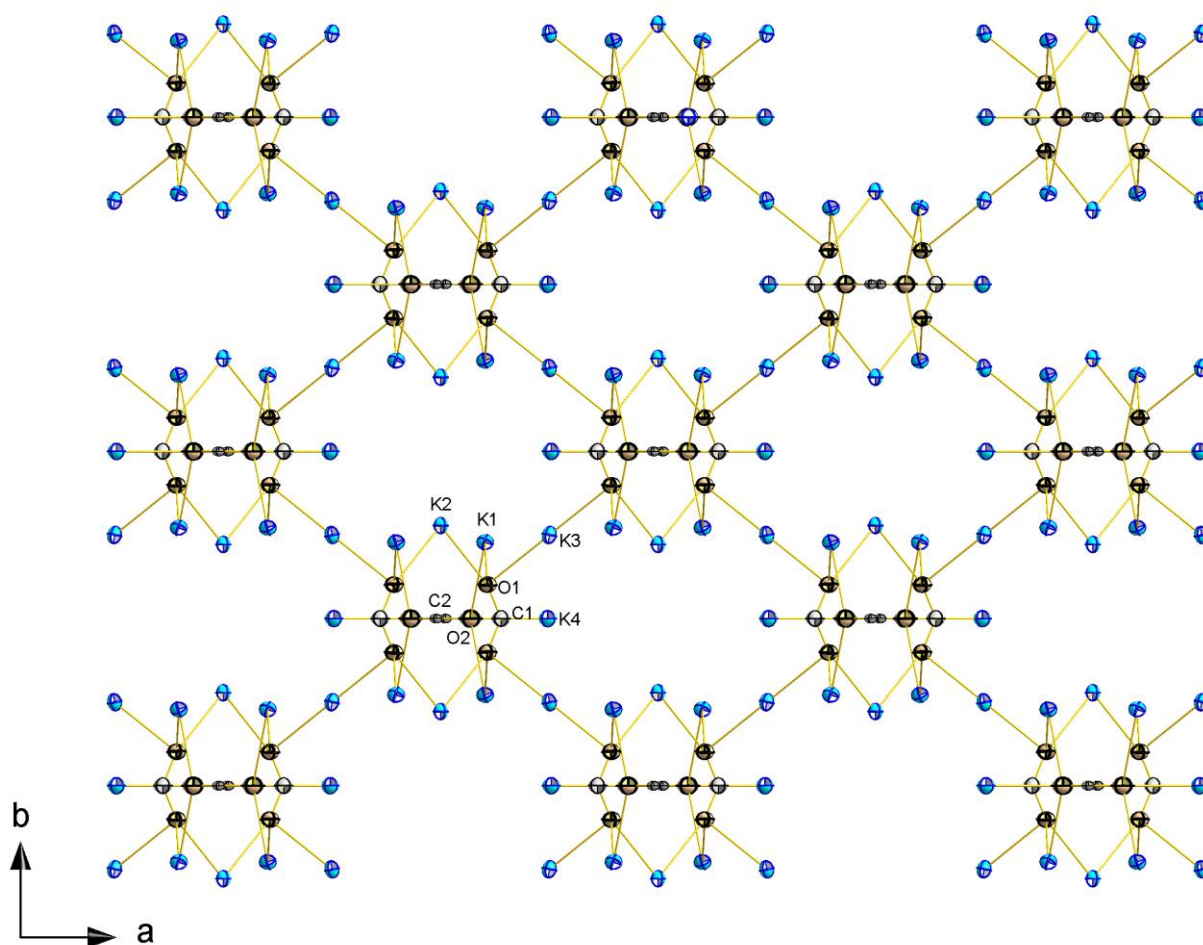


Figure S3. Representation of the packing of anions and cations in the crystal structure of **3**. View along [001]. Ellipsoids are drawn at 50% probability.

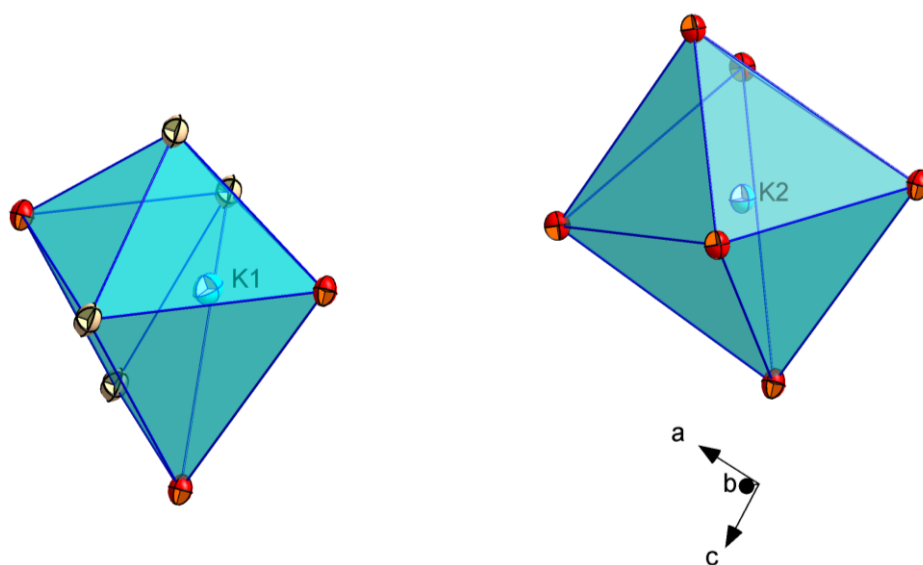


Figure S4. Representation of the K⁺ environment in the crystal structure of **4**. Ellipsoids are drawn at 50% probability.

