Incorporation of Sulfate or Selenate Groups into Oxotellurates(IV): III. Compounds with Magnesium or Zinc

Matthias Weil*[a] and Mahdi Shirkhanlou^[a]

Abstract. The mixed oxochalcogenate compounds $Mg_2(SO_4)(TeO_3)-(H_2O)$, $Mg_3(SO_4)(TeO_3)(OH)_2(H_2O)_2$, $Zn_2(SeO_4)(TeO_3)$, and $Zn_4(SO_4)(TeO_3)_3$ were obtained under hydrothermal conditions (210 °C, autogenous pressure). Structure analyses using single-crystal X-ray data revealed tellurium in all four compounds to be present in oxidation state +IV, whereas sulfur or selenium atoms exhibit an oxidation state of +VI. In the crystal structures of the two magnesium compounds, $[MgO_5(H_2O)]$ octahedra $[Mg_2(SO_4)(TeO_3)(H_2O)$ structure, isotypic with the Co and Mn analogues] or $[MgO_4(OH)_2]$ and $[MgO_4(OH)_2(H_2O)_2]$ octahedra $[Mg_3(SO_4)(TeO_3)(OH)_2(H_2O)_2$ structure.

Introduction

A determining factor in the crystal chemistry of oxotellurates(IV)^[1,2] is the presence of the $5s^2$ lone electron pair at the tellurium(IV) atom that – in the majority of cases – is stereochemically active.^[3] The shapes of the resulting oxotellurate(IV) anions, with coordination numbers of the Te^{IV} atom ranging from three to five, are considered to have significant influence for a possible formation of non-centrosymmetric crystal structures, a precondition for non-linear optical or other interesting physical properties.^[4]

In recent projects we have investigated the incorporation of tetrahedral sulfate or selenate anions into metal oxotellurate-(IV) frameworks with the objective to use these building units as spacers and to obtain new phases with non-centrosymmetric crystal structures. For this purpose we have originally chosen systems with divalent metal ions having large radii (Hg, Cd, Ca, Sr, and Pb), that were reacted hydrothermally with precursors of Te^{IV} and S^{VI} or Se^{VI [5-7]} The goal of the current project was to investigate whether sulfate or selenate anions can also be incorporated under hydrothermal conditions into oxotellurates(IV) of metals with smaller ions, resulting in noncentrosymmetric structures. For this purpose, we chose magnesium and zinc, and succeeded in the preparation and structural characterization of four new double salts with composition $Mg_2(SO_4)(TeO_3)(H_2O),$ Mg₃(SO₄)(TeO₃)(OH)₂(H₂O)₂, $Zn_2(SeO_4)(TeO_3)$, and $Zn_4(SO_4)(TeO_3)_3$.

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ture, novel structure type] as well as trigonal-pyramidal TeO₃²⁻ anions make up metal oxotellurate sheets, which are bridged by SO₄²⁻ anions. The polar crystal structure of Zn₂(SeO₄)(TeO₃) is isotypic with Zn₂(MoO₄)(TeO₃) and consists of [ZnO₄] tetrahedra, [ZnO₆] octahedra, SeO₄²⁻ and TeO₃²⁻ anions as principal building units that are connected into a framework structure. Such a structural arrangement, with basically the same coordination polyhedra as in Zn₂(SeO₄)(TeO₃) but with SO₄²⁻ instead of SeO₄²⁻ anions, is also found in the telluriumrich compound Zn₄(SO₄)(TeO₃)₃ that crystallizes in a novel structure type.

Experimental Section

Synthesis: Selenic acid was prepared by oxidizing SeO_2 in aqueous solution with an H_2O_2/HNO_3 mixture. Zinc selenate pentahydrate was prepared by dissolving basic zinc carbonate in an excess of selenic acid and the solution evaporated nearly until dryness. The obtained product was recrystallized from water and checked by powder X-ray diffraction for purity. All other chemicals were used from commercial sources.

Hydrothermal syntheses were conducted in sealed Teflon containers (capacity ca. 5–10 mL) in steel autoclaves at autogenous pressure at 210 °C for one week. Experimental details are described elsewhere.^[7] Magnesium and zinc compounds in form of their oxides, chlorides, sulfates or selenates were mixed in stoichiometric amounts with TeO₂. For batches starting from oxides or chlorides, concentrated selenic acid (ca. 80 wt%) or sulfuric acid (ca. 94 wt%) were added; for some experiments KOH or NaOH were also added to ensure slightly basic conditions. The solid products were filtered off, washed subsequently with mother liquor, water and ethanol. 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 on a PANalytical X'PertPro system.

Thermogravimetry: The samples were heated in alumina crucibles in a stream of argon (10 mL·min⁻¹) with a heating rate of 10 K·min⁻¹ in the temperature interval 30–1000 °C with a Netzsch TG F3 Tarsus system.

