Supplementary Material (ESI) for Chemical Communications

Fine-Tuning of Optical Properties with Salts of Discrete or Polymeric, Heterobimetallic Telluride Anions $[M_4(\mu_4\text{-Te})(SnTe_4)_4]^{10-}$ (M = Mn, Zn, Cd, Hg) and $^{3}_{\infty}\{[Hg_4(\mu_4\text{-Te})(SnTe_4)_3]^{6-}\}$

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SUPPORTING INFORMATION

Experimental Details

General. All synthesis steps were performed with strong exclusion of air and moisture (N_2 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. $[K_4(H_2O)_{0.5}][SnTe_4]$ and $[Cs_4(H_2O)_2][SnTe_4]$ were synthesized by application of a method described in ref. [1].

Synthesis of $[K_{10}(H_2O)_{20}][M_4(\mu_4\text{-}Te)(SnTe_4)_4]$ (M = Mn (1), Zn (2), Cd (3a), Hg (4)) and $[Rb_{10}(H_2O)_{20}][Cd_4(\mu_4\text{-}Te)(SnTe_4)_4]$ (3b)). 0.079 g (0.1 mmol) of $[K_4(H_2O)_{0.5}][SnTe_4]$ or 0.107 g (0.1 mmol) of $[Rb_4(H_2O)_2][SnTe_4]$ were dissolved in 5 mL of H_2O (**1** – **3**) or 5 mL of MeOH (**4**) [2, 3] and added to a solution of 0.020 g (0.1 mmol) of $MnCl_2 \cdot 4H_2O$, 0.014 g (0.1 mmol) of $ZnCl_2$, 0.018 g (0.1 mmol) of $CdCl_2$ or 0.027 g (0.1 mmol) of $HgCl_2$, respectively, in 5 mL of H_2O, whereupon the reaction mixture immediately turned dark red(dish black). After stirring for 24 hours, a reddish black precipitate of binary telluride was removed by filtration. The filtrate was layered by 10 mL of THF. Black rhombic dodecahedra of **1**, **2**, **3**, or **4** – that are soluble in water – crystallized after two days. Yields with respect to Sn: **1**: 54 mg ($1.5 \cdot 10^{-2}$ mmol, 75%); **2**: 19 mg ($0.5 \cdot 10^{-2}$ mmol, 26%); **3a**: 51 mg ($1.3 \cdot 10^{-2}$ mmol, 66%); **3b**: 53 mg ($1.2 \cdot 10^{-2}$ mmol, 61%); **4**: 43 mg ($1.0 \cdot 10^{-2}$ mmol, 51%).

Synthesis of $[Cs_6(H_2O)_4][Hg_4(\mu_4\text{-}Te)(SnTe_4)_3]$ (5). 0.239 g (0.2 mmol) of $[Cs_4(H_2O)_2][SnTe_4]$ were dissolved in 3 mL of H_2O and added to a solution of 0.054 g (0.2 mmol) of $HgCl_2$ in 3 mL of H_2O, whereupon the reaction mixture immediately turned dark red. After stirring for 24 hours, traces of a black precipitate was removed by filtration. The filtrate was layered by 6 mL of THF. Small black cuboids of **5** formed after two days Yield of **5** with respect to Sn: 66 mg ($1.8 \cdot 10^{-2}$ mmol, 45%).

Stability of the crystalline material of 1 – 5. Single crystals of the compounds can be isolated under inert conditions from the mother liquor without decomposition. For X-ray diffraction measurements, polyfluorether oil-wrapped individuals were mounted on the glass fiber of the goniometer head, which was thereupon positioned in a cooled N_2 stream.

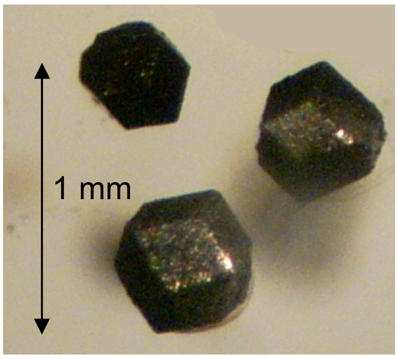

Figure 1. Single crystals of compound **1**.

