Incorporation of Sulfate or Selenate Groups into Oxotellurates(IV): II. Compounds with Divalent Lead

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Abstract. Four mixed oxochalcogenate compounds in the systems $Pb^{II}/X^{VI}/Te^{IV}/O/(C)$, $(X^{VI} = S \text{ and } Se)$ were obtained as minority phases under hydrothermal conditions (210 °C, one week). Their compositions as determined on the basis of single-crystal X-ray diffraction data are $Pb_3(SeO_4)(TeO_3)_2$, $Pb_7O_4(SeO_4)_2(TeO_3)_2$, $Pb_5(SeO_4)_2(TeO_4)_2(TeO_3)_3$, and $Pb_2(SO_4)(TeO_3)_3$. All crystal structures are centrosymmetric, and in each case the oxochalcogenate anions are isolated from each

Introduction

In continuation of our previous investigations on the effect of introducing tetrahedral oxochalcogenate(VI) anions as spacers into framework structures of divalent metal oxotellurates-(IV) (metal = mercury, cadmium, calcium, strontium)^[1,2] to possibly obtain compounds with non-centrosymmetric structures, we have expanded these studies to lead(II) oxotellurates-(IV). Next to the structure-directing, i.e. stereochemically active, 5s² lone electron pair at the tellurium atom of respective oxotellurate(IV) anions, the presence of the 6s² lone electron pair at the Pb²⁺ cation might additionally trigger the formation of non-centrosymmetric structures. In fact, from the four structurally determined lead(II) oxotellurates(IV) reported up to date, α -PbTeO₃,^[3] β -PbTeO₃,^[4] Pb₂Te₃O₈,^[5] and PbTe₅O₁₁,^[6] only β -PbTeO₃ crystallizes in a non-centrosymmetric space group and is reported to have ferroelectric properties.^[7]

In this article we report on hydrothermal formation and crystal structures of four new mixed oxochalcogenate(IV,VI) compounds with compositions $Pb_3(SeO_4)(TeO_3)_2$, $Pb_7O_4(SeO_4)_2(TeO_3)$, $Pb_5(SeO_4)_2(TeO_4)(CO_3)$, and $Pb_2(SO_4)$ -(TeO₃).

Experimental Section

Synthesis: Hydrothermal syntheses were conducted in sealed Teflon containers (capacity ca. 10 mL) in steel autoclaves at autogenous pressure. Lead(II) compounds in form of lead oxide, lead acetate, or lead oxide carbonate were mixed in stoichiometric amounts with TeO₂ and concentrated selenic acid (ca. 80 wt %, prepared by oxidizing SeO₂ in aqueous solution with an H_2O_2/HNO_3 mixture) or sulfuric acid (ca.

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other. The Pb²⁺ cations exhibit distorted coordination polyhedra with coordination numbers ranging from six to ten, in the majority of cases with a "one-sided" coordination by oxygen atoms. The presence of the very rare square-pyramidal Te^{IV}O₄⁴⁻ anion distinguishes the structure of Pb₅(SeO₄)₂(TeO₄)(CO₃) from the other structures, where the oxo-tellurate(IV) anions exist in the TeO₃²⁻ trigonal-pyramidal configuration.

94 wt %); for some experiments KOH was also added to ensure slightly basic conditions. The respective mixture was placed in the Teflon container, filled up with water to about two-thirds of the container volume and sealed with a Teflon lid. The sealed container was placed in the autoclave and heated at 210 °C for one week. Afterwards, the autoclave was cooled to room temperature overnight. The solid products were filtered off, washed subsequently with mother liquor, water, and ethanol. All reaction batches consisted of phase-mixtures when inspected optically under a polarizing microscope. These findings were confirmed by subsequent powder X-ray diffraction studies of the bulk products. Representative results of the hydrothermal experiments are gathered in Table 1.

Powder X-ray Diffraction (PXRD): Samples of the bulk material were ground, fixed with small amounts of petroleum jelly on silicon wafers and measured with $\text{Cu-}K_{\alpha 1,2}$ radiation in Bragg-Brentano geometry with a PANalytical X'PertPro system.

Single Crystal Diffraction: Crystals of good optical were pre-selected under a polarizing microscope, embedded in perfluorinated polyether and then mounted on MiTeGen MicroLoopsTM. Diffraction data were recorded at room temperature or at 100 K using Mo- K_{α} radiation with a Bruker APEX-II CCD diffractometer (ω - and φ -scans),^[11] aiming at data sets of the complete reciprocal sphere. After integration of the data with the program SAINT,^[11] absorption corrections were performed on indexed faces with SADABS^[11] or by optimization of the crystal shape using HABITUS;^[12] for the data sets of the two-domain crystals (see below) of Pb₃(SeO₄)(TeO₃)₂ and Pb₇O₄(SeO₄)₂(TeO₃), TWINABS^[11] was used for absorption correction. All crystal structures were solved by direct methods and were refined using the SHELXTL program package.^[13]

For data collections of Pb₃(SeO₄)(TeO₃)₂ and Pb₇O₄(SeO₄)₂(TeO₃) splitting of reflections indicated multi-domain crystals. A close inspection of their diffraction data with the program RLATT^[11] revealed two distinct domains for both data sets. For Pb₃(SeO₄)(TeO₃)₂ one twin domain was rotated by 180° about the reciprocal a^* axis relative to the other twin domain; for Pb₇O₄(SeO₄)₂(TeO₃) one twin domain was rotated by 180° about reciprocal axis [014] (corresponding to a rotation about the *c* axis in direct space). Both data sets were reduced to intensity values with overlap information using SAINT^[11] into a HKFL5format reflection file. An absorption correction was applied with the

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Table 1. Details of representative experiments for phase formation studies in the systems Pb/X/Te/O/(H) (X = S and Se) performed under hydrothermal conditions.

