The New Oxometallates $Cs_4[FeO_3]$, $Cs_4[ZnO_3]$ and $Cs_3[BO_3]$ with Trigonal-planar Anions – Decomposition Products of Alkali Metal Suboxometallates

Constantin Hoch

Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Reprint requests to Dr. Constantin Hoch. Fax: (+49) 711 685 64241.
E-mail: hoch@iac.uni-stuttgart.de

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Three new cesium oxometallates with trigonal-planar $[MO_3]^{n-}$ anions (M = Zn, Fe, B) were observed as products of reactions aimed at the formation of alkali metal suboxometallates A_9MO_4 (A = Rb, Cs; M = Al, Ga, In, Fe, Sc), or as decomposition products thereof. $Cs_4[FeO_3]$, $Cs_4[ZnO_3]$ and $Cs_3[BO_3]$ crystallize with new structure types ($Cs_4[FeO_3]$: triclinic, space group $P\bar{1}$, a = 7.0652(1), b = 7.125(1), c = 9.939(2) Å, α = 80.74(2), β = 71.32(2), γ = 64.04(2)°, Z = 2, $Cs_4[FeO_3]$: monoclinic, space group $P2_1/c$, a = 7.146(4), b = 18.572(1), c = 7.050(4) Å, β = 115.47(4)°, Z = 4, $Cs_3[BO_3]$: orthorhombic, space group $Pnma$, a = 10.967(1), b = 10.967(1), c = 10.353(1) Å). In all structures the trigonal-planar anions have no or low point symmetry, but deviate only marginally from ideal $\bar{6}m2$ symmetry. The new crystal structures can be derived from simple and highly symmetrical packings of spheres or from known binary structure types.

Key words: Oxometallates, Cesium, Ferrates, Zincates, Borates, Crystal Structure, Topology

Introduction

Oxometallates of the heavy alkali metals with low or no connectivity between the individual oxometallate anions, *e. g.* ortho- or dimetallates, are scarcely known. They are especially difficult to synthesize because the resulting crystal structures with relatively small and highly charged anions and large cations with low charge have low lattice energies, following Paulings second law for ionic crystals [1].

Conventional synthetic approaches, *e. g.* heating mixtures of the binary oxides, often result in oxometallates with higher condensation of the orthometallate building units, and the reaction temperatures of two oxides often are very high. Solid-state reactions are slow and often do not yield single crystals but powders, complicating the structure elucidation of new products. In this work a new synthetic approach towards metal-rich oxometallates is presented with the examples of three new structures which all contain isolated trigonal-planar oxometallate anions $[MO_3]^{n-}$. Decomposing alkali metal suboxometallates [2] at low temperatures has already been described as a convenient access to several new ortho- and dimetallates with tetrahedral $[MO_4]^{n-}$ anions [3].

From all known oxometallates with the formal compositions A_3MO_3 or A_4MO_3 only a small group of structures show isolated planar $[MO_3]^{3-}$ or $[MO_3]^{4-}$ anions [4]. The majority exhibit either *pseudo*-tetrahedral anions with stereochemically active lone pairs of electrons [5], dimers $[M_2O_6]^{6-}$ of edge-sharing $[MO_4]$ tetrahedra [6], or other, less common structural motifs (edge- and corner-sharing square pyramids [7], dimers of edge-sharing squares [8], edge-sharing octahedra [9], or chains of corner-linked tetrahedra [10]). Examples for structures with trigonal-planar anions which can be described as isosteric analogs to carbonates or nitrates are only known from borates, ferrates, cobaltates, and zincates so far, and the structures we report on here corroborate this finding.

Experimental Section

Sample preparation

As the three cesium oxometallates presented here are extremely hygroscopic and were produced from reaction mixtures containing metallic cesium and cesium oxide, all handling was carried out in a glove box filled with argon. The reactions took place in mechanically sealed tantalum crucibles placed in small steel autoclaves to prevent cesium from dis-