Details of the X-ray diffraction measurements, structure solutions and refinements

Data of the X-ray structural analyses: T = 203 K, graphite monochromator, imaging plate detector Stoe IPDS. Structure solution by direct methods, full-matrix-least-squares refinement against F^2; software used: SHELXS-97 and SHELXL-97.[4] Further details on the X-ray analyses, atomic coordinates, displacement parameters and full structural parameter lists are summarized in the cif files, equally provided in the Internet.

Table 1. Crystallographic and refinement details of **1 – 5** at 203 K [4].

Compound	**1**	**2**	**3a**	**3b**	**4**	**5**
Empirical formula	$H_{40}K_{10}O_{20}Mn_4Sn_4Te_{17}$	$H_{40}K_{10}O_{20}Zn_4Sn_4Te_{17}$	$H_{40}K_{10}O_{20}Cd_4Sn_4Te_{17}$	$H_{40}Rb_{10}O_{20}Cd_4Sn_4Te_{17}$	$H_{40}Hg_4K_{10}O_{20}Sn_4Te_{17}$	$H_8Cs_6O_4Hg_4Sn_3Te_{13}$
Formula weight /g·mol^{-1}	3615.04	3656.76	3844.88	4308.58	4197.64	3686.78
Crystal color and shape	black rhombic dodecahedron	fragment of a black rhombic dodecahedron	black rhombic dodecahedron	black rhombic dodecahedron	black rhombic dodecahedron	black cuboid
Crystal size /mm^3	0.40×0.40×0.40	0.08×0.08×0.04	0.24×0.24×0.24	0.30×0.30×0.30	0.15×0.15×0.15	0.10×0.10×0.08
Radiation (λ /Å)	$Ag_{K\alpha}$ (0.56087)	$Ag_{K\alpha}$ (0.56087)	$Ag_{K\alpha}$ (0.56087)	$Mo_{K\alpha}$ (0.71073)	$Mo_{K\alpha}$ (0.71073)	$Mo_{K\alpha}$ (0.71073)
Crystal system	cubic	cubic	cubic	cubic	cubic	trigonal
Space group	*I*–43*m* (No. 217)	*I*–43*m* (No. 217)	*I*–43*m* (No. 217)	*I*–43*m* (No. 217)	*I*–43*m* (No. 217)	*R*3*m* (No. 160)
***a* /Å**	16.0889(19)	15.9651(18)	16.1423(19)	16.1002(19)	16.0760(19)	15.880(2)
***c* /Å**						17.367(4)
***V* /Å^3**	4164.7(9)	4069.3(8)	4206.3(9)	4173.4(9)	4154.6(9)	3793.0(11)
Z	2	2	2	2	2	3
ρ_{calc} /g·cm^{-3}	2.883	2.984	3.036	3.429	3.355	4.842
$\mu(Mo_{K\alpha})$ /mm^{-1}	4.287	4.677	4.460	13.828	14.930	25.170
Absorption correction type	semiempirical	semiempirical	semiempirical	semiempirical	semiempirical	semiempirical
Min/max transmission	0.23851 / 0.28808	0.26679 / 0.71571	0.23666 / 0.32484	0.44051 / 0.54977	0.21109 / 0.28773	0.21489 / 0.39132
2Θ range /°	5-42	5-40	5-44	9-50	5-48	5-50
No. of measured reflections	9978	6709	7857	17132	3873	2415
***R*(int)**	0.0759	0.1584	0.1450	0.1062	0.1384	0.0840
No. of independent reflections	785	539	940	576	463	1173
No. of indep. reflections ($I > 2\sigma(I)$)	739	420	727	542	400	963
No. of parameters^a	68	38	52	51	50	67
R_1 ($I > 2\sigma(I)$)	0.0625	0.0621	0.0530	0.0319	0.0635	0.0474
wR_2 (all data)	0.1638	0.1977	0.1376	0.0652	0.1236	0.1050
***S* (all data)**	1.055	0.880	1.072	1.086	1.095	0.950
BASF for TWIN refinement^b	0.25(6)	0.45(6)	0.07(4)	0.17(6)	0.17(3)	0.483(19)
Largest diff. peak/hole /e$^-$·10^{-6}pm^{-3}	–0.653 / 0.526	–0.047 / 0.032	–0.828 / 1.544	–0.552 / 0.473	–0.516 / 0.449	-2.538 / 2.049