Amounts of starting materials and stoichiometric ratios	Phases determined by X-ray powder diffraction of the $bulk^{a)}$	Additional phase determined by single- crystal X-ray diffraction
PbO 0.180 g, H ₂ SeO ₄ 0.17 mL, TeO ₂ 0.084 g, KOH 0.09 g;	"PbTeO ₃ •0.33H ₂ O" ^b), Pb ₂ Te ₃ O ₈ ^[5] , PbTe ₅ O ₁₁ ^[6]	$Pb_3(SeO_4)(TeO_3)_2^{c)}$
PbO:H ₂ SeO ₄ :TeO ₂ :KOH = 1.5:2:1:2 PbO 0.180 g, H ₂ SeO ₄ 0.17 mL, TeO ₂ 0.084 g, KOH 0.18 g;	$Pb_2Te_3O_8^{[5]}$, $PbTe_5O_{11}^{[6]}$, "PbTeO ₃ ·0.33H ₂ O" ^{b)}	$Pb_7O_4(SeO_4)_2(TeO_3)^{c)}$
PbO:H ₂ SeO ₄ :TeO ₂ :KOH = 1.5:2:1:4 PbCO ₃ ·Pb(OH) ₂ 0.205 g, H ₂ SeO ₄ 0.17 mL, TeO ₂ 0.084 g;	Pb ₂ Te ₃ O ₈ ^[5] , Pb ₅ (CO ₃) ₃ O(OH) ₂ ^[9]	$Pb_5(SeO_4)_2(TeO_4)(CO_3)^{c)}$
PbCO ₃ ·Pb(OH) ₂ :H ₂ SeO ₄ :TeO ₂ = 1.3:2:1 Pb(OAc) ₂ 0.319 g, H ₂ SO ₄ 0.15 mL, TeO ₂ 0.078 g; Pb(OAc) ₂ :H ₂ SO ₄ :TeO ₂ = 2:2:1	PbSO ₄ ^[10] , Pb ₂ Te ₃ O ₈ ^[5]	$Pb_2(SO_4)(TeO_3)^{c)}$

a) Main phases appear first, minor phases last in terms of semi-quantitative phase analysis. For all batches additional reflections were present that could not be assigned to known phases or the new phases given in the right column. b) This lead(II) oxotellurate was reported to be a hydrous phase with an approximate water content of 0.33 mol per formula unit.^[8] Our very recent structure determination revealed that this phase in fact does not contain any water and represents the third PbTeO₃ polymorph. Results will be published in a forthcoming communication. c) This work.

multi-scan approach implemented in TWINABS; reflections were merged according to Laue class 2/m for Pb₃(SeO₄)(TeO₃)₂ and to $\overline{1}$ for Pb₇O₄(SeO₄)₂(TeO₃). This resulted in the following intensity statistics for Pb₃(SeO₄)(TeO₃)₂: mean $I/\sigma = 2.0$ for domain 1 only; mean $I/\sigma =$ 2.1 for domain 2 only; mean $I/\sigma = 6.8$ for reflections belonging to both

domains, with a refined ratio of the two twin domains of 0.52:0.48; for $Pb_7O_4(SeO_4)_2(TeO_3)$: mean $I/\sigma = 12.6$ for domain 1 only; mean $I/\sigma = 13.9$ for domain 2 only; mean $I/\sigma = 14.25$ for reflections belonging to both domains, with a refined ratio of the two twin domains of 0.58:0.42.

Table 2. Details of data collections and structure refinements.

	Pb ₃ (SeO ₄)(TeO ₃) ₂	$Pb_7O_4(SeO_4)_2(TeO_3)$	$Pb_5(SeO_4)_2(TeO_4)(CO_3)$	$Pb_2(SO_4)(TeO_3)$
M _R	1115.73	1975.85	1573.48	686.04
Crystal size /mm ³	$0.01 \times 0.08 \times 0.10$	$0.01 \times 0.01 \times 0.04$	$0.01 \times 0.03 \times 0.04$	$0.05 \times 0.06 \times 0.09$
Temperature /°C	23	23	-173	23
Radiation; $\lambda / \text{Å}$		Mo-K _o	; 0.71073	
Diffractometer	Bruker APEX-II	Bruker APEX-II	Bruker APEX-II	Bruker APEX-II
Crystal color; form	colorless, block	colorless, lath	colorless, block	colorless, plate
Space group (no.)	C2/c (15)	$P\bar{1}$ (2)	<i>Cmcm</i> (63)	$P2_1/n$ (14)
Formula units Z	4	2	4	4
a /Å	16.0853(4)	7.3191(5)	5.5097(3)	7.36480(10)
b /Å	11.7365(3)	10.3696(6)	14.6016(7)	10.7296(2)
c /Å	6.0788(1)	11.6317(8)	17.8552(9)	9.3268(2)
a /°	90	73.534(2)	90	90
β /°	107.599(1)	89.982(2)	90	111.463(1)
γ /°	90	87.431(2)	90	90
$V/Å^3$	1093.88(4)	845.67(10)	1436.46(13)	685.91(2)
μ /mm ⁻¹	54.652	75.483	65.544	53.488
X-ray density /g·cm ⁻³	6.775	7.759	7.276	6.643
Range $\theta_{\min} - \theta_{\max}$	2.19-30.04	1.83-27.00	2.28-40.10	3.02-46.12
Range	$-22 \le h \le 21$	$-9 \le h \le 9$	$-9 \le h \le 9$	$-14 \le h \le 14$
	$0 \le k \le 16$	$-12 \le k \le 13$	$-26 \le k \le 26$	$-21 \le k \le 21$
	$0 \le l \le 8$	$0 \le l \le 14$	$-32 \le l \le 32$	$-18 \le l \le 18$
Measured reflections	26577	44953	68540	86178
Independent reflections	1610	3700	2441	5967
Observed reflections $[I > 2\sigma(I)]$	1472	2796	1896	5013
R _i	-	_	0.1071	0.0812
Absorption correction	TWINABS	TWINABS	HABITUS	SADABS
Transmission coefficients T_{\min} ; T_{\max}	0.295; 0.746	0. 249; 0. 747	0.240; 0.475	0.0924; 0.1970
Number of parameters	76	152	48	101
Extinction coefficient (SHELXL)	0.00019(5)	_	_	0.00277(10)
Difference electron densities max.; min. / e^{-} ·Å ⁻³ (distance /Å, atom)	3.35 [1.10, Pb2];	4.86 [0.81, O13];	4.06 [0.62, Te1];	3.36 [0.59, Pb1];
	-2.97 [1.15, Pb2]	-4.64 [1.07, Pb4]	-3.08 [0.41, O3]	-2.91 [0.48, Pb2]
$R [F^2 > 2\sigma(F^2)]$	0.0307	0. 0624	0.0220	0.0276
wR_2 (F^2 all)	0.0905	0. 1779	0.0351	0.0614
GooF	1.124	1.096	0.927	1.108