Empirical formula	$Cs_4[FeO_3]$	$Cs_4[ZnO_3]$	$Cs_3[BO_3]$
Crystal system	triclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$Pbam$ (no. 55)
Z	2	4	8
a, Å	7.0652(14)	7.146(4)	10.9364(12)
b, Å	7.1255(14)	18.572(10)	10.9779(13)
c, Å	9.9390(18)	7.050(4)	10.3564(13)
α, deg	80.735(15)	90	90
β, deg	71.323(15)	115.47(4)	90
γ, deg	64.041(15)	90	90
V, Å^3	426.06(14)	844.7(8)	1245.2(2)
Calc. density, g cm^{-3}	4.95	5.07	4.88
Crystal color	red	– colorless –	
Crystal shape	fragment	flat rod	fragment
Diffractometer	– IPDS 2 –		IPDS 1
	(Stoe & Cie, Darmstadt, Germany)		
Radiation, wavelength, Å	– MoK_α, 0.71073 –		AgK_α, 0.56083
Data collection mode	– ω scans –		φ scans
$h_{\mathrm{min/max}}$	−8/8	−8/8	−13/13
$k_{\mathrm{min/max}}$	−8/8	−22/18	−13/13
$l_{\mathrm{min/max}}$	−12/12	−8/8	−12/12
$2\vartheta_{\mathrm{min/max}}$, deg	7.1/63.2	6.6/52.0	40.0
Corrections	– Lorentz, polarization, absorption (numerical) [13] –		
Structure solution	– Direct Methods [14] –		
Structure refinement	– full-matrix least-squares refinement on $F_o{}^2$ [14] –		
No. of l. s. parameters	74	74	76
No. of reflections	3045	3892	9836
No. of independent reflections	1568	1558	1254
No. of independent reflections [$I \geq 2\sigma(I)$]	1146	907	1035
R_{int}	0.0608	0.1489	0.0877
R_σ	0.0759	0.1501	0.0408
$R1$ [$F_o^2 \geq 2\sigma(F^2{}_o$]	0.0664	0.0610	0.0373
$R1$ (all $F_o{}^2$)	0.0899	0.1175	0.0481
$wR2$ [$F_o{}^2 \geq 2\sigma(F^2{}_o$]	0.2017	0.1365	0.0591
$wR2$ (all $F_o{}^2$)	0.2118	0.1532	0.0611
Absorption coeff., mm^{-1}	18.5	19.8	9.2
Min. transmission	0.095	0.071	0.311
Max. transmission	0.281	0.389	0.747
Min. res. el. density, e Å^{-3}	−2.81	−2.40	−1.01
Max. res. el. density, e Å^{-3}	2.61	2.29	1.02

Table 1. Details on data collection, structure solution and refinement, and crystallographic data for $Cs_4[FeO_3]$, $Cs_4[ZnO_3]$ and $Cs_3[BO_3]$.

tilling during heating. The steel autoclaves were placed in argon-filled glass tubes and heated in a vertical tube furnace. Cesium metal was obtained from a reaction of cesium chloride with calcium metal as described by Hackspill [11]. Cesium oxide Cs_2O was produced following a procedure described previously [2]. All other educts were commercially available oxides with purities of at least 99.9 %.

$Cs_4[FeO_3]$ was first observed as a byproduct resulting from a reaction of cesium metal, cesium oxide Cs_2O and iron oxide Fe_2O_3 in the molar ratio $Cs : Cs_2O : Fe_2O_3 = 8 : 5 : 1$ (total amount of sample: 1.500 g). The reaction was aimed at the formation of Cs_9FeO_4 [2, 12] which appeared as the main product. The reactands were heated to 300 °C within 5.5 h, held at this temperature for 2 h, cooled to 200 °C within 10 h, and then to r. t. by switching off the furnace. $Cs_4[FeO_3]$ forms brittle xenomorphic crystals of red color. It is also formed as the main decomposition product when the suboxometallate Cs_9FeO_4 is heated to about 200 °C [2].

An analogous reaction of cesium metal, cesium oxide Cs_2O and zinc oxide ZnO in the molar ratio of $Cs : Cs_2O : ZnO = 1 : 3 : 3$ (total sample amount: 1.500 g) aimed at the formation of Cs_9ZnO_4 did not yield the desired product. Instead, $Cs_4[ZnO_3]$ in form of clear colorless flat rods embedded in a bronze-colored liquid matrix of cesium suboxides was obtained from which the crystals were separated by centrifugation. The reaction mixture was treated with the same temperature program as described above for $Cs_4[FeO_3]$.