[a] Different numbers of parameters in **1 – 3** result from a different extent of disorder observed for counterions and solvent molecules, which had to be taken into consideration by individual assignment of respective split positions; these have been adapted manually during the refinement procedure to result in the best possible model for the assignment of residual electron density within the "solid solution" type arrangement of K^+ ions and H_2O molecules.

[b] All so far examined crystals of **1 – 5** show racemic twinning which has been considered by refinement using the TWIN command. For **1 – 4** the assignment of the space group was not trivial. *I*–43*m* showed to lead to best results, although large ellipsoids at the terminal Te ligands indicate a possible description as a primitive structure (according to space group *P*–43*m*) with slightly differing orientations of the P1 cluster anions at the unit cell corners or center, respectively. However, refinement in one of the primitive space group did not produce satisfying *R* values and thermal ellipsoids

without assignment of heavy atom split positions. Further reduction of the symmetry was not indicated; another possible solution was found in space group *I*23, however with worse final *R* values on average, distinctly larger ellipsoids, and more splitting of atomic positions needed. For additional comments regarding compound **2**, see Table 2 and Figure 2.

Table 2. Selected interatomic distances [Å] and angles [°] observed in compounds **1** – **5**.

Compound	**1**	**2**^{d}	**3a**	**3b**	**4**	**5**
A, M	K, Mn	K, Zn	K, Cd	Rb, Cd	K, Hg	Cs, Hg
Sn–Te$_t$^{b}	2.726(4)	2.709(17)	2.731(3)	2.723(2)	2.688(7)	—
Sn–(μ-Te)^a	2.755(2)	2.756(9)	2.7459(15)	2.7463(12)	2.748(4)	2.745(4), 2.748(3)
Sn–(μ^t-Te)^a	—	—	—	—	—	2.728(3)
M–(μ_4-Te)	2.725(4)	2.701(11)	2.7876(19)	2.7900(15)	2.763(2)	2.744(7), 2.795(2)
M–(μ-Te)^a	2.759(2)	2.639(7)	2.8159(14)	2.8197(12)	2.826(3)	2.790(2), 2.824(3)
Hg–(μ^t-Te)^a	—	—	—	—	—	2.827(4)
A…Te^c	3.52 – 4.07	3.55 – 4.01	3.66 – 4.27	3.69 – 4.13	3.36 – 4.08	3.858(3) – 4.234(3)
A…O^c	2.53 – 3.07	2.56 – 3.10	2.50 – 3.13	2.70 – 3.18	2.54 – 3.13	3.07(14) – 3.60(16)
(μ-Te)–Sn–Te$_t$	106.35(6)	107.2(2)	105.67(4)	105.76(3)	105.70(9)	—
(μ-Te)–Sn–(μ-Te)	112.40(5)	111.66(19)	112.99(4)	112.91(3)	112.97(7)	113.24(8), 115.52(15)
(μ-Te)–Sn–(μ^t-Te)	—	—	—	—	—	101.75(7), 109.86(13)
(μ_4-Te)–M–(μ-Te)	111.03(9)	111.3(3)	109.79(4)	109.73(3)	110.12(8)	110.51(8), 111.66(8)
(μ_4-Te)–Hg–(μ^t-Te)	—	—	—	—	—	110.89(6)
(μ-Te)–M–(μ-Te)	107.87(10)	107.6(3)	109.15(4)	109.21(3)	108.81(8)	108.42(8), 110.78(10)
(μ-Te)–Hg–(μ^t-Te)	—	—	—	—	—	100.40(14)
Sn–(μ-Te)–M	104.79(11)	105.3(3)	105.35(6)	105.51(5)	105.04(12)	103.07(8), 103.89(12)
Sn–(μ^t-Te)–Hg	—	—	—	—	—	97.70(11)
M–(μ_4-Te)–M	109.47	109.47	109.47	109.47	109.47	107.24(12), 111.61(11)