Table 3. Selected interatomic distances	Å as well as results of bond valence sum calculations	/v.u. ^{a)} .
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Pb ₃ (SeO ₄)(TeO ₃) ₂		$Pb_7O_4(SeO_4)_2(TeO_3)$			Pb ₅ (Se	$Pb_5(SeO_4)_2(TeO_4)(CO_3)$				$Pb_2(SO_4)(TeO_3)$					
Pb1 Pb1 Pb1 Pb1 Pb2 Pb2 Pb2 Pb2 Se1 Se1 Se1 Se1 Te1 Te1 Te1		05 04 04 05 02 02 01 03 03 03 03 01 01 01 01 04 05 03	2.289(7) 2.537(7) 2.604(8) 2.606(8) 2.628(7) 2.927(8) 2.332(7) 2.527(7) 2.527(7) 2.527(7) 2.527(7) 1.625(7) 1.625(7) 1.628(7) 1.628(7) 1.874(7) 1.874(7) 1.878(7)	Pb1 Pb1 Pb1 Pb1 Pb1 Pb1 Pb2 Pb2 Pb2 Pb2 Pb2 Pb2 Pb3 Pb3 Pb3 Pb3 Pb3 Pb3 Pb3 Pb3 Pb3 Pb3		03 01 02 04 06 07 09 014 03 03 01 08 07 013 04 02 04 05 06 013 014 012 04 03 01 02 04 05 06 013 014 012 04 05 06 013 014 012 04 05 06 013 014 012 04 05 06 013 014 012 04 05 06 013 014 012 04 05 06 013 014 012 04 05 06 013 014 012 04 05 06 013 014 012 04 05 06 013 014 012 04 05 06 013 014 012 04 05 06 013 014 012 04 05 06 013 014 012 04 05 06 013 014 012 04 05 06 013 014 012 04 05 06 013 014 012 04 05 06 013 014 012 04 05 06 013 014 012 04 05 06 013 010 07 06 015 02 06 015 07 06 015 07 06 015 07 06 015 07 06 015 07 06 015 07 06 015 07 06 015 07 06 05 09 010 011 014 015 07 06 05 09 010 011 014 015 07 06 05 09 010 011 014 015 07 06 05 09 010 011 014 011 014 015 07 06 05 09 011 014 016 017 011 014 016 017 017 010 011 014 016 017 011 016 011 016 017 011 016 017 016 011 016 017 016 011 016 011 016 017 017 010 016 017 010 016 017 010 010 010 012 015 011 016 011 016 017 017 016 017 010 016 017 010 010 016 011 016 017 010 010 010 010 010 010 010	$\begin{array}{c} 2.33(3)\\ 2.41(3)\\ 2.44(3)\\ 2.51(2)\\ 2.99(4)\\ 3.01(4)\\ 3.02(3)\\ 3.50(4)\\ 2.28(3)\\ 2.29(3)\\ 2.41(3)\\ 2.28(3)\\ 2.29(3)\\ 2.41(3)\\ 2.28(3)\\ 2.29(3)\\ 2.41(3)\\ 2.29(3)\\ 2.41(3)\\ 2.27(4)\\ 2.97(3)\\ 3.05(3)\\ 2.20(2)\\ 2.30(3)\\ 2.34(2)\\ 2.67(3)\\ 3.16(3)\\ 3.16(3)\\ 3.16(3)\\ 3.16(3)\\ 2.22(3)\\ 2.23(4)\\ 2.30(6)\\ 2.30(3)\\ 2.53(2)\\ 2.54(4)\\ 2.90(4)\\ 3.20(4)\\ 3.20(4)\\ 3.20(4)\\ 3.20(4)\\ 3.20(4)\\ 3.20(4)\\ 3.20(4)\\ 3.25(3)\\ 2.95(4)\\ 2.98(4)\\ 3.05(4)\\ 2.21(3)\\ 2.48(4)\\ 2.57(3)\\ 2.98(6)\\ 3.11(5)\\ 3.44(3)\\ 1.59(3)\\ 1.61(3)\\ 1.61(3)\\ 1.61(3)\\ 1.61(3)\\ 1.61(3)\\ 1.61(3)\\ 1.61(3)\\ 1.61(3)\\ 1.61(3)\\ 1.61(3)\\ 1.61(3)\\ 1.63(4)\\ 1.82(4)\\ 1.84(2)\\ 1.87(3)\\ \end{array}$	Pb1 Pb1 Pb1 Pb2 Pb2 Pb3 Pb3 Pb3 Pb3 Se1 Se1 Se1 Se1 C1 C1		02 03 04 01 02 03 06 02 03 05 04 04 04 04 05 01 02 03 06	$\begin{array}{c} 2.345(3) \ (2 \times) \\ 2.502(5) \\ 2.673(3) \ (2 \times) \\ 2.8910(12) \ (2 \times) \\ 3.358(3) \ (2 \times) \\ 2.423(3) \ (4 \times) \\ 2.865(4) \ (2 \times) \\ 3.392(3) \ (4 \times) \\ 2.4760(13) \\ 2.500(3) \ (2 \times) \\ 2.840(5) \\ 2.8893(12) \ (2 \times) \\ 2.907(3) \ (2 \times) \\ 3.032(3) \ (2 \times) \\ 1.642(4) \\ 1.653(4) \\ 1.995(3) \ (4 \times) \\ 1.278(6) \ (2 \times) \\ 1.318(9) \end{array}$	Pb1 Pb1 Pb1 Pb1 Pb1 Pb2 Pb2 Pb2 Pb2 Pb2 Pb2 Pb2 Pb2 S1 S1 S1 Te1 Te1 Te1		02 02 03 07 04 05 01 06 03 03 01 01 02 05 04 06 05 04 07 05 06 04 03 02 01	2.397(3) 2.536(3) 2.594(3) 2.632(3) 2.677(3) 2.789(3) 2.993(3) 3.107(4) 3.206(3) 2.335(3) 2.375(3) 2.384(3) 2.753(3) 2.981(4) 3.029(3) 3.164(3) 3.200(4) 3.455(3) 1.462(3) 1.476(3) 1.488(3) 1.488(3) 1.488(3) 1.895(3)