$Cs_3[BO_3]$ was the main product of a reaction of cesium metal, cesium oxide Cs_2O and boron oxide B_2O_3 in the molar ratio $Cs : Cs_2O : B_2O_3 = 4 : 2.5 : 0.5$ (total amount of sample: 1.500 g). The mixture was heated to 300 °C within 3 h, kept at this temperature for 3 h and cooled to r. t. by switch-

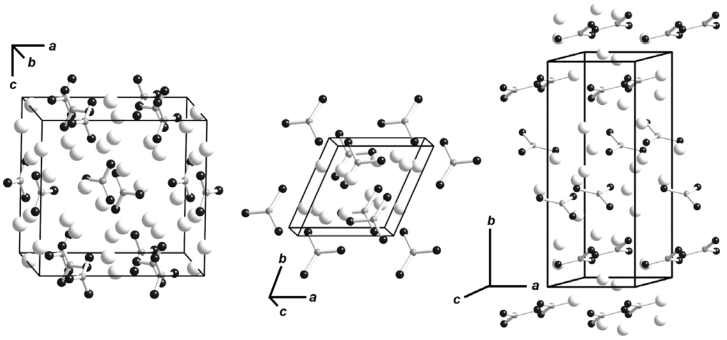

Fig. 1. The unit cells of $Cs_4[ZnO_3]$ (left), $Cs_4[FeO_3]$ (middle) and $Cs_3[BO_3]$ (right). Oxygen atoms are drawn in black, cesium atoms in light gray and Zn, Fe and B atoms, respectively, in middle gray.

ing off the furnace. The reaction was aimed at the production of Cs_9BO_4 which was not observed in the product mixture containing $Cs_3[BO_3]$ and liquid bronze-colored cesium suboxides as the only characterized phases. $Cs_3[BO_3]$ forms colorless transparent crystal rods.

X-Ray structure determinations

The moisture-sensitive crystals were selected from the product mixtures under K-dried paraffin oil, sealed in oil-filled glass capillaries (∅ = 0.1 mm) and mounted on either a one-circle (IPDS 1, Stoe & Cie, Darmstadt, Germany) or a two-circle goniometer (IPDS 2). After checking the crystal quality with either Ag$K\alpha$ (IPDS 1) or Mo$K\alpha$ radiation (IPDS 2, both graphite-monochromatized), data of the accessible part of half the Ewald sphere were collected. After data reduction, Lorentz, polarization and absorption corrections (numerical, optimized crystal shape [13]) were performed. Reflection statistics and absence conditions were used to find suitable space groups for the structure solution with Direct Methods [14]. The structure refinements were carried out with full-matrix least-squares techniques on F^2 [14] treating the displacement factors of all atoms anisotropically. Information on data collection, structure determination, and the crystallographic data are compiled in Table 1. Standardized fractional atomic parameters [15] and equivalent isotropic displacement parameters can be found in Table 2. Tables 3 and 4 show the anisotropic displacement factors and selected interatomic distances and angles.

Further details of the crystal structure investigations are available from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition numbers CSD-423336 ($Cs_4[FeO_3]$), CSD-423335 ($Cs_4[ZnO_3]$) and CSD-423334 ($Cs_3[BO_3]$).

Results and Discussion

Table 2. Fractional atomic coordinates in standardized setting [15], Wyckoff numbers and equivalent isotropic displacement parameters (pm^2) for $Cs_4[FeO_3]$, $Cs_4[ZnO_3]$ and $Cs_3[BO_3]$ at r. t. Standard deviations of the last digit are given in parentheses.