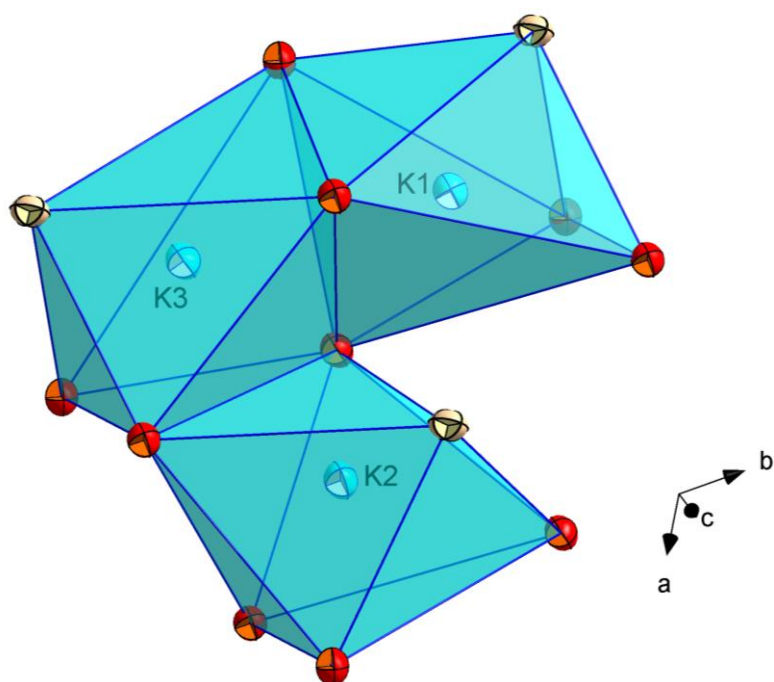


Figure S5. Representation of the K^+ environment in the crystal structure of **5**. Ellipsoids are drawn at 50% probability.

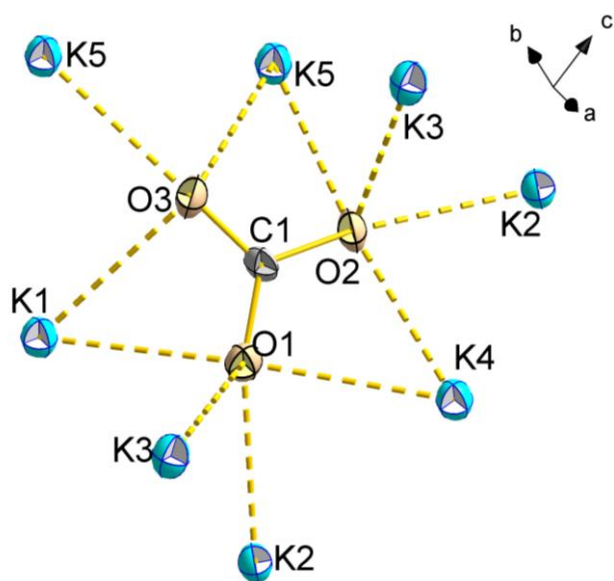


Figure S6. Representation of the $[\text{CO}_3]^{2-}$ environment in the crystal structure of **6**. Ellipsoids are drawn at 50% probability.

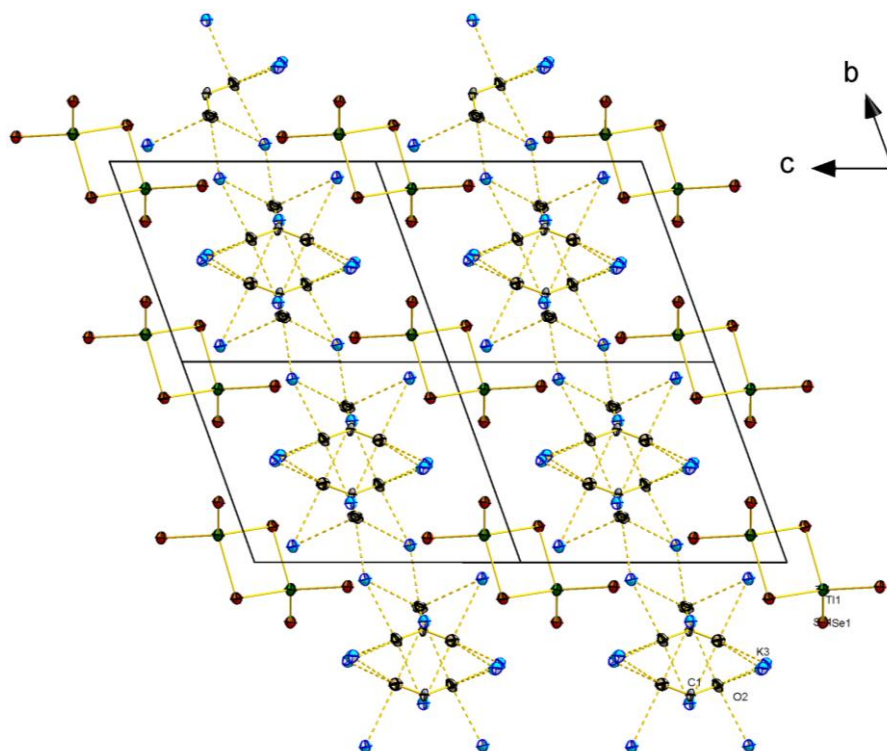


Figure S7. Representation of the packing of cations and anions in the crystal structure of **6**. View along [100]. Ellipsoids are drawn at 50% probability.