Pb₃(SeO₄)(TeO₃)₂

Pb1 2.01 [1.87], Fb2 1.58 [1.91], Se1 6.19, Te1 4.03, O1 1.85 (1Se, 2Pb) [1Se; 1.54]; O2 2.06 (1Se, 2Pb), O3 2.09 (1Te, 2Pb), O4 1.99 (1Te, 2Pb), O5 2.10 (1Te, 2Pb).

 Pb₇O₄(SeO₄)₂(TeO₃)

 Pb1 1.99 [1.59], Pb2 1.89 [1.66], Pb3 1.99 [1.81], Pb4 1.81 [1.53], Pb5 1.97 [1.50], Pb6 1.82 [1.13], Pb7 1.91 [1.48], Se1 6.36, Se2 6.30, Te1 4.27, O1 1.99 (4Pb), O2 1.97 (4Pb), O3 1.96 (4Pb), O4 2.00 (4Pb), O5 2.13 (1Te, 3Pb), O6 2.15 (1Te, 4Pb) [1.87; 1Se, 1Pb], O7 2.00 (1Se, 4Pb) [1.67; 1Se, 1Pb], O8 2.43 (1Te, 4Pb), O9 1.95 (1Se, 3Pb) [1.50; 1Se], O10 2.01 (1Se, 3Pb) [1.71; 1Se], O11 1.92 (1Se, 2Pb) [1.68; 1Se], O12 2.00 (1Se, 2Pb) [1.87; 1Se, 1Pb], O13 2.13 (1Te, 4Pb) [1.79; 1Te, 1Pb], O14 1.98 (1Se, 4Pb) [1.56; 1Se], O15 1.83 (1Se, 2Pb) [1.65, 1Se]

Pb₅(SeO₄)₂(TeO₄)(CO₃) Pb1 2.14 [1.72], Pb2 2.10 [1.57], Pb3 2.00 [1.02], Se1 5.89, Te1 3.81, C1 3.92, O11.75 (1Se, 3Pb) [1.44; 1Se], O2 2.14 (1Te, 3Pb), O3 1.86 (1C, 2Pb) [1.69; 1C, 1Pb], O4 2.04 (1Se, 4Pb) [1.72; 1Se, 1Pb], O5 1.78 (1Se, 2Pb) [1.48; 1Se], O6 1.92 (1C, 2Pb).

Pb₂(SO₄)(TeO₃)

Pb1 1.97 [1.67], Pb2 1.98 [1.523], S1 5.95, Te1 3.82, O1 2.22 (1Te, 3Pb) [2.10; 1Te, 2Pb], O2 2.26, O3 2.13 (1Te, 3Pb) [2.05; 1Te, 2Pb], O4 1.84 (1S, 3Pb) [1.68; 1S, 1Pb], O5 (1.88 1S, 3Pb) [1.68; 1S, 1Pb], O6 1.64 (1S, 2 Pb) [1S; 1.46], O7 1.80 (1S, 1Pb).

a) For bond valence sum calculations, Pb–O distances up to 3.55 Å were used; in brackets the results only for "short" Pb–O distances up to 2.80 Å are considered. For O atoms the number and type of the coordinated atoms are given.