Atom	W.-site	x	y	z	U_{equiv}
			$Cs_4[FeO_3]$		
Fe1	2*i*	0.6844(7)	0.2054(6)	0.2365(5)	313(10)
O1	2*i*	0.132(4)	0.012(4)	0.676(3)	540(60)
O2	2*i*	0.453(4)	0.180(4)	0.207(3)	570(70)
O3	2*i*	0.730(4)	0.447(3)	0.177(3)	460(60)
Cs1	2*i*	0.0200(3)	0.2563(3)	0.4066(2)	406(6)
Cs2	2*i*	0.2064(3)	0.2051(3)	0.0107(2)	381(6)
Cs3	2*i*	0.2677(4)	0.6523(3)	0.1467(2)	425(6)
Cs4	2*i*	0.4423(3)	0.2117(3)	0.6200(2)	408(6)
			$Cs_4[ZnO_3]$		
Zn1	4*e*	0.2862(5)	0.38359(17)	0.2876(4)	241(7)
O1	4*e*	0.041(3)	0.4075(10)	0.311(2)	320(50)
O2	4*e*	0.309(3)	0.4026(12)	0.034(3)	410(60)
O3	4*e*	0.508(3)	0.1643(11)	0.019(2)	350(50)
Cs1	4*e*	0.1555(3)	0.57548(10)	0.1560(2)	333(5)
Cs2	4*e*	0.2103(3)	0.19706(10)	0.1774(2)	337(5)
Cs3	4*e*	0.2940(3)	0.00031(10)	0.2066(2)	309(5)
Cs4	4*e*	0.6748(3)	0.30389(10)	0.2148(3)	331(5)
			$Cs_4[BO_3]$		
B1	4*g*	0.2558(12)	0.0331(11)	0	140(30)
O11	8*i*	0.1980(6)	0.4911(5)	0.1167(8)	252(15)
O12	4*g*	0.1658(8)	0.1205(7)	0	201(19)
B2	4*h*	0.4665(12)	0.2569(11)	1/2	170(30)
O21	8*i*	0.0077(5)	0.1972(6)	0.3845(7)	239(14)
O22	4*h*	0.3793(7)	0.1637(8)	1/2	200(18)
Cs1	8*i*	0.25359(4)	0.24472(4)	0.24943(6)	184(2)
Cs2	4*h*	0.17079(8)	0.01446(7)	1/2	193(2)
Cs3	4*g*	0.01823(7)	0.32937(7)	0	192(2)
Cs4	4*f*	0	1/2	0.31498(8)	196(2)
Cs5	4*e*	0	0	0.18440(8)	195(2)

$Cs_4[FeO_3]$ crystallizes in a new triclinic structure type (see Fig. 1). The sole crystallographically independent trigonal-planar $[FeO_3]^{4-}$ anion has no special point symmetry, however, the deviations from ideal $\bar{6}m2$ symmetry are very small (see Table 4), with bond angles O–Fe–O between 118.7(10) and 121.2(11)° and the sum of all angles $\Sigma_{\angle\text{O-Fe-O}} = 360.0(11)°$. The anion is coordinated by 13 Cs atoms (see Fig. 2). The oxygen atoms have either a distorted octahedral 5+1

Table 3. Anisotropic displacement parameters (pm^2) for $Cs_4[FeO_3]$, $Cs_4[ZnO_3]$ and $Cs_3[BO_3]$ at r. t. Standard deviations of the last digit are given in parentheses.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
			$Cs_4[FeO_3]$			
Fe1	400(20)	330(20)	310(30)	-1(17)	-101(19)	-238(18)
O1	610(150)	500(140)	690(190)	-30(120)	-170(130)	-390(120)
O2	690(160)	470(130)	900(200)	230(130)	-670(160)	-370(120)
O3	530(130)	460(120)	470(150)	10(100)	80(110)	-440(110)
Cs1	486(11)	402(11)	467(13)	10(9)	-193(10)	-271(9)
Cs2	411(10)	367(10)	445(13)	-10(8)	-129(9)	-227(8)
Cs3	489(12)	379(11)	460(14)	-25(9)	-162(10)	-203(9)
Cs4	520(12)	359(10)	418(13)	-25(8)	-102(9)	-263(9)
			$Cs_4[ZnO_3]$			
Zn1	281(18)	316(17)	176(12)	4(12)	145(12)	7(14)
O1	410(120)	370(130)	240(80)	260(70)	190(90)	180(90)
O2	440(130)	740(170)	200(80)	-60(80)	270(90)	90(90)
O3	300(120)	660(140)	140(80)	10(80)	120(80)	-90(90)
Cs1	325(11)	433(11)	243(7)	9(7)	125(7)	8(8)
Cs2	400(11)	409(11)	251(8)	-31(7)	188(8)	-16(9)
Cs3	339(10)	409(10)	226(7)	8(6)	164(7)	10(8)
Cs4	337(11)	392(10)	333(8)	-48(7)	210(8)	-26(8)
			$Cs_3[BO_3]$			
B1	130(60)	140(50)	140(70)	0	0	-20(50)
O11	240(40)	290(30)	220(40)	-20(30)	-10(30)	-80(30)
O12	160(40)	200(40)	240(50)	0	0	80(30)
B2	100(50)	120(60)	290(80)	0	0	80(50)
O21	280(40)	280(30)	150(30)	-40(30)	-30(30)	110(30)
O22	170(40)	260(40)	170(50)	0	0	-40(40)
Cs1	180(3)	185(3)	186(3)	03(2)	-23(2)	-1(2)
Cs2	140(4)	189(4)	249(5)	0	0	-25(3)
Cs3	173(4)	148(3)	253(5)	0	0	28(3)
Cs4	192(4)	255(4)	141(4)	0	0	-49(3)
Cs5	233(4)	199(4)	153(4)	0	0	-24(3)