Single Crystal Diffraction and Structure Analysis: Crystals were pre-selected under a polarizing microscope. Indexing procedures of selected single crystals revealed unknown unit cells for some crystals. Intensity data of these crystals were measured either at room temperature (Siemens SMART) or at -173 °C in a stream of cold nitrogen (Bruker APEX-II). Data strategies were optimized with APEX2^[8] using φ - and ω -scans and with SMART^[8] using ω -scans. Intensity data were integrated with SAINT^[8] and absorption corrections were applied

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

Amounts of starting materials and stoichiometric ratios	Phases determined by X-ray powder diffraction of the $\text{bulk}^{a)}$	(Additional) phases determined by sin- gle-crystal X-ray diffraction
Strong acidic media (phase	s crystallized from solution after hydrothermal expe	riment)
MgO 0.13 g, TeO ₂ 0.10 g, H ₂ SO ₄ 1 mL;	$Te_2O_3(SO_4)^{[16]}$	$Te_2O_3(SO_4)$
$MgO:TeO_2:H_2SO_4 = 5:1:>10$		
ZnO 0.15 g, TeO ₂ 0.10 g, H ₂ SO ₄ 1 mL;	$ZnSO_4 \cdot H_2O^{[17]}, Te_2O_3(SO_4)$	$Te_2O_3(SO_4)$
$ZnO:TeO_2:H_2SO_4 = 3:1:>10$		
MgO 0.13 g, TeO ₂ 0.10 g, H ₂ SeO ₄ 1 mL;	$H_6 TeO_6^{[18]}$	H ₆ TeO ₆
$MgO:TeO_2:H_2SeO_4 = 5:1:>8$		
ZnO 0.15 g, TeO ₂ 0.10 g, H ₂ SeO ₄ 1 mL;	H_6TeO_6 , $ZnSeO_4 \cdot H_2O^{[19]}$	
$ZnO:TeO_2:H_2SeO_4 = 3:1:>8$		
Slightly basic media (pH ≈ 9	-10; phases obtained directly after hydrothermal exp	periment)
MgCl ₂ ·2H ₂ O 0.38 g, TeO ₂ 0.18 g, H ₂ SO ₄ 0.3 mL,	$Mg_2Te_3O_8^{[15]}, MgTe_2O_5^{[20]}$	$Mg_2(SO_4)(TeO_3)(H_2O)^{b)}$
NaOH 0.09 g;		
$MgCl_2 \cdot 2H_2O:TeO_2:H_2SO_4:NaOH = 2.5:1:2:2$		
MgSO ₄ •7H ₂ O 0.38 g, TeO ₂ 0.10 g, KOH 0.07 g;	$Mg_2Te_3O_8$	$Mg_3(SO_4)(TeO_3)(OH)_2(H_2O)_2^{b)}$
$MgSO_4 \cdot 7H_2O:TeO_2:KOH = 2.5:1:2$		$Mg_2Te_3O_8$,
		$Mg_2(SO_4)(OH)_2$ (caminite) ^[21] ,
		$K_2Mg_3(OH)_2(SO_4)_3 \cdot 2H_2O^{[22]}$
ZnO 0.106 g, TeO ₂ 0.136 g, H ₂ SeO ₄ 0.2 mL, KOH 0.076 g;	$Zn_2Te_3O_8^{[23]}$, $TeO_2^{[24]}$, $ZnO^{[25]}$	$Zn_2(SeO_4)(TeO_3)^{b)}$
$ZnO:TeO_2:H_2SeO_4:KOH = 1.6:1:1:1.6$		
ZnSeO ₄ •5H ₂ O 0.47 g, TeO ₂ 0.10 g, KOH 0.07 g;	$Zn_2Te_3O_8$	$Zn_2(SeO_4)(TeO_3)^{b)}$
$ZnSeO_4 \cdot 5H_2O:TeO_2:KOH = 2.5:1:2$	$Zn_2(SeO_4)(TeO_3)^{b)}$	
ZnSO ₄ •7H ₂ O 0.36 g, TeO ₂ 0.10 g, KOH 0.07 g;	$Zn_3(TeO_3)_3(SO_4)^{b)}$	$Zn_3(TeO_3)_3(SO_4)^{b)}$
$ZnSO_4 \cdot 7H_2O:TeO_2:KOH = 2:1:2$		

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 work.

with SADABS.^[8] The crystal structures were solved by direct methods and refined using the SHELXTL program package.^[9]

The hydrogen atoms of the water molecule in the structure of $Mg_2(SO_4)(TeO_3)(H_2O)$ were clearly discernible from a difference map

Table 2. Details of data collections and structure refinements.