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For the final structure refinement of $Pb_7O_4(SeO_4)_2(TeO_3)$ and $Pb_5(SeO_4)_2(TeO_4)(CO_3)$, oxygen atoms were refined with isotropic displacement parameters, whereas for refinement of $Pb_3(SeO_4)(TeO_3)_2$ and $Pb_2(SO_4)(TeO_3)$ they were refined with anisotropic displacement parameters. Numerical data of the data collections and structure refinements are summarized in Table 2 and selected bond lengths are listed in Table 3. A complete list of bond length including symmetry codes to generate symmetry-related sites is given as Supporting Information. For the four structure models bond valence sum calculations^[14] were performed by using values of $R_0 = 1.963$, B = 0.49 for Pb–O interactions,^[15] as well as $R_0 = 1.624$, B = 0.37 for S–O, $R_0 = 1.788$, B = 0.37 for Se–O, $R_0 = 1.917$, B = 0.37 for Te–O and $R_0 = 1.390$, B = 0.37 for C–O interactions;^[16] results of the calculations are compiled in Table 3. Drawings of structural details were produced using the program ATOMS.^[17]

Further details of the crystal structures investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Germany (Fax: +49-7247-808-666; Leopoldshafen, E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request-fordeposited-data.html) on quoting the depository numbers CSD-432394 [Pb₃(SeO₄)(TeO₃)₂], CSD-432395 [Pb₇O₄(SeO₄)₂(TeO₃)], CSD-432396 $[Pb_{5}(SeO_{4})_{2}(TeO_{4})(CO_{3})],$ CSD-432397 and [Pb₂(SO₄)(TeO₃)].

Supporting Information (see footnote on the first page of this article): Detailed list of selected bond lengths and angles including symmetry codes.

Results and Discussion

Formation

As previously pointed out.^[2] multi-phase formation of hydrothermally synthesized products is a common observation and also applies for the present $Pb^{II}/X^{VI}/Te^{IV}/O/(C)$ (X = S and Se) systems. All experiments resulted in the formation of multi-phase products; representative batches with reagents used and product phases determined are compiled in Table 1. Just like in the related systems $M^{II}/X^{VI}/Te^{IV}/O$, where lead is replaced by divalent metals of comparable size (M = Ca, Sr,Cd, Hg^[1,2]), in the present study compounds containing both tellurium and sulfur/selenium are minority products, whereas compounds containing tellurium as the only chalcogen are majority products. Likewise, formation of Te- and S/Se-containing phases becomes more successful at basic conditions (pH 9-11), which also explains the formation of the "basic" compound $Pb_7O_4(SeO_4)_2(TeO_3)$ (for a discussion of "basic" features in this compound, see below). One batch using basic lead carbonate PbCO₃·Pb(OH)₂ as the lead source resulted in an incorporation of carbonate (pH of the resulting solution was ca. 6), whereas for other lead sources [lead(II)-acetate or -nitrate] under similar conditions an incorporation of the respective anion was not observed.

Crystal Structures - Common Features

The lone electron pair situated at the Pb²⁺ cation is associated with a non-spherical charge distribution which, in the majority of cases, causes a disposition of ligands around the cation resulting in an identifiable void: the lone electron pair is said to be "stereochemically active". According to Shimoni-Livny et al., the coordination environment around lead(II) can be classified into two categories, viz. holodirected, in which the bonds to the ligands are directed throughout the surface of an encompassing sphere, and hemidirected, in which the bonds are directed throughout only a part of the encompassing sphere, leading to an identifiable void or gap.^[18] The distinction whether the coordination sphere around a Pb²⁺ cation is considered to be holo- or hemidirected is not unproblematic and clearly depends on the radius of the defined coordination sphere (or the respective coordination number of the central atom). It appears obvious that for large coordination spheres the tendency for a holodirected coordination increases (then accompanied with higher coordination numbers and a disparate bond lengths distribution), whereas for only small coordination spheres the tendency for hemidirected coordination prevails. However, since the coordination number is somewhat subjective,^[19] in particular for large ions, the threshold for the radius of the first coordination sphere is not clearly definable.

Our approach for the definition of the first coordination sphere of the Pb²⁺ cation in the title structures is based (a) on the sum of the van der Waals radii of Pb and O (2.02 and 1.52 Å, respectively)^[20] and (b) on bond valence calculations. A Pb–O bond of 3.5 Å still accounts for 2.2% of the overall bond valence sum (BVS). Therefore Pb-O interactions up to 3.55 Å were considered for BVS calculations, in agreement with the sum of the van der Waals radii given above. Based on the Pb-O bond length distributions (Table 3), "short" Pb-O bonds might be considered for distances less than 2.80 Å and consequently "long" bonds greater than this boundary. However, from the BVS calculations it is obvious that "long" Pb–O bonds (> 2.80 Å) significantly contribute to the valence sum of an individual lead atom. Inclusions of these "long" bonds raise the bond valence sums at some of the lead and oxygen atoms to much more reasonable values, cf. Table 3. For the sake of clarity, crystal structure plots (Figure 2, Figure 5, Figure 8, Figure 10) in this communication include only Pb-O bonds up to 2.80 Å, whereas individual [PbO_x] polyhedra for each structure are shown with all relevant Pb-O contacts, distinguishing short Pb-O distances with filled and long Pb-O distances with open bonds, respectively (Figure 1, Figure 3, Figure 6, Figure 9).