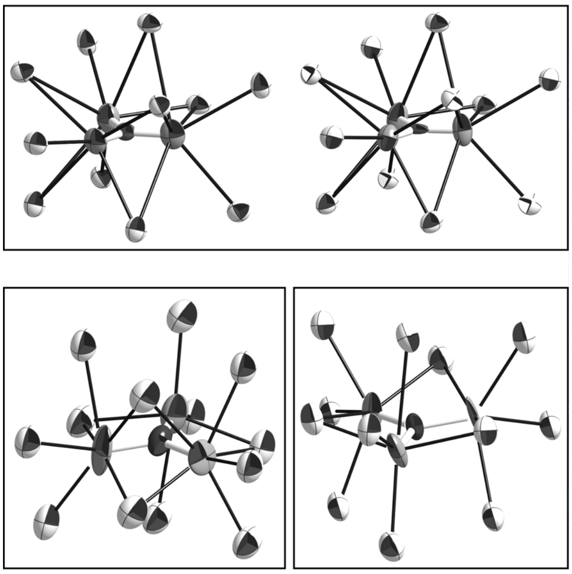

Fig. 2. Synopsis of the oxometallate anions and their coordinations by cesium cations in $Cs_3[BO_3]$ (upper frame, around B1 at left and around B2 at right), $Cs_4[FeO_3]$ (lower frame, left) and $Cs_4[ZnO_3]$ (lower frame, right). All ellipsoids are drawn at a probability level of 90 %.

or a 6+1 coordination by Cs and Fe atoms with Cs–O distances in the range between 2.89(2) and 3.74(3) Å. This is in good agreement with the sum of the Shannon radii for Cs^+ and O^{2-} [16] and with the respective distances found in many other cesium oxometallates [4–6, 8, 17]. The $[Cs_{13}FeO_3]$ clusters can be regarded as roughly spherical entities that build up the total crystal structure by sharing common Cs atoms. They are packed in a slightly distorted hexagonal close packing with the layers oriented parallel to the *ab* plane of the unit cell (see Fig. 3). The metric of the unit cell with very similar *a* and *b* vectors and γ close to 60° reflects this underlying structural motif of a hexagonal close packing. The vector of the stacking direction of the hexagonal layers $c^{\text{hex}} = \sin\alpha \cdot c$ has the length 9.809 Å. The ratio $c^{\text{hex}}/a^{\text{hex}} = 1.382$ with a^{hex} being the mean value of the lattice vectors *a* and *b* is smaller than the one for ideal hexagonal close packing with $c/a = \sqrt{\frac{8}{3}} \approx 1.633$.

$Cs_4[ZnO_3]$ crystallizes in a new monoclinic structure type (see Fig. 1). The structure is built up from planar $[FeO_3]^{4-}$ anions coordinated by 13 cesium

Table 4. Selected interatomic distances (Å) and angles (deg) for $Cs_4[FeO_3]$, $Cs_4[ZnO_3]$ and $Cs_3[BO_3]$ at r. t. Standard deviations of the last digit are given in parentheses.