[a] Sn–(μ-Te) or Mn–(μ-Te) denote atomic distances in Sn–(μ-Te)–Mn bridges in **1** – **5**, whereas Sn–(μ^t-Te) or M–(μ^t-Te) denotes distances within Sn–(μ-Te)–Hg bridges between adjacent cluster fragments in **5**.

[b] Sn–Te$_t$ denotes distances between Sn atoms and terminal Te atoms in **1** – **4**.

[c] Owing to high disorder of K or Rb and O atomic positions in **1** – **4**, Te…A and A…O distances are afflicted with high standard deviations; therefore only rough ranges are provided.

[d] Owing to systematically very small, poorly scattering crystals of compound **2**, data sets are of poor quality (see Table 1) resulting in relatively high esds.

Thermal ellipsoid representations of the ternary anions in compounds **1** – **5** are given in figures 2 and 3 with the labeling scheme.

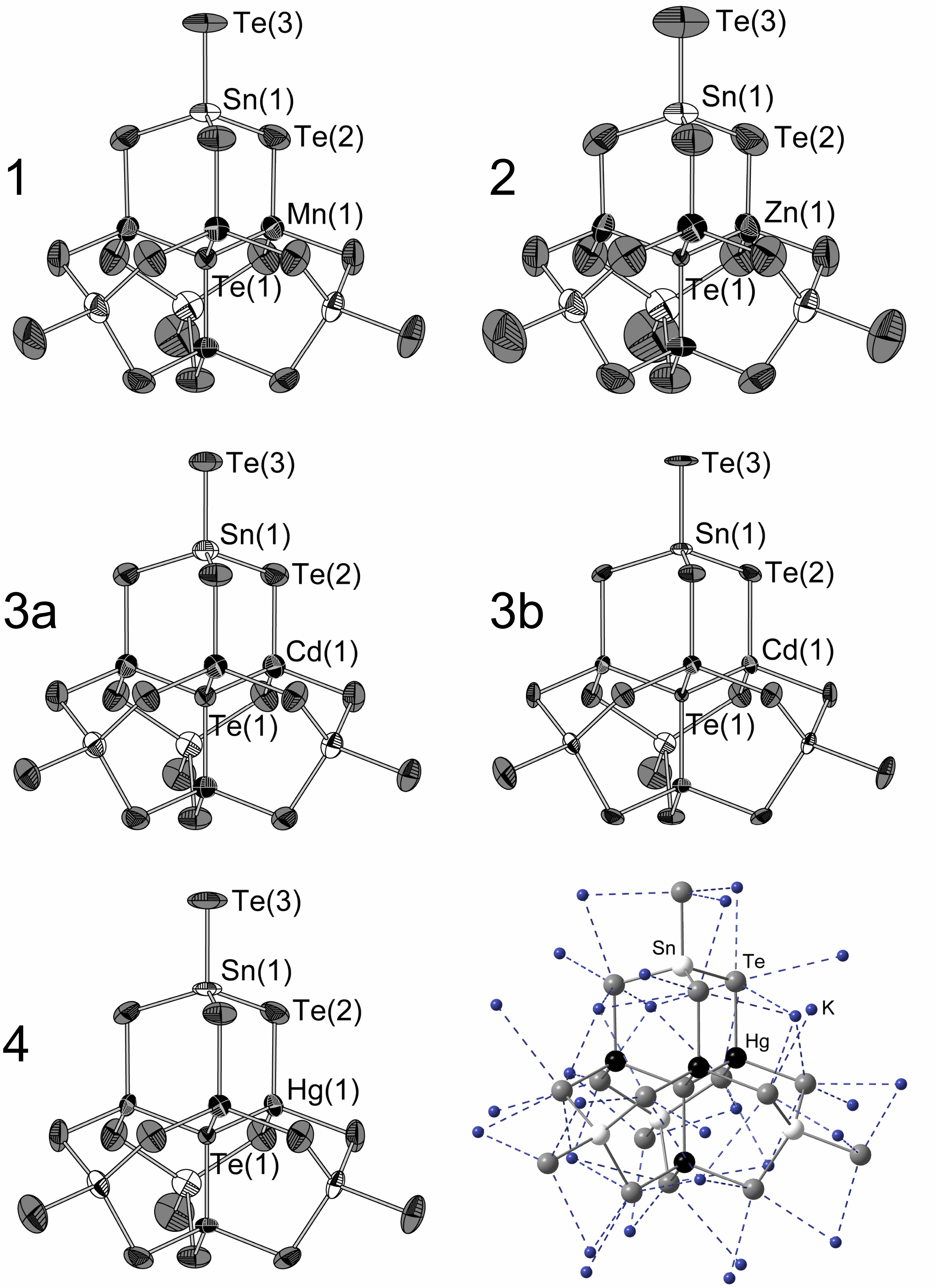

Figure 2. Thermal ellipsoid representation (40% probability) of the ternary anions in compounds **1**, **2**, **3a**, **3b**, and **4** with the labeling scheme; for **4**, the coordination to next K^+ ions is also given (disorder of K^+ ions omitted for clarity). The poor crystal quality which is immanent to compound **2** is clearly reflected by unsatisfying results of the structure refinement; significant enlargement of the thermal ellipsoids indicate rotation of the anions within the crystal that might be responsible for the poor crystal quality; attempts to describe atoms Te(2) and Te(3) by disordered positions do not lead to better results