All four title structures are centrosymmetric and contain tetrahedral XO_4^{2-} anions (X = Se and S). The observed bond lengths (average 1.63 Å for the three selenate structures and 1.48 Å for the sulfate structure) and angles are characteristic for selenate and sulfate groups.^[21,22] In three out of four structures, the oxotellurate(IV) anion has a trigonal-pyramidal configuration, representing the most frequently observed shape of isolated oxotellurate(IV) anions.^[23] The mean Te–O distances and O–Te–O angles in the three structures are very similar (Pb₃(SeO₄)(TeO₃)₂ 1.87 Å, 95°, Pb₇O₄(SeO₄)₂(TeO₃) 1.85 Å, 97°, Pb₂(SO₄)(TeO₃) 1.89 Å, 92°) and conform with literature data.^[23,24] In all of the four structures, the XO_4^{2-} (X = S and Se) anions and the oxotellurate(IV) anions are separated from each other.

$Pb_3(SeO_4)(TeO_3)_2$

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In the asymmetric unit one of two Pb sites, viz. Pb2, as well as the Se site is located on a twofold rotation axis (Wyckoff position 4*e*); all other sites (the second Pb, the Te and five O sites) are situated on general positions. Pb1 has a coordination number of six if only short Pb–O bonds are taken into account. One markedly short Pb–O bond is present with ≈ 2.29 Å, followed by five similar bond lengths between 2.54 and 2.65 Å. The coordination number of Pb1 increases to seven under consideration of an additional long bond of 2.93 Å. In the same view Pb2 has coordination numbers of four using only short bonds [pairs with d(Pb-O) = 2.33 and 2.53 Å] and of six taking into account also the long bonds [a pair with d(Pb-O) =2.84 Å]. The resulting coordination spheres around both Pb²⁺ cations are considerably distorted and are displayed in Figure 1.



Figure 1. The coordination polyhedra of the two Pb^{2+} cations in the crystal structure of $Pb_3(SeO_4)(TeO_3)_2$. For symmetry codes, see: Supporting Information.

The crystal structure of Pb₃(SeO₄)(TeO₃)₂ (Figure 2) can be rationalized as being divided into columns extending parallel [001]. Each column consists of a centrosymmetric pair of building units of the same kind stacked along the direction of propagation. The so formed {Pb1}₂, {Pb2}₂, {Se1}₂, and {Te1}₂ columns are arranged in such a way that the {Pb}₂ columns alternate with {Te1}₂ or {Se1}₂ columns along [100] leading to a packing sequence [{Pb2}₂ - {Te1}₂ - {Pb1}₂ - {Se1}₂ - {Pb1}₂ - {Te1}₂ - {Pb1}₂ - {Se1}₂ - {Pb1}₂ - {Te1}₂ - {Pb1}₂ - {Se1}₂ along this direction to build up "sheets". Adjacent "sheets" are shifted according to the *c* glide along [010]. Individual columns are linked by common oxygen atoms into a framework, whereby neither TeO₃²⁻ nor SeO₄²⁻ anions are condensed together or among themselves.

 $Pb_3(SeO_4)(TeO_3)_2$ has the same formula type as the two isotypic structures of $Hg_3(SeO_4)(TeO_3)_2^{[1]}$ and $Ca_3(SeO_4)$ - $(TeO_3)_2^{[2]}$ but shows no structural relation to the latter two. These compounds crystallize with polar structures in space group type $P2_1$, and their structural set-up is organized in metal oxotellurate(IV) layers held together by intermediate selenate anions.

$Pb_7O_4(SeO_4)_2(TeO_3)$

This compound has the highest lead content of the four title compounds, with seven unique Pb sites in the asymmetric unit,



Figure 2. The crystal structure of $Pb_3(SeO_4)(TeO_3)_2$ in a projection along [001]. Te atoms and TeO_3^{2-} trigonal pyramids are given in red, Se atoms and SeO_4^{2-} tetrahedra in orange, Pb^{2+} cations in blue, O atoms are white. Displacement ellipsoids are drawn at the 50% probability level.

completed by two Se, one Te and 15 O sites, all on general positions.

For a rational description and structural classification of mineral and synthetic lead(II) oxocompounds, Krivovichev and co-workers introduced the concept of oxo-centered [OPb₄] tetrahedra.^[25] This motif is representative for "basic" O²⁻ anions in the structure, i.e. oxygen atoms that are exclusively surrounded by lead atoms. In the title structures, [OPb₄] tetrahedra are solely present in Pb₇O₄(SeO₄)₂(TeO₃), apparently because in this structure the Pb:X ratio (X = central atom of anoxoanion) is with 7:3 the highest in comparison with the three other structures. Four such [OPb4] units are present in $Pb_7O_4(SeO_4)_2(TeO_3)$, all in form of distorted tetrahedra. The corresponding Pb-O distances are the shortest in the structure and range from 2.20 to 2.50 Å (Figure 3). All four [OPb₄] tetrahedra share the Pb1 atom. In this way a $\{O_4Pb_9\}$ subunit is made up by condensation of two edges of each [OPb₄] tetrahedron. Adjacent subunits are linked by edge-sharing on two sides (Pb2···Pb2'; Pb···Pb3'; ' denotes the symmetry-related counterpart) of each subunit into zigzag chains of overall composition ${}^{1}_{\infty}$ [O₄Pb₇]⁶⁺, with the propagation of the chains parallel [001] (Figure 4). The periodicity of the ${}^{1}_{\infty}$ [O₄Pb₇]⁶⁺ chains is 2, with an identity period of 11.6317(8) Å, a value that corresponds with the length of the c axis. Although lead(II) compounds comprising oxo-centered tetrahedra with a O:Pb ratio of 4:7 are known for the isotypic phosphate and arsenate phases $Pb[Pb_7O_4]O(XO_4)_2$ (X = P and As)^[25], the connectivity





Figure 3. The coordination polyhedra of the seven Pb^{2+} cations in the crystal structure of $Pb_7O_4(SeO_4)_2(TeO_3)$. For symmetry codes, see: Supporting Information.

of the $[OPb_4]$ tetrahedra into a layered arrangement is different than in $Pb_7O_4(SeO_4)_2(TeO_3)$, where chains of condensed $[OPb_4]$ tetrahedra are present. This makes the structural unit of ${}_{\infty}^{1}[O_4Pb_7]^{6+}$ chains unprecedented in the classification of basic lead(II) oxocompounds.

The ${}^{1}_{\infty}$ [O₄Pb₇]⁶⁺ chains are flanked by Te1O₃²⁻ pyramids that are connected to the outer lead atoms of the chains through Pb-O bonds with the shortest Pb-O distance around 2.50 Å for each of the three O atoms of the $Te1O_3^{2-}$ pyramid; more remote lead atoms situated between 2.65 and 3.20 Å complete the coordination sphere of these oxygen atoms. In this way the ${}^{1}_{\infty}[O_4Pb_7]^{6+}$ chains are linked by the oxotellurate(IV) units into sheets with composition ${}^{1}_{\infty}[O_4Pb_7(TeO_3)]^{4+}$ parallel (010). The remaining SeO_4^{2-} tetrahedra occupy the remaining space between adjacent sheets and are only loosely bound through rather weak contacts between the oxygen and lead atoms of the sheets (Table 3, Figure 5). In this sense the SeO_4^{2-} tetrahedra have the role as spacers between the ${}^{1}_{\infty}$ [O₄Pb₇(TeO₃)]⁴⁺ sheets. Some of the corresponding selenate oxygen atoms (e.g. O10, O11, O14, O15) have their shortest contacts to the lead atoms at distances greater than 2.9 Å, which explains their comparatively high displacement param-



Figure 4. The unprecedented motif of a ${}^{1}_{\infty}[O_4Pb_7]^{6+}$ chain of condensed [OPb₄] tetrahedra in the crystal structure of Pb₇O₄(SeO₄)₂(TeO₃). Displacement ellipsoids are drawn at the 74% probability level.



Figure 5. The crystal structure of $Pb_7O_4(SeO_4)_2(TeO_3)$ in a projection along [100]. Color codes are as in Figure 2; displacement ellipsoids are drawn at the 74% probability level.

eters and a significant underbonding with respect to the results of BVS calculations (Table 3). A similar behavior was observed for some structures with mixed oxochalcogenate anions where the metals are calcium, cadmium, or strontium.^[2]

ARTICLE

$Pb_5(SeO_4)_2(TeO_4)(CO_3)$

Pb₅(SeO₄)₂(TeO₄)(CO₃) is the only mixed oxochalcogenate title compound containing an additional anionic group, viz. a carbonate anion. All cations and all central atoms of the oxo anions are situated on special positions of space group *Cmcm*: Pb1, Pb3, Se1 on Wyckoff position 8*g* (site symmetry *.m*), Pb2, Te1, and C1 on Wyckoff position 4*c* (*m*2*m*). Lead atom Pb1 shows a [4+4] coordination, whereas the coordination spheres of atoms Pb2 and Pb3 can be divided into a [4+6] and a [3+7] mode, respectively (Figure 6). The coordination polyhedron of the tellurium atom is unique in comparison with the three other title structures (each containing trigonal TeO₃^{2–} pyramids) and represents the very rare case of a tetragonal TeO₄^{4–} pyramid with the Te atom at the apex.



Figure 6. The coordination polyhedra of the three Pb^{2+} cations in the crystal structure of $Pb_5(SeO_4)_2(TeO_4)(CO_3)$. For symmetry codes, see: Supporting Information.

In comparison with the trigonal-pyramidal TeO₃²⁻ anions (average Te-O bond length 1.87 Å in the three structures), the four oxygen ligands in the TeO4⁴⁻ anion require more space and the bond length increases to 1.995(3) Å. The main structural features of the two types of anions are comparatively displayed in Figure 7. Although a coordination number of four is not uncommon for oxotellurate(IV) units^[23,24], with TeO₄ disphenoids as the most frequently observed coordination polyhedra, the configuration of a tetragonal TeO₄⁴⁻ pyramid is only known from the rare mineral nabokoite, K[Cu₇(TeO₄)- $(SO_4)_5$]Cl.^[26] In the Pb₅(SeO₄)₂(TeO₄)(CO₃) structure the point group symmetry of the TeO_4^{4-} pyramid is m2m whereas it is 4. in the structure of nabokoite, however with similar Te-O bond lengths and O-Te-O angles: 1.995(3) Å and 130.5(1), 80.3(2), 79.5(2)° in Pb₅(SeO₄)₂(TeO₄)(CO₃) and 2.029 Å and 124.22, 77.36° in nabokoite.

The two different C–O bond lengths $[2 \times 1.278(6)]$ and 1.318(9) Å] average to 1.291 Å, in very good agreement with the reported mean distance of 1.284 Å for the carbonate anion.^[27] In the crystal structure (Figure 8) the lead atoms



Figure 7. Structural features of the trigonal-pyramidal TeO_3^{2-} anion in the crystal structures of $\text{Pb}_3(\text{SeO}_4)(\text{TeO}_3)_2$, $\text{Pb}_7\text{O}_4(\text{SeO}_4)_2(\text{TeO}_3)$ and $\text{Pb}_2(\text{SO}_4)(\text{TeO}_3)$ with averaged values (left), and of the tetragonal-pyramidal TeO_4^{4-} anion (right) in the crystal structure of $\text{Pb}_5(\text{SeO}_4)_2(\text{TeO}_4)(\text{CO}_3)$.

make up a three-dimensional network with oxygen atoms of the TeO_4^{4-} , SeO_4^{2-} , and CO_3^{2-} polyhedra (taking into account also the long Pb–O bonds). In this connection the TeO_4^{4-} and CO_3^{2-} polyhedra alternate with each other along [010] and are aligned into sheets parallel (001) at $z = \frac{1}{4}$; the SeO₄²⁻ tetrahedra are likewise organized in sheets at $z \approx \frac{1}{4}$. This arrangement leaves space for the lone electron pairs of the Pb²⁺ cations and the TeO_4^{4-} anion. In a very simple view based on the Pb–O bond lengths distribution around the lead atoms, the orientation and the shape of the corresponding $[PbO_r]$ polyhedra relative to each other or to the TeO_4^{4-} tetragonal pyramid, and the site symmetries of the lead and tellurium atoms, the orientations of the lone pairs of electrons can be assumed. From there it appears that they point towards each other for the symmetryrelated pairs Pb1...Pb1' and Pb3...Pb3', and for the pair Pb2...Te1. However, the long distances of 3.4817(4), 4.9926(4), and 5.0225(5) Å, respectively, between corresponding atoms does not allow a significant E···E interaction to occur.



Figure 8. The crystal structure of $Pb_5(SeO_4)_2(TeO_4)(CO_3)$ in a projection approximately along [100]. C atoms and CO_3^{2-} triangles are grey; color codes of other atoms and polyhedra and displacement ellipsoids are as in Figure 2.

$Pb_2(SO_4)(TeO_3)$

The asymmetric unit of the sulfate phase comprises of two Pb, one S, one Te, and seven O sites. The coordination spheres



of the two lead cations are markedly different (Figure 9). Under consideration of only short Pb-O bonds, cation Pb1²⁺ is surrounded by six oxygen atoms in the range 2.4–2.8 Å whilst cation Pb2²⁺ has only four coordination partners, three at \approx 2.35 Å and one at 2.75 Å. If more remote Pb-O bonds are considered, then the coordination numbers expand to nine for both Pb1 and Pb2. In the crystal structure, the lead cations are organized in a layered arrangement extending parallel (001) at $z \approx 0, \frac{1}{2}$, whereby the lead atoms in these layers are stacked into columnar packets along [010]. Anion polyhedra of the same kind are likewise arranged into columnar arrangements along [010], alternating along [100]. In this manner, anion layers are formed which extend parallel (001) at $z \approx \frac{1}{4}$ and $\frac{3}{4}$. In the final arrangement of the crystals structure, the metal and anion layers alternate along [001] and build up the threedimensional framework (Figure 10). The structure of $Pb_2(SO_4)(TeO_3)$ is isotypic with that of the oxochromate(VI) analogue Pb₂(CrO₄)(TeO₃) which was very recently obtained by solid state reactions from PbO, TeO₂ and chromium(III) precursors.[28]



Figure 9. The coordination polyhedra of the two Pb^{2+} cations in the crystal structure of $Pb_2(SO_4)(TeO_3)$. For symmetry codes, see: Supporting Information.



Figure 10. The crystal structure of $Pb_2(SO_4)(TeO_3)$ in a projection along [010]. S atoms and SO_4^{2-} triangles are orange; color codes of the other building units and displacement ellipsoids are as in Figure 2.

Conclusions

Although incorporation of tetrahedral XO_4^{2-} anions (X = S and Se) into lead oxotellurate(IV) under hydrothermal conditions led to four compounds obtained as minority phases with compositions $Pb_3(SeO_4)(TeO_3)_2$, $Pb_7O_4(SeO_4)_2(TeO_3)$, $Pb_{5}(SeO_{4})_{2}(TeO_{4})(CO_{3})$, and $Pb_{2}(SO_{4})(TeO_{3})$, the primary goal to obtain phases with non-centrosymmetric structures could not be accomplished. Despite the presence of two structure-directing building units with stereochemically active lone electron pairs, viz. Pb²⁺ cations and oxotellurate(IV) anions, that might facilitate the formation of non-centrosymmetric crystal structures, all compounds crystallize in centrosymmetric space group types. In all four structures, the respective oxoanions (SeO₄²⁻ or SO₄²⁻ tetrahedra, TeO₃²⁻ trigonalpyramids or the very rare TeO_4^{4-} tetragonal pyramid, as well as the trigonal-planar CO_3^{2-} anion) are isolated in the crystal structures.

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Keywords: Crystal engineering; Hydrothermal synthesis; Oxotellurates(IV); Lead; Mixed oxochalcogenates; Crystal structure

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· PbO · Pb-acetate · PbCO₃·Pb(OH)₂ · TeO₂ · H₂SeO₄/H₂SO₄ · KOH

Hydrothermal conditions 210 °C, one week

→

 $\begin{array}{l} \mathsf{Pb}_{3}(\mathsf{SeO}_{4})(\mathsf{TeO}_{3})_{2} \\ \mathsf{Pb}_{7}\mathsf{O}_{4}(\mathsf{SeO}_{4})_{2}(\mathsf{TeO}_{3}) \\ \mathsf{Pb}_{5}(\mathsf{SeO}_{4})_{2}(\mathsf{TeO}_{4})(\mathsf{CO}_{3}) \\ \mathsf{Pb}_{2}(\mathsf{SO}_{4})(\mathsf{TeO}_{3}) \end{array}$

ARTICLE

<i>M. Weil</i> , * <i>M.</i>	M. Shirkhanlou							
Incorporation	of	Sulfate	or	Selenate	Groups	into	Oxo-	
tellurates(IV): II. Compounds with Divalent Lead								