Atoms	Distance	Atoms	Distance	Atoms	Distance	Atoms	Distance
			$Cs_4[FeO_3]$				
Fe1–O1	1.83(3)	Cs1–O1	2.89(2)	Cs2–O2	2.95(2)	Cs3–O1	3.01(3)
Fe1–O2	1.84(2)	Cs1–O2	2.93(3)	Cs2–O3	2.96(2)	Cs3–O3	3.04(2)
Fe1–O3	1.86(2)	Cs1–O1	3.08(3)	Cs2–O3	3.05(2)	Cs3–O2	3.06(2)
Atoms	Angle	Cs1–O3	3.28(3)	Cs2–O2	3.29(3)	Cs3–O3	3.40(3)
O1–Fe1–O2	118.7(10)					Cs3–O2	3.74(3)
O1–Fe1–O3	121.2(11)						
O2–Fe1–O3	120.1(11)						
			$Cs_4[ZnO_3]$				
Atoms	Distance	Atoms	Distance	Atoms	Distance	Atoms	Distance
Zn1–O1	1.88(2)	Cs1–O1	2.99(2)	Cs2–O3	2.86(2)	Cs3–O2	2.89(2)
Zn1–O2	1.90(2)	Cs1–O3	3.00(2)	Cs2–O2	2.95(2)	Cs3–O1	2.91(2)
Zn1–O3	1.93(2)	Cs1–O2	3.03(2)	Cs2–O1	3.04(2)	Cs3–O1	3.11(1)
Atoms	Angle	Cs1–O1	3.52(2)	Cs2–O3	3.54(2)	Cs3–O2	3.20(2)
O1–Zn1–O2	119.9(7)	Cs1–O2	3.62(2)				
O1–Zn1–O3	119.4(7)						
O2–Zn1–O3	120.6(8)						
			$Cs_3[BO_3]$				
Atoms	Distance	Atoms	Distance	Atoms	Distance	Atoms	Distance
B1–O12	1.38(2)	Cs1–O22	3.069(4)	Cs2–O22	2.812(8)	Cs3–O12	2.805(8)
B1–O11	1.39(1)	Cs1–O12	3.074(5)	Cs2–O21	2.940(6)	Cs3–O11	2.915(6)
B1–O11	1.39(1)	Cs1–O21	3.082(6)	Cs2–O21	2.940(6)	Cs3–O11	2.915(6)
B2–O21	1.37(1)	Cs1–O11	3.092(6)	Cs2–O21	3.263(7)	Cs3–O11	3.311(7)
B2–O21	1.37(1)	Cs1–O11	3.147(6)	Cs2–O21	3.263(7)	Cs3–O11	3.311(7)
B2–O22	1.40(2)	Cs1–O21	3.182(6)	Cs4–O22	2.940(6)	Cs5–O12	2.949(7)
Atoms	Angle	Atoms	Angle	Cs4–O11	2.990(8)	Cs5–O21	2.995(7)
O12–B1–O11	119.5(5)	O21–B2–O21	121.0(11)	Cs4–O21	3.399(7)	Cs5–O11	3.386(7)
O11–B1–O11	121.0(11)	O21–B2–O22	119.5(6)				

atoms and of almost perfect trigonal-planar shape, although the unique crystallographically independent anion has no special point symmetry. The bond angles O–Zn–O range from 119.4(7) to 120.6(8)°, and sum up to $\Sigma_{\angle \text{O-Zn-O}} = 359.9(8)^\circ$ (see Table 4). The oxygen atoms again show either a distorted octahedral 5+1 or a 6+1 coordination by Cs and Zn atoms, and the respective Cs–O distances ranging from 2.86(2) to 3.62(2) Å are in good agreement with the sum of the Shannon radii as well as with the Cs–O distances observed in $Cs_4[FeO_3]$ and other cesium oxometallates [4–6, 8, 17]. For $Cs_4[ZnO_3]$ no significant twinning according to $\begin{pmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$ was observed, although this was expected from the *pseudo*-hexagonal basis vectors (see Table 1). They result, in analogy to the structure of $Cs_4[FeO_3]$, in a packing of hexagonal layers of the roughly spherical $[Cs_{13}ZnO_3]$ clusters (see Fig. 3). These layers are stacked in the *b* direction in an ...ABCD... sequence. The doubled periodicity with respect to the hexagonal close packing in $Cs_4[FeO_3]$ results in a monoclinic *b* axis which is about twice as long as the stacking vector in $Cs_4[FeO_3]$.

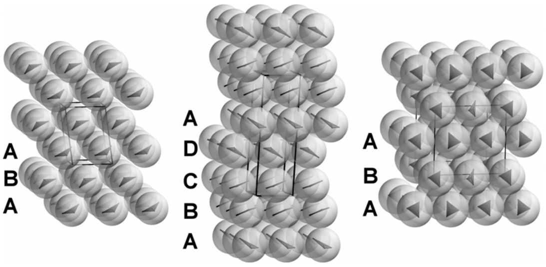

Fig. 3. Packing of the roughly sherical clusters $[Cs_xMO_3]$ in $Cs_4[FeO_3]$ (left), $Cs_4[ZnO_3]$ (middle) and $Cs_3[BO_3]$ (right). The coordination polyhedra depicted in Fig. 2 are represented by transparent grey spheres with radii corresponding to the longest Cs–O distance found for the respective cluster. In the center of these spheres the trigonal-planar $[MO_3]^{n-}$ anions and their respective orientation can be seen as dark triangles. The stacking vectors c^{hex} (for $Cs_4[FeO_3]$, see text), *b* (for $Cs_4[ZnO_3]$) and *c* (for $Cs_3[BO_3]$) are pointing upwards.

$Cs_3[BO_3]$ crystallizes in a new orthorhombic structure type (see Fig. 1). All analyzed crystals showed twinning according to $\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix}$ due to the similar lattice parameters *a* and *b* (see Table 1). The *pseudo*-tetragonal lattice already indicates an underlying struc-

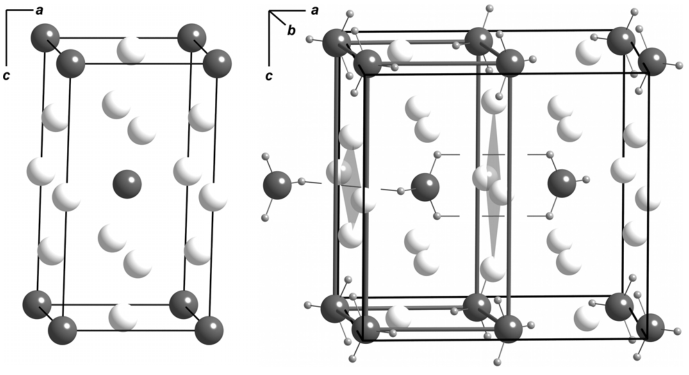

Fig. 4. Topologic relation between the tetragonal unit cell of *InPd*$_3$ [18] (left) and the orthorhombic unit cell of $Cs_3[BO_3]$ (right) with about doubled volume. In and Pt atoms are depicted as dark and light grey spheres, respectively, and so are the related atoms B and Cs in $Cs_3[BO_3]$. Additionally, oxygen atoms (small spheres) with their respective orientation (see text) are emphasized by dashed lines.

ture motif of higher symmetry. The *pseudo*-tetragonal symmetry requires two topologically identical but crystallographically independent $[BO_3]^{3-}$ anions (see Fig 2) with B atoms at Wyckoff positions 4*g* and 4*h*, respectively, and point symmetry *m*. Their respective coordination by 12 cesium atoms is almost identical: one oxygen atom is situated on the mirror plane (O12 and O22, respectively, see Table 2) and shows a strongly distorted octahedral coordination by one boron and five cesium atoms. The other two oxygen atoms belong to one crystallographic position (O11 and O21, respectively) and show a 6+1 coordination. In all cases, the Cs–O distances are in the range between 2.8205(8) and 3.399(7) Å with the longest distances in the 6+1 coordination (see Table 4). Again, these interatomic distances are in good agreement with the sum of the Shannon radii and the distances observed in $Cs_4[FeO_3]$ and $Cs_4[ZnO_3]$ and many other cesium oxometallates [4 – 6, 8, 17]. Also, the deviation of the anion shapes from ideal $\bar{6}m2$ symmetry is very small with O–B–O angles ranging from 119.5(5) to 121.0(11)° and the sum of the angles $\Sigma_{\angle\text{O-B-O}} = 360.0(11)^\circ$ (see Table 4).

In analogy of the sphere packing topologies mentioned above, the structure of $Cs_3[BO_3]$ also can be rationalized by a packing of the roughly spherical $[Cs_{12}BO_3]$ clusters, but here no hexagonal nets are formed. Instead, square nets of $[Cs_{12}BO_3]$ clusters are packed in an ...ABAB... sequence along the *c* direction (see Fig. 3). These square nets are the topological reason for the underlying *pseudo*-tetragonal symmetry.

The structure of $Cs_3[BO_3]$ can be rationalized yet in another way, as the arrangement of the Cs and B atoms corresponds to a slightly distorted $InPd_3$ [18] pattern (see Fig. 4). The distortion is caused by filling in oxygen atoms in the structure and by the orientation of the $[BO_3]^{3-}$ anions. One of the $[Pd_4]$ squares on the *ac* faces of the $InPd_3$ structure is distorted towards an oblate rhombus with its center at (1/2, 0, 1/2) in the $Cs_3[BO_3]$ structure and another one towards a prolate rhombus with its center at (1/2, 1/2, 1/2). On the basis of this description it would also be possible to rationalize the structures of $Cs_4[FeO_3]$ and $Cs_4[ZnO_3]$ by analyzing the underlying AB_4 structures of the packing of Cs and Fe resp. Zn atoms, however