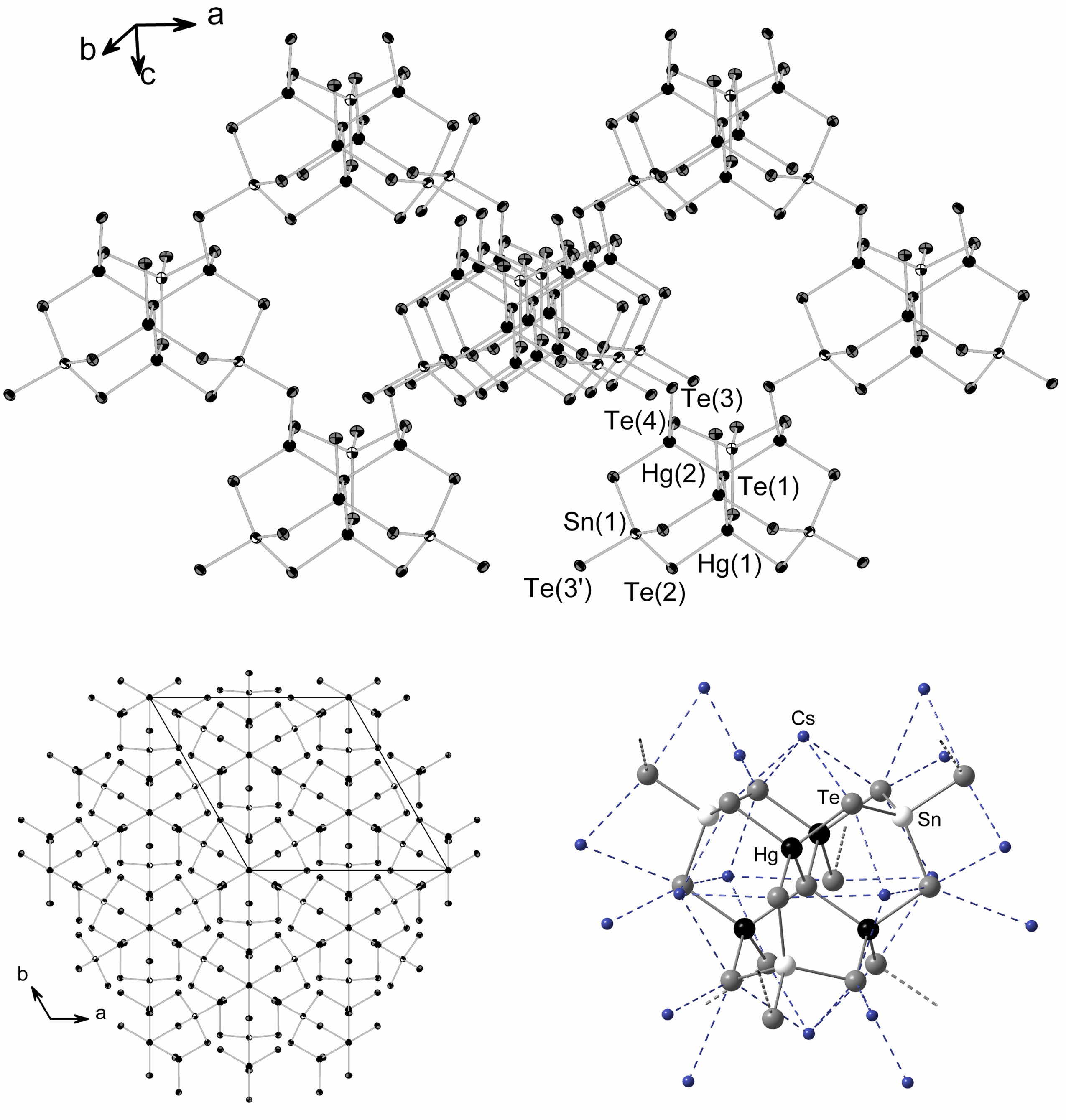

Figure 3. Thermal ellipsoid representation (50% probability) of the ternary anionic network in compound **5** with the labeling scheme (view perpendicular to crystallographic *c* axis (top), atom Te(3') being generated *via* -y+2/3, x-y+1/3, z+1/3; view along crystallographic *c* axis (bottom left), and coordination of one monomeric unit to next Cs^+ ions (bottom right; continuation of the structure is indicated by dashed lines).

Quantum chemical investigations

Density functional (DFT) calculations [5] of the anion in **1** were performed using the program system TURBOMOLE [6] (RIDFT program,[7] Becke-Perdew functional (B-P-86) [8]). Basis sets were of TZVPP quality (triple zeta valence plus multiple polarization functions).[7b] Relativistically corrected effective core potentials (ECP) were used for the Sn and Te atoms (ECP-28).[9] Compensation of the negative charges of all calculated molecules was achieved by simulating mirror charges employing the COSMO model.[10] Thus, all orbital energies were calculated to be negative and structural parameters improved compared to computation of free anions. The use of the unrestricted Kohn-Sham (UKS) modus allowed for systematic investigations of ground state occupations. All geometry optimizations were performed without symmetry restrictions (C_1 symmetry), therefore convergence into local minimum structures can be assumed. Mullikan population analyses of the DFT wave function revealed the presence of 4.6 – 4.7 d electrons at each Mn atom which corresponds to intact d^5 shells within the limits of the method used. The spin orientation of the minimum was $S = 0$ with two Mn atoms possessing $S = +^5/_2$ and two Mn atoms possessing $S = -^5/_2$ which represents an $S = 0$ ground state in the sum. In further calculations, the spin orientation was stepwise inverted, leading to two further species fulfilling the *aufbau* principle with $S = 5$ or $S = 10$, respectively, that are only slightly higher in energy (0.1 or 0.3 eV, respectively).

UV-Vis spectroscopy

UV-Vis spectra were recorded on a PERKIN ELMER LAMBDA900 spectrometer, employing double-beam technique. The samples were measured as suspensions in Nujol that were prepared by grinding single crystals under N_2 atmosphere in a drop of Nujol. The mixture was given between two quartz plates and rapidly brought into the UV-Vis beam. Wavelengths of the onset of absorption and the beginning of the plateau were assigned graphically at the cross-over point of the respective tangents.

References for the Supporting Information

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