	Mg ₂ (SO ₄)(TeO ₃)(H ₂ O)	Mg ₃ (SO ₄)(TeO ₃)(OH) ₂ (H ₂ O) ₂	Zn ₂ (SeO ₄)(TeO ₃)	Zn ₄ (SO ₄)(TeO ₃) ₃
M _R	338.30	414.64	449.30	884.34
Crystal size /mm ³	$0.08 \times 0.10 \times 0.12$	$0.009 \times 0.009 \times 0.280$	$0.02 \times 0.06 \times 0.25$	$0.06 \times 0.12 \times 0.22$
Temperature /°C	-173	-173	23	-173
Diffractometer	Bruker APEX-II	Bruker APEX-II	Siemens SMART	Bruker APEX-II
Radiation; $\lambda / \text{Å}$		Mo- K_{a} ; 0.710	073	
Crystal color; form	colorless, parallelepiped	colorless, needle	colorless, lath	colorless, bar
Space group (no.)	<i>Pbcm</i> (57)	<i>Pnma</i> (62)	$P2_{1}(4)$	$P2_1/c$
Formula units, Z	4	4	2	4
a /Å	7.4239(3)	9.8038(7)	5.1889(9)	15.7405(9)
b /Å	10.1841(5)	6.0940(5)	8.1373(12)	5.1943(3)
c /Å	8.3958(4)	15.2895(11)	7.1710(12)	13.9917(8)
β /°	90	90	101.465(5)	101.3320(14)
$V/Å^3$	634.77(5)	913.46(12)	296.74(8)	1121.67(11)
μ /mm ⁻¹	5.220	3.743	19.018	16.359
X-ray density /g·cm ⁻³	3.540	3.015	5.028	5.237
Range $\theta_{\min} - \theta_{\max}$	2.74-35.15	2.47-30.21	2.90-31.42	2.97-37.99
Range	$-12 \le h \le 12$	$-13 \le h \le 13$	$-7 \le h \le 7$	$-26 \le h \le 26$
-	$-16 \le k \le 16$	$-8 \le k \le 8$	$-11 \le k \le 11$	$-8 \le k \le 8$
	$-13 \le l \le 13$	$-21 \le l \le 21$	$-10 \le l \le 10$	$-23 \le l \le 23$
Measured reflections	41730	27973	4627	35830
Independent reflections	1484	1467	1902	3785
Observed reflections $[I > 2\sigma(I)]$	1382	1112	1866	3566
R _i	0.0453	0.117	0.027	0.047
Absorption correction	SADABS	SADABS	SADABS	SADABS
Transmission coefficients	0.609;	0.650;	0.439;	0.281;
$T_{\min}; T_{\max}$	0.747	0.746	0.746	0.747
Number of parameters	67	95	101	191
Difference electron density	0.76 [0.67, O5];	1.54 [1.00, Te1];	1.34 [0.89, Te];	2.63 [0.65, Te3];
max; min / e^{-} ·Å ⁻³ (dist. /Å, atom)	-1.10 [1.23, Te1]	-1.75 [0.61, Te1]	-1.01 [0.96, O2]	-2.07 [0.46, Te3]
Flack parameter	_	_	0.070(11)	_
$R [F^2 > 2\sigma(F^2)]$	0.0173	0.0437	0.0198	0.0271
$wR_2 (F^2 \text{ all})$	0.0314	0.1025	0.0456	0.0716
GooF	1.186	1.102	1.018	1.201

Table 3. Selected interatomic distances /Å and angles /° as well as results of bond valence sum calculations /v.u., with coordination partners for oxygen atoms in parentheses.