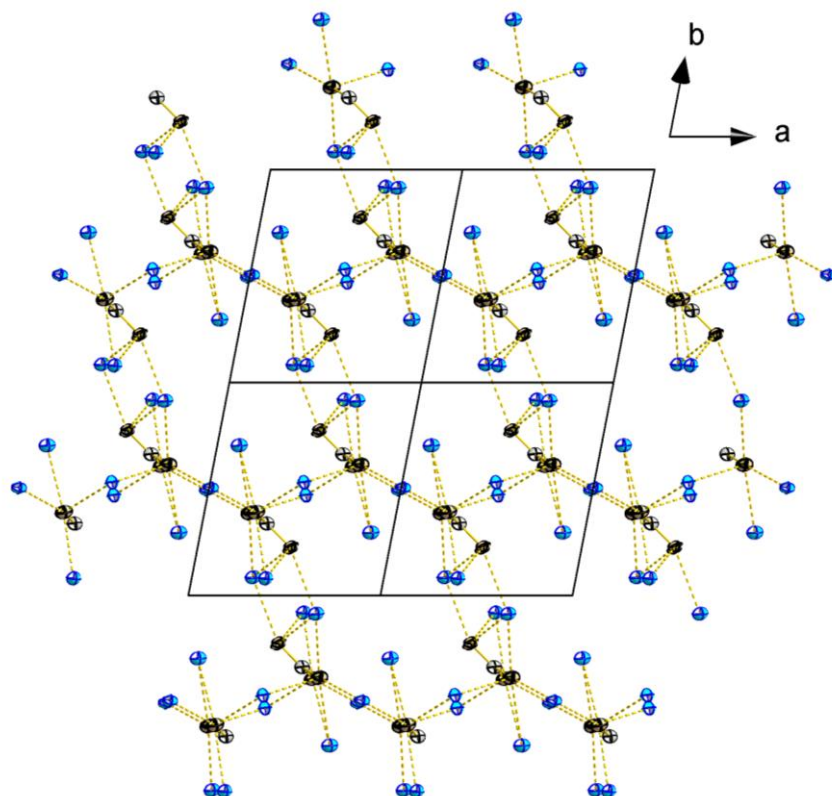


Figure S8. Representation of the packing of cations and anions in the crystal structure of **6**. View along [001]. Ellipsoids are drawn at 50% probability.

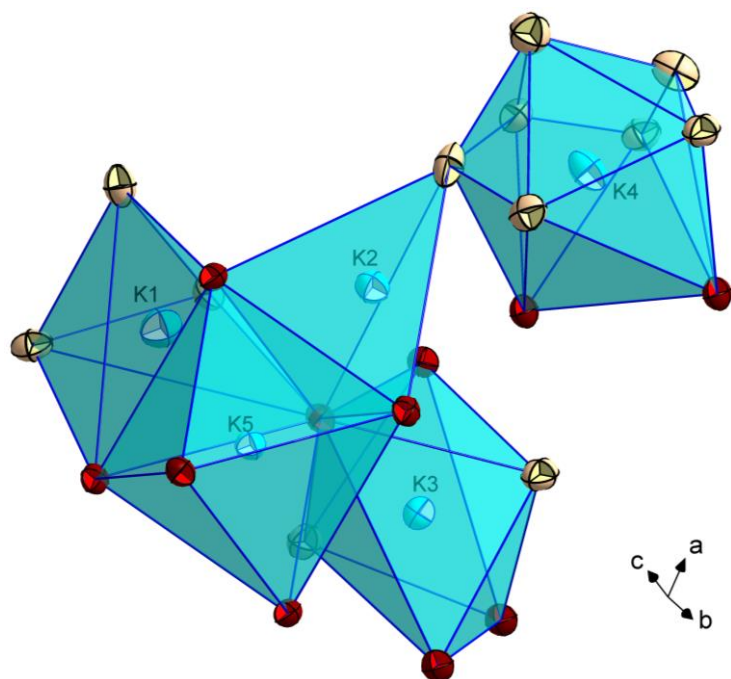


Figure S9. Representation of the K^+ environment in the crystal structure of **8**. Ellipsoids are drawn at 50% probability.

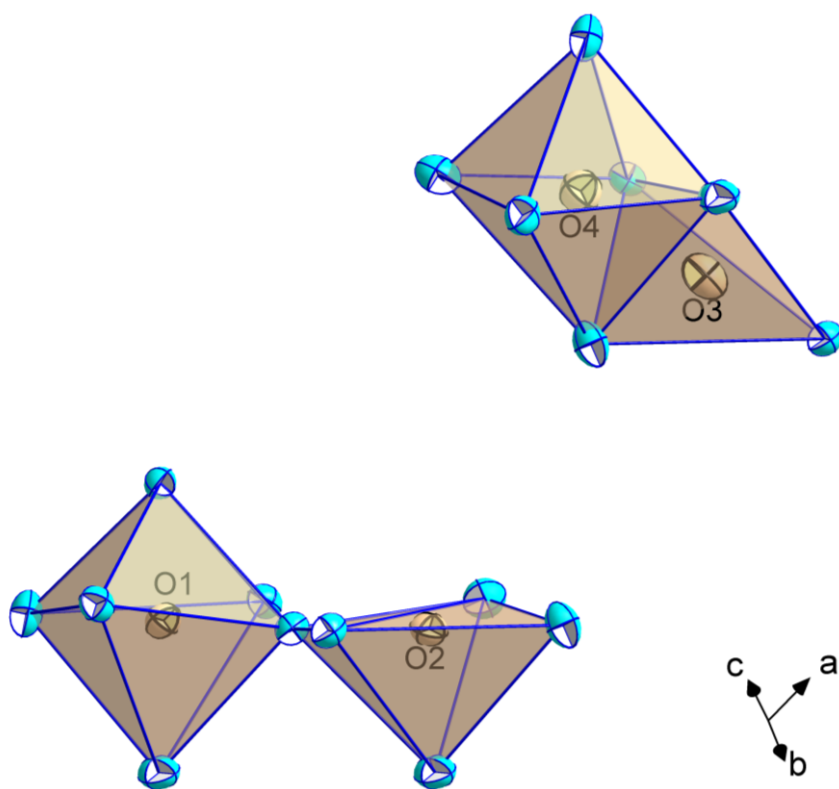


Figure S10. Representation of the O environment in the crystal structure of **8**. Ellipsoids are drawn at 50% probability.

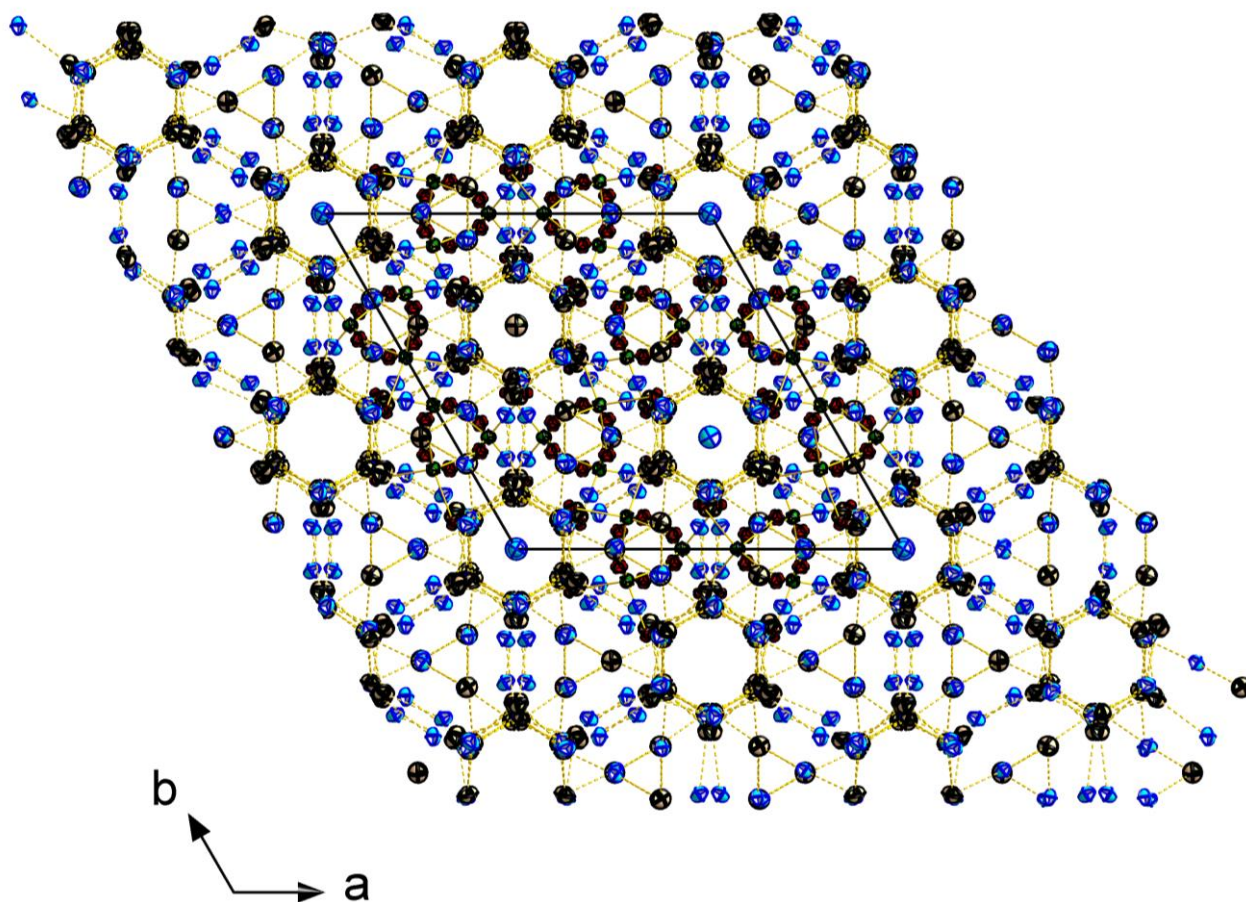


Figure S11. Representation of the packing of cations and anions in the crystal structure of **8**. View along [001]. Ellipsoids are drawn at 50% probability.

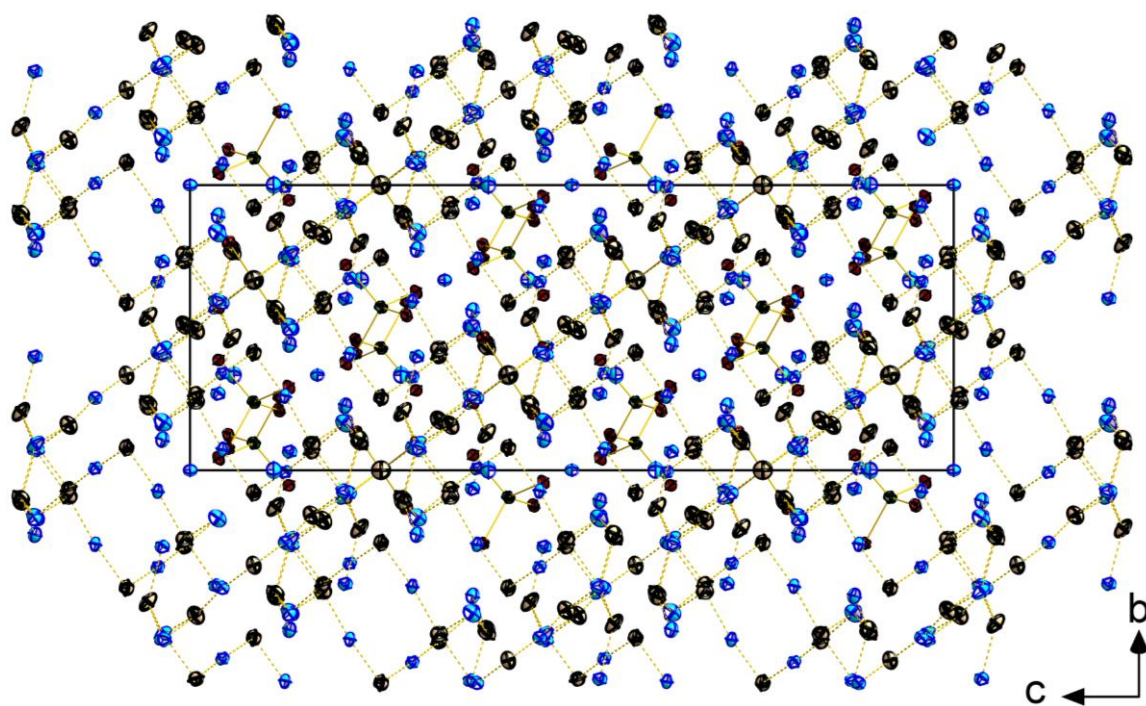


Figure S12. Representation of the packing of cations and anions in the crystal structure of **8**. View along [100]. Ellipsoids are drawn at 50% probability.

Details on quantum chemical calculations

All molecular electronic structure calculations were carried out with the TURBOMOLE program package V6.6.^[7] COSMO was used for the compensation of negative charges, applying the default parameters with $\epsilon = \infty$.^[8] Structure optimizations were undertaken by employment of the RIDFT program, using the BP86 functional^[9] and def2-TZVP basis sets with respective ECPs.^[10] The optimized structures were confirmed to be local minima on the energy hypersurface by means of calculations of the 2nd derivative of the energy. Figure S14-S17 summarize all calculated species along with their total energy values.

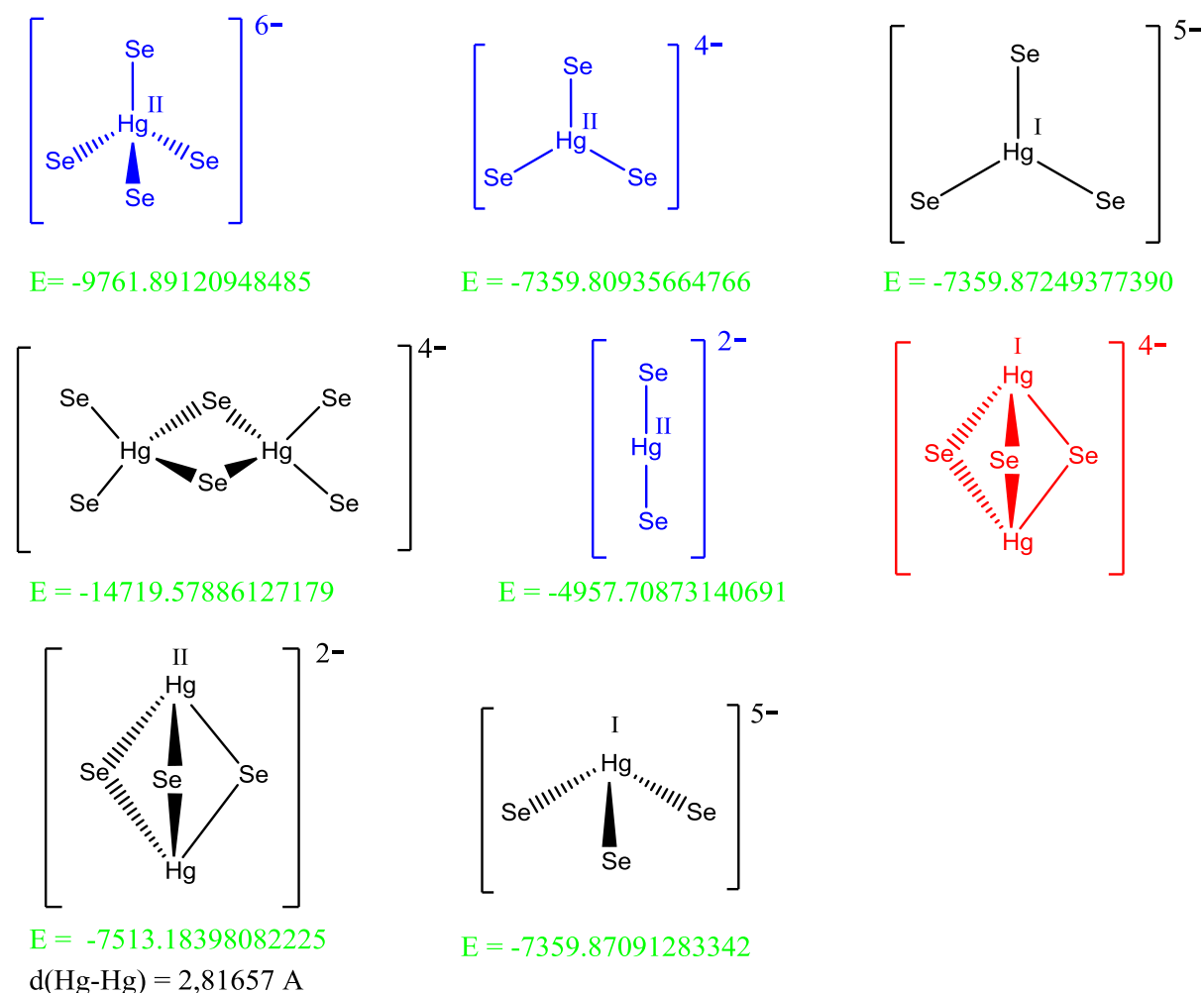


Figure S14. Schematic drawing of chalcogenidoplumbate anions calculated by means of quantum chemical methods, along corresponding total energies. Red coloured structures indicate that no convergence could be achieved. Blue coloured structures indicate experimentally determined structural motifs. Green coloured energy values indicate (local) minima on the energy hypersurface. All energy values in Hartree.

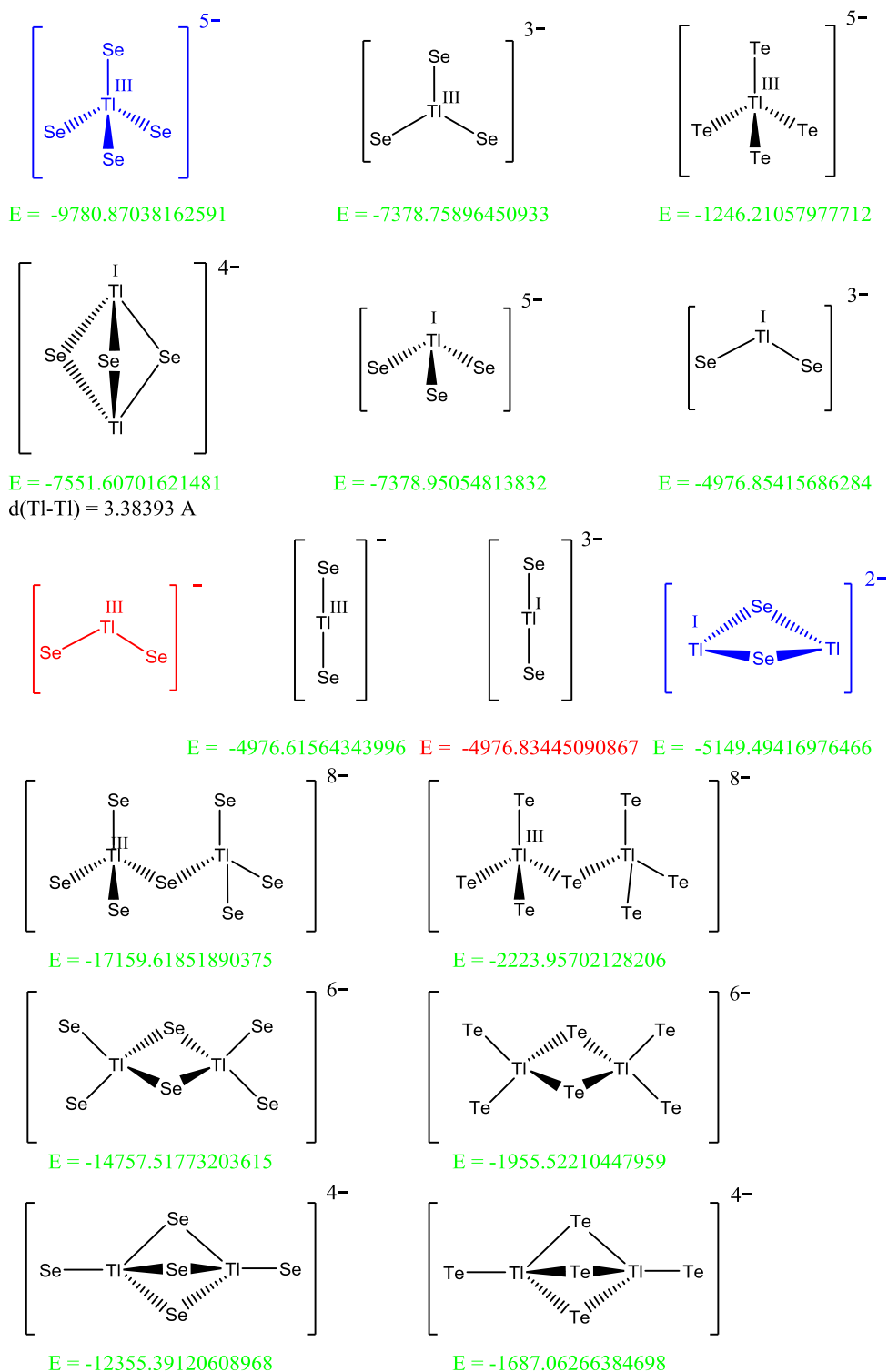


Figure S15. Schematic drawing of selenidothallate anions calculated by means of quantum chemical methods, along with corresponding total energies. Red coloured structures indicate that no convergence could be achieved. Blue coloured structures indicate experimentally determined structural motifs. Green coloured energy values indicate (local) minima on the energy hypersurface. Red coloured energy value indicate imaginary vibrational modes. All energy values in Hartree.

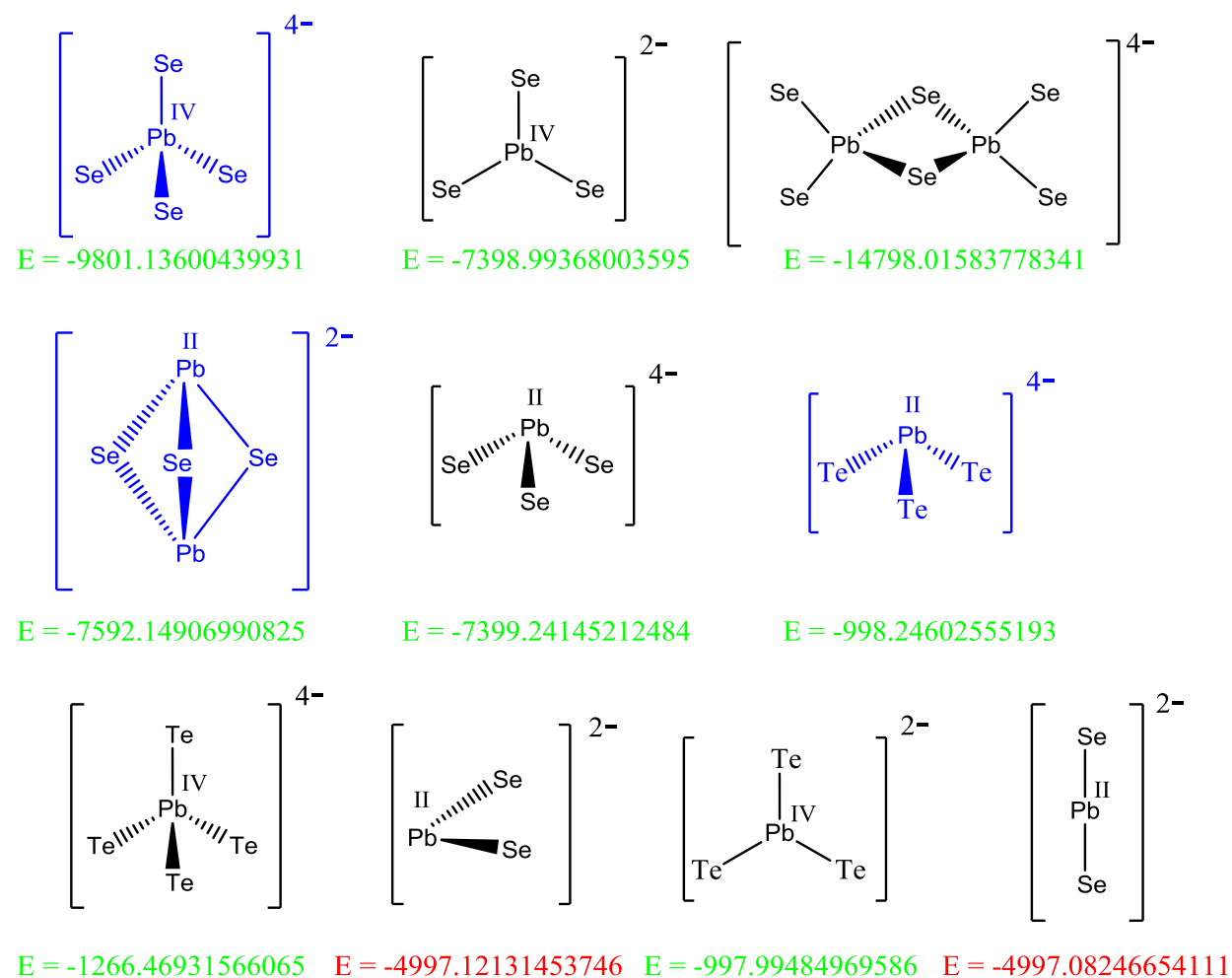


Figure S16. Schematic drawing of chalcogenidoplumbate anions calculated by means of quantum chemical methods, along with corresponding total energies. Blue coloured structures indicate experimentally determined structural motifs. Green coloured energy values indicate (local) minima on the energy hypersurface. Red coloured energy value indicate imaginary vibrational modes. All energy values in Hartree.

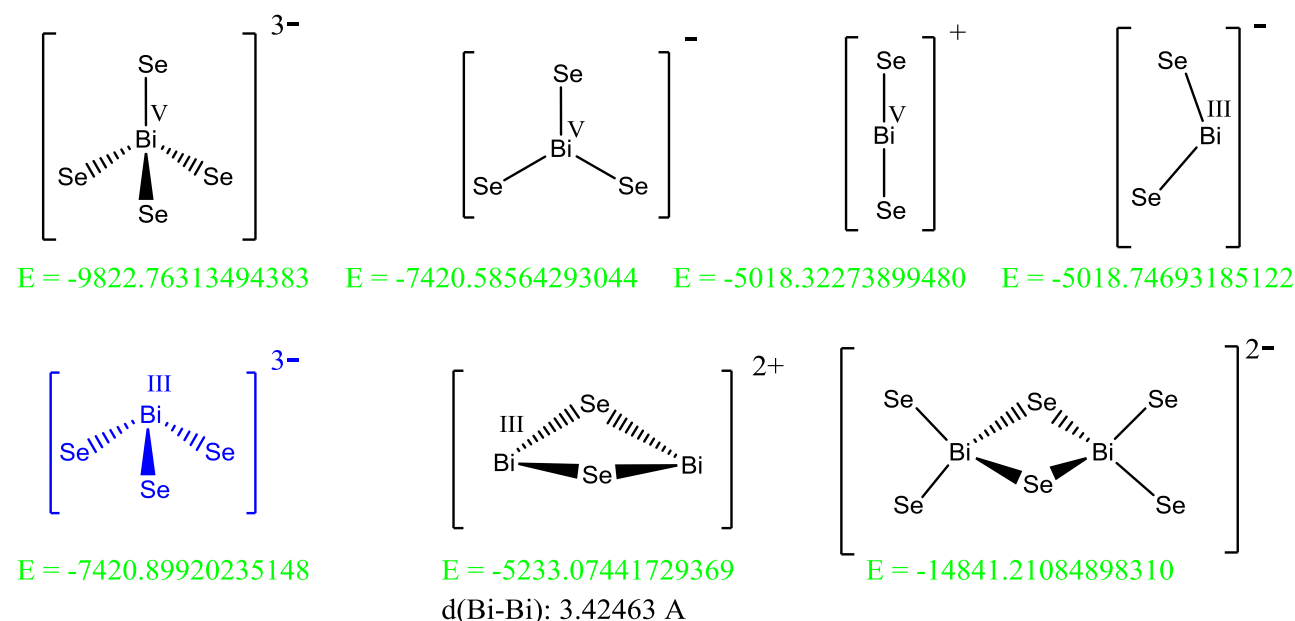


Figure S17. Schematic drawing of selenidobismuthate anions calculated by means of quantum chemical methods, along with corresponding total energies. Blue coloured structures indicate experimentally determined structural motifs. Green coloured energy values indicate (local) minima on the energy hypersurface. All energy values in Hartree.

References for the Supporting Information

- 1 W. Bronger, A. Donike, D. Schmitz, *Z. Anorg. Allg. Chem.*, 1996, **622**, 1003.
- 2 Louis J. Farrugia, *WinGX for MS-Windows V2013-7*, University of Glasgow, United Kingdom, 2013.
- 3 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *Appl. Cryst.* 2009, **42**, 339.
- 4 G. M. Sheldrick, *SHELXL-2014/7*, University of Göttingen, Germany, 2014.
- 5 X-Area version 1.56, Stoe & Cie GmbH, Darmstadt, Germany, 2011.
- 6 Bruker (2007). SADABS Bruker AXS Inc., Madison, Wisconsin, USA.
- 7 Turbomole Version 6.6, Turbomole GmbH 2014. Turbomole is a development of University of Karlsruhe and Forschungszentrum Karlsruhe 1989–2007, Turbomole GmbH since 2007; F. Furche, R. Ahlrichs, C. Hättig, W. Klopper, M. Sierka, F. Weigend, *WIREs Comput. Mol. Sci.*, 2014, **4**, 91; F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057.
- 8 A. Klamt, G. Schuurmann, *J. Chem. Soc. Perkin Trans.*, 1993, **2**, 799.
- 9 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098; J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.
- 10 F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297; F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057; M. Dolg, H. Stoll, A. Savin, H. Preuss, *Theor. Chim. Acta*, 1989, **75**, 173; H. Stoll, B. Metz, M. Dolg, *J. Comput. Chem.*, 2002, **23**, 767.