20	1							
Mg ₂ (SO ₄)(TeO	3)(H ₂ O)				Zn ₂ (SeO ₄)(7	TeO ₃)		
Mg1	_	03		2.0453(10)	Zn1	_	05	1.925(3)
Mg1	_	04		2.0515(12)	Zn1	_	07	1.941(3)
Mg1	_	04		2.0638(11)	Zn1	_	04	1.958(3)
Mg1	_	O6		2.0860(11)	Zn1	_	01	2.067(3)
Mg1	_	01		2.1118(9)	Zn2	_	06	2.032(3)
Mg1	_	05		2.2229(11)	Zn2	_	05	2.043(3)
S1	_	O6		$1.4667(11)(2 \times)$	Zn2	_	03	2.046(3)
S1	_	02		1.4844(15)	Zn2	_	07	2.104(3)
S1	_	05		1.4938(16)	Zn2	_	04	2.180(3)
Te1	_	03		1.8499(15)	Zn2	_	02	2.398(3)
Te1	_	04		$1.8715(10) (2 \times)$	Se	_	03	1.635(3)
					Se	_	06	1.638(3)
					Se	_	01	1.643(3)
					Se	_	02	1.652(3)
$D-H\cdots A$	D-H	H•••A	D····A	≤ <i>D</i> –H••• <i>A</i>	Те	_	04	1.864(3)
01-H1···02	0.82(3)	1.79(3)	2.5816(12)	162(3)°	Те	_	05	1.870(3)
	0102(0)			(-)	Te	_	07	1.897(3)
					Te	_	02	2 533(3)
Mg1 2 04 S1 4	5 94 Tel 4 0'	7 01 (2 Mo-	H atoms not	considered) 0.65	Zn1 1 96 Z	n2 1 98 Se1 5 94	Te 3 93 (CN 3) 4	16 (CN 4) O1 (Zn Se)
$\Omega_{2}^{2}(S) 1.46 \Omega$	$3 (2 M_{\rm ff} T_{\rm e})$	$218 \ O4 \ (2)$	Mg Te) 2.08	O5 (2 Mg S) 1.90	1.86 02 (S	a_2 and long bonds t	o Zn and Te consi	(21, 4), 01 (21, 50)
$O6 (M_{0} \le 1.40, 0)$	2 (2 191 <u>8</u> , 10)	2.10, 04 (2		55 (2 mig, 5) 1.90,	1.00, 02 (3)	7n Te) 2.14 OS 6	$2 7_n$ Tel 2 20 Ω	5 (7n Se) = 1.02, 0.5 (211, 35)
CO (mg, 5) 1.0					1.51, 04(2) Te) 2.11	2.1.4, 03 (2 ZII, ICJ 2.29, U	(LII, 3C) 1.91, 07 (2 LII,
					10) 2.11.			
wig ₃ (SO ₄)(1eO	3)(UII) ₂ (H ₂ U	0112		2.020(1)	0117		0.011	
Mg1	-	O1H		2.038(4)	O1H	•••	O2H	2.744 (7)
Mg1	-	O2H		2.055(4)	O1H	•••	03	2.696 (6) (2×)
Mg1	-	O3		2.069(4)	O2H	•••	O1WA	$2.821(10)(2 \times)$
Mg1	-	O4		2.072(4)	O2H	•••	O3	2.835 (6) (2×)
Mg1	-	O2		2.097(4)	O2H	•••	O1WB	2.924 (11)
Mg1	-	O1		2.114(4)				
Mg2	-	O2H		2.015(6)				
Mg2	_	O1H		2.062(6)				
Mg2	-	O1WB		2.096(10) (2×)	O1WA	•••	O5	2.740 (11)
Mg2	_	O3		$2.127(4)(2 \times)$	O1WA	•••	O1WA	2.76 (2)
Mg2	_	O1WA		$2.199(10) (2 \times)$	O1WA	•••	O3	2.786 (11)
S1	_	O5		1.467(5)	O1WA	•••	O1WB	2.797 (17)
S1	_	O2		$1.467(4) (2 \times)$	O1WA	•••	O4	2.983 (12)
S1	_	O1		1.496(5)	O1WB	•••	05	2.808 (11)
Te1	_	O3		$1.853(4) (2 \times)$	O1WB	•••	05	2.823 (11)
Te1	_	04		1.860(5)	O1WB	•••	O1H	3.000 (11)
Mg1 2.15, Mg2	2 2.00. S 6.00). Tel 4.17. ()1H (3 Mg) 1	.16. O2H (3 Mg) 1.1	7. O1 (S. 2 N	Ag) 2.05, O2 (S, M	(g) 1.87. O3 (Te. 2	2 Mg) 2.07. O4 (Te. 2 Mg)
2.09, O5 (S) 1.	53, O1WA (1	Mg) 0.26, O2	WB (Mg) 0.3	4.	., (,		.8,, (, -	
$\overline{Zn_4(SO_4)(TeO_3)}$	1)3							
Zn1	_	08		2,015(3)	Te1		03	1.867(3)
Zn1	_	08		2.037(3)	Te1	_	08	1.880(3)
Zn1	_	012		2.057(3)	Te1	-	02	1 801(2)
Zn1	_	06		2.000(3) 2.144(3)	Te1	-	06	2587(2)
Z111 7n1	—	00		2.144(3) 2.207(2)	Ten	_	07	2.307(2) 1.888(2)
Z111 7n1	_	01		2.207(2) 2.325(3)	102 Te2	-	011	1.000(2) 1.007(2)
Z111 7n2	_	011		2.525(5) 1.045(2)	102 To2	-	00	1.907(3)
Z_{n2}	_	04		1.943(3) 1.074(2)	102 To2	-	012	1.909(2)
	-	04		1.974(3)	1e2 To2	-	013	2.347(3)
Z112 7-2	-	010		1.975(2)	1e5 T-2	-	015	1.841(3)
Zn2	-	010		2.007(3)	1e3	-	04	1.867(3)
Zn3	-	0/		2.003(3)	1e3	-	010	1.901(2)
Zn3	-	02		2.014(3)	SI	-	01	1.469(3)
Zn3	-	011		2.072(3)	S1	-	012	1.481(3)
Zn3	_	09		2.109(3)	S1	-	05	1.484(3)
Zn3	_	O10		2.128(3)	S1	-	06	1.484(3)
Zn3	-	O13		2.465(3)				
Zn4	-	09		1.962(2)				
Zn4	_	O2		1.967(3)				
Zn4	_	O3		1.973(2)				
77 4	_	05		1 997(3)				

Zn1 1.96, Zn2 1.93, Zn3 2.03, Zn4 1.93, Te1 3.91 (CN3; 4.10 CN4), Te2 3.68 (CN3; 4.05; CN4) Te3 4.02, S1 5.92, O1 (S, Zn) 1.71, O2 (Te, 2 Zn) 2.19, O3 (Te, 2 Zn) 2.09, O4 (Te, Zn) 1.83, O5 (S, Zn) 1.92, O6 (S, Zn) 1.76 (S, Zn + long Te) 1.96, O7 (Te, 2 Zn) 2.20, O8 (Te, 2 Zn) 2.15, O9 (Te, 2 Zn) 2.03, O10 (Te, 2 Zn) 1.99, O11 (Te, 2 Zn) 2.10, O12 (S, Zn) 1.85, O13 (Te) 1.44 (Te, long bond Te, long bond Zn) 1.94.

and were refined freely. The oxygen atom of the water molecule in the structure of $Mg_3(SO_4)(TeO_3)(OH)_2(H_2O)_2$ is disordered relative to a mirror plane and was refined with two statistically occupied sites (O1WA and O1WB), for which no restraints were applied during refinement. Hydrogen atom positions in the structure of $Mg_3(SO_4)(TeO_3)(OH)_2(H_2O)_2$ could not be located reliably and hence were excluded from the model. Nevertheless, bond valence sum calculations (BVS), for which bond valence parameters of *Brese* and *O'Keeffe*^[10] or *Brown*^[11] were used, clearly revealed the oxygen atoms belonging to water molecules or OH groups.

Details of the data collections and structure refinements are listed in Table 2. Selected bond lengths and angles are compiled in Table 3, together with the results of BVS calculations. A complete list of bond length including symmetry codes to generate symmetry-related sites is given as Supporting Information. Drawings of structural details were produced using the program ATOMS.^[12]

Further details of the crystal structures investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request-fordeposited-data.html) on quoting the depository numbers CSD-432345 [Mg₂(SO₄)(TeO₃)(H₂O)], CSD-432392 [Mg₃(SO₄)(TeO₃)-(OH)₂(H₂O)₂], CSD-432346 [Zn₂(SeO₄)(TeO₃)], and CSD-432381 [Zn₄(SO₄)(TeO₃)₃].

Supporting Information (see footnote on the first page of this article): Detailed list of selected bond lengths and angles including symmetry codes; X-ray powder diffraction pattern of $Zn_4(SO_4)(TeO_3)_2$; Thermogravimetric measurement of $Zn_4(SO_4)(TeO_3)_2$.

Results and Discussion

To the best of our knowledge, double salts of magnesium or zinc in combination with oxotellurate(IV) and oxochalcogenate(VI) anions are unknown. Our first approaches with respect to the preparation of such compounds were simple coprecipitation reactions in aqueous solutions. For this purpose we used a concentrated solution of magnesium (zinc) sulfate or selenate in excess, to which a half-concentrated solution of sodium oxotellurate(IV) was slowly added. In all reactions white precipitates formed which were left in the mother liquor overnight. As revealed by PXRD, in the case of ZnSO₄ or ZnSeO₄ + Na₂TeO₃, amorphous solids had formed, whereas in the case of MgSO₄ or MgSeO₄ + Na₂TeO₃, a mixed oxotellurate sodium magnesium with composition Na₂Mg(TeO₃)₂·3H₂O was obtained as revealed by isotypism with the hexagonal Na₂M(TeO₃)₂·3H₂O structures (M = Co, Zn).^[13] The diffraction patterns of the precipitates showed broad peaks indicating a rather poor crystallinity of the materials; refined lattice parameters^[14] on the basis of the Na₂Co(TeO₃)₂·3H₂O structure model^[13] in space group $P6_3/m$ are a = 9.415(2), c = 7.719(2) Å, and V = 592.5(3) Å³ at room temperature. Reacting the obtained product in the mother liquor under the same hydrothermal conditions as described in more detail above led to single phase formation of spiroffitetype Mg₂Te₃O₈.^[15]

Attempts for crystal growth under hydrothermal conditions in strong acidic media with excessive acid resulted in colorless solutions in all cases. After partial evaporation of these solutions at ca. 40 °C for several days, colorless crystalline masses were obtained that were separated by filtration. Identified phases are compiled in Table 1; novel phases were not obtained under these conditions. The stronger oxidation power of selenic acid led to an oxidation of Te^{IV} to yield telluric acid, whereas use of sulfuric acid yielded Te₂O₃(SO₄)^[16] without changing the oxidation state of tellurium. Basic conditions (pH 9-10) on the other hand are beneficial for formation of mixed oxochalcogenate phases, as was already shown for other systems M/Se/Te/O (M = Hg,^[5] Cd, Ca, Sr,^[6] Pb^[7]). For M = Mg, Zn, four new double salts with compositions $Mg_2(SO_4)(TeO_3)$ - (H_2O) , $Mg_3(SO_4)(TeO_3)(OH)_2(H_2O)_2$, $Zn_2(SeO_4)(TeO_3)$, and $Zn_4(SO_4)(TeO_3)_3$ were obtained, albeit in the majority of cases with low yields and as parts of multi-phase products. Except for $Zn_4(SO_4)(TeO_3)_3$ that could be prepared as a single-phase product (see Figure S1, Supporting Information), optical inspection of the reaction products under a polarizing microscope revealed multi-phase formation for all batches. These findings were confirmed by subsequent single crystal and powder X-ray diffraction of the bulk (Table 1). Apart from the identified phases, additional weak reflections were present in the diffraction pattern of all batches that could not be assigned to any known phase(s).

Crystal Structures

$Mg_2(SO_4)(TeO_3)(H_2O)$

The compound crystallizes with four formula units in the centrosymmetric space group *Pbcm* and is isotypic with its Co and Mn analogues.^[26] The asymmetric unit contains one Mg site in a general position 8e, one S and one Te site on a mirror plane (4d), six O sites, two of which in general positions (8e; O4, O6), three on a mirror plane (4d, O2, O3, O5), and one on a twofold rotation axis (4c; O1), as well as one H site in a general position. The principal building units are one [MgO₅(H₂O)] octahedron, one trigonal-pyramidal TeO₃²⁻, and one tetrahedral SO_4^{2-} anion, all with bond lengths and angles distributions characteristic for their respective configurations.^[1,2,27-29] Individual [MgO₅(H₂O)] octahedra are condensed by sharing two edges (O3···O5; O4···O4'; ' denotes the symmetry-related counterpart) into zigzag chains running parallel to [001]. Individual chains are linked along [010] by sharing water molecules (O1) into undulating layers extending parallel (100).

The tellurium atoms are situated between the chains and have a bridging function, with two atoms (O4, O4') to one chain and O3 to the neighboring chain, thus forming a metal oxotellurate(IV) layer ${}^2_{\infty}$ [Mg₂O₃(H₂O)(TeO₃)]⁴⁻. The lone electron pair of the trigonal-pyramidal TeO₃²⁻ anion points in the opposite direction relative to the water molecule towards the open space of this arrangement. Adjacent ${}^2_{\infty}$ [Mg₂O₃(H₂O)-(TeO₃)]⁴⁻ layers are linked by the sulfur atoms along [100], whereby an individual sulfur atom shares two oxygen atoms with one layer (O6, O6') and one oxygen atom (O5) of the other layer (Figure 1). Atom O2 completes the tetrahedral coordination of the sulfur atom and is exclusively bonded to the

latter. Its rather low bond valence sum of 1.46 valence units can be readily explained by its additional role as an acceptor of a rather strong hydrogen bond involving the water molecule $[O\cdots O \text{ distance: } 2.5816(12) \text{ Å}, OH\cdots O \text{ angle: } 162(3)^{\circ}].$



Figure 1. The crystal structure of $Mg_2(SO_4)(TeO_3)(H_2O)$ in a projection along [001]. [MgO₆] octahedra are turquoise, SO_4^{2-} anions orange and TeO_3^{2-} anions red. Displacement ellipsoids are drawn at the 90% probability level.

$Mg_{3}(SO_{4})(TeO_{3})(OH)_{2}(H_{2}O)_{2}$

Two Mg sites, one Te, one S, and nine O sites are present in the asymmetric unit of Mg₃(SO₄)(TeO₃)(OH)₂(H₂O)₂ that crystallizes with four formula units in the space group *Pnma*. Except one of the Mg sites, the disordered O sites belonging to the water molecule and two O sites on general positions (8d), all other sites are located on mirror planes (4c). Both Mg²⁺ cations in this novel structure type exhibit a distorted octahedral environment. Mg1 is bound to four O atoms and two cis-disposed OH groups, whereas Mg2 is bound to two oxygen atoms, two cis-disposed OH groups and two transdisposed water molecules, with Mg-O distances ranging from 2.038(4) to 2.199(10) Å. The [Mg1O₄(OH)₂] octahedra share edges O1...O4 and OH1...OH2 to make up infinite chains extending along [010]. These chains are bridged by [Mg2O₂(OH)₂(H₂O)₂] octahedra through corner-sharing of O2H and edge-sharing of O3···O1H and their symmetry-related counterparts, giving rise to a fused system of six-membered rings. The rings are organized into a corrugated layer extending parallel (001), whereby each of the two OH groups (O1H, O2H) is bonded to three Mg^{2+} cations, the corresponding bond lengths being the shortest of the two octahedra. The open space of the ring system is occupied above and below the ring plane by tellurium atoms, which are bonded to three oxygen atoms of the ring in the shape of slightly distorted trigonal prisms. The positions of the tellurium atoms alternate (along [100]) in an up and down mode, with the lone electron pair pointing away from the layer.

The resulting ${}^{2}_{\infty}$ [Mg₃O₃TeO₃(OH)₂(H₂O)₂]⁴⁻ layers (Figure 2) are connected along [001] by sulfur atoms. Three oxygen bonding partners of the sulfur atom originate from the layers (two, O2, O2', from one and one, O1, from the other layer), the forth oxygen atom (O5) being solely bonded to the sulfur atom (Figure 3). The displacement parameters of this oxygen atom show no conspicuous features, making it highly



Figure 2. The ${}^{2}_{\infty}$ [Mg₃O₃TeO₃(OH)₂(H₂O)₂]⁴⁻ layer in the crystal structure of Mg₃(SO₄)(TeO₃)(OH)₂(H₂O)₂ in a projection along [001]. Colour codes are as in Figure 1; oxygen atoms belonging to OH groups are green, and those of water molecules (only the average position of the disordered water molecule is shown) are lilac. Displacement ellipsoids are drawn at the 97 % probability level.



Figure 3. The crystal structure of $Mg_3(SO_4)(TeO_3)(OH)_2(H_2O)_2$ in a projection along [010]. Color codes are as in Figure 1 and Figure 2. Displacement ellipsoids are drawn at the 97% probability level.

probable that it is hydrogen-bonded to the disordered water molecules at medium strengths (OW···O5 distances: 2.74– 2.82 Å), in agreement with the rather low bond valence parameter of 1.53 v.u. for O5. Other interpolyhedral O···O distances (Table 2) involving the OH groups and water molecules both as donor and acceptor atoms as well as framework oxygen atoms (O3, O4) as acceptor atoms point to a rather complex hydrogen-bonding network of medium to weak strengths (O···O distances between 2.7 and 3.0 Å). The various possibilities for hydrogen bonding interactions deem it possible that the hydrogen atoms are disordered over several sites which might be the reason why a reliable localization of hydrogen atoms was not possible from difference maps on the basis of the current diffraction data.

$Zn_2(SeO_4)(TeO_3)$

 $Zn_2(SeO_4)(TeO_3)$ crystallizes with Z = 2 in the polar space group $P2_1$ and is isotypic with $Zn_2(MoO_4)(TeO_3)$ and Zn₂(MoO₄)(SeO₃).^[4] All atoms are located on general positions. Zn1 is tetrahedrally coordinated and Zn2 octahedrally, both coordination polyhedra being considerably distorted. Zn1 shows three similar Zn-O bond lengths of about 1.94 Å and one longer bond of 2.07 Å, with angles ranging from 93–123°; Zn2 has three similar short Zn–O bonds (2.04 Å), two intermediate bonds (2.11–2.17 Å), and one long bond (2.40 Å). The O-Zn-O angles range from 74-118° for cisoid and from 146-163° for transoid bonds. The [Zn2O₆] octahedron shows a higher distortion than the two corresponding polyhedra in the isotypic Zn₂(MoO₄)(SeO₃) and Zn₂(MoO₄)(SeO₃) structures,^[4] where the bond lengths range from 1.986(3)-2.227(3)and 2.016-2.155(5) Å, respectively. The angular distortions of the SeO_4^{2-} anion are small (range 107–112°) and all Se–O bonds are very similar, with the mean value of 1.642 Å in very good agreement with literature data.^[29]

The tellurium(IV) atom can be described as [3+1] coordinated, with three short bonds around 1.88 Å (trigonal-pyramidal configuration) and one considerably longer bond around 2.53 Å (bisphenoidal configuration). Whereas a consideration of the long Te-O bond has no high relevance for the tellurium(IV) atom itself (the bond valence sum increases from 3.93 v.u. considering only the three short bonds to 4.16 v.u. if the long bond is also taken into account), it appears to be important for the remote O2 atom. This atom shows the longest Se-O bond and is also bonded to the Zn²⁺ cation at the longest distance. Hence the contributions of the long Zn-O and Te-O bonds, equivalent to 0.15 v.u. and 0.23 v.u., respectively, cannot be ignored and participate to the saturation of this oxygen atom. However, for the following description the trigonal-pyramidal configuration for the TeO_3^{2-} anion is used.

In the crystal structure the principal building units are linked through common corners into a three-dimensional framework (Figure 4) that can be rationalized as being composed of sheets stacked along [001]. The first sheet comprises of alternately assembled rows of $[ZnO_6]$ octahedra and SeO_4^{2-} anions (Figure 5a); the second sheet is made up from likewise alternating



Figure 4. The crystal structure of $Zn_2(SeO_4)(TeO_3)$ in a projection along [100]. [ZnO₆] octahedra are turquoise, [ZnO₄] tetrahedra lightblue, SeO_4^{2-} anions orange, and TeO_3^{2-} anions red. Displacement ellipsoids are drawn at the 74 % probability level.



Figure 5. The sheets in the crystal structure of $Zn_2(SeO_4)(TeO_3)$, viewed in a projection along [103]. Color code and displacement ellipsoids are as in Figure 4. (a) The sheet composed of $[ZnO_6]$ polyhedra and SeO_4^{2-} anions; (b) the sheet composed of $[ZnO_4]$ polyhedra and TeO_3^{2-} anions.

rows of $[ZnO_4]$ tetrahedra and TeO_3^{2-} anions, whereby the lone electron pairs of the tellurium(IV) atoms are alternately oriented in an up and down fashion for every row, pointing towards the empty space (Figure 5b). The two types of sheets are linked by edge- and corner-sharing of individual polyhedra with TeO_3^{2-} and SeO_4^{2-} anions remaining isolated from each other.

$Zn_4(SO_4)(TeO_3)_3$

All sites (four Zn, one S, three Te, and 13 O) in this centrosymmetric structure (Z = 4, $P2_1/c$) are located on general positions of this novel structure type. Just like in the $Zn_2(SeO_4)$ -(TeO₃) structure, the Zn²⁺ cations display different coordination numbers, with two of them (Zn1, Zn3) in octahedral and two (Zn2, Zn4) in tetrahedral coordination. The octahedral coordination spheres are considerably distorted, showing two noticeable longer bonds for Zn1 [2.207(2) and 2.325(3) Å] and one longer bond for Zn3 [2.465(3) Å], while both tetrahedral coordination spheres display a rather uniform bond lengths distribution between 1.945(3) and 2.007(3) Å for Zn2 and 1.962(2) and 1.997(3) Å for Zn4. The SO_4^{2-} tetrahedron shows only minute deviations from ideal values and has typical bond lengths and angles (bond lengths range 1.469(3)-1.484(3) Å; angular range 107.50(17)-110.99(15)°]. The coordination numbers of the three tellurium(IV) atoms are [3+1] for Te1 and Te2, and [3] for Te3. Again, like in the $Zn_2(SeO_4)(TeO_3)$ structure described above, three oxygen atoms are bonded at short distances around 1.88 Å in the shape of a trigonal pyramid, and the remotely bonded oxygen atoms lead to a higher saturation of the bond valence for the coordination partners. In this regard O6, bonded to Te1 at 2.587(2) Å, and O13, bonded at Te2 at 2.347(3) Å, increase the bond valence sum by 0.19 and 0.37 v.u., respectively, resulting in overall distorted bisphenoidal coordination environments. For clarity, the following crystal structure description is solely based on trigonalpyramidal TeO₃²⁻ coordination polyhedra.

Another similarity with the $Zn_2(SeO_4)(TeO_3)$ structure pertains to the connection of the principal building units, viz. $[ZnO_6]$ and $[ZnO_4]$ polyhedra, TeO_3^{2-} and XO_4^{2-} anions (here X = S), into a framework structure. $[ZnO_6]$ and $[ZnO_4]$ polyhedra share corners, resulting in the formation of sheets extending parallel (201). Adjacent sheets are connected along [001] through corner-sharing with the SO_4^{2-} and the $Te3O_3^{2-}$ anions. The two remaining tellurium atoms bridge the zinc oxide sheets in such a way that the lone electron pairs point away from the mean plane of the sheet, and the apices of all three TeO_3^{2-} anions are oriented towards the empty space of the framework. Likewise for all other structures, a condensation of the oxochalcogenate anions is not observed, and the TeO_3^{2-} and SO_4^{2-} anions again remain isolated in the structure (Figure 6).

A thermogravimetric measurement (see Figure S2, Supporting Information) revealed this phase to be stable up to 860 °C (onset). The decomposition is accompanied with a constant mass loss up to 1000 °C (end of measurement). The final product of this heat treatment was a glass.



Figure 6. The crystal structure of $Zn_4(SO_4)(TeO_3)_3$ in a projection along [010]. Color codes as in Figure 4 with SO_4^{2-} anions in yellow. Displacement ellipsoids are drawn at the 97% probability level.

Conclusions

Low yields and multi-phase formation during hydrothermal synthesis prevented further examination of physical properties for $Mg_2(SO_4)(TeO_3)(H_2O)$, $Mg_3(SO_4)(TeO_3)(OH)_2(H_2O)_2$, and $Zn_2(SeO_4)(TeO_3)$. $Zn_4(SO_4)(TeO_3)_3$ could be obtained as a single phase and is stable up to 860 °C as revealed by thermogravimetry. From the four compounds, only $Zn_2(SeO_4)(TeO_3)$ crystallizes in a non-centrosymmetric space group. Optimization of the hydrothermal reaction conditions for preparation of single phase material requires adjustment of variable interdependent parameters (educt materials, filling degree, pH, temperature, duration etc.) and is currently in progress. This includes also studies whether other divalent first row transition metals (Mn, Fe, Co, Ni, Cu) form new oxotellurate(IV) oxochalcogenate(VI) double salts under similar conditions.

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

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Incorporation of Sulfate or Selenate Groups into Oxotellurates(IV): III. Compounds with Magnesium or Zinc

· MgO
· MgCl ₂
· ZnO
· TeO ₂
$\cdot H_2 SeO_4/H_2 SO_4$
· KOH/NaOH

Hydrothermal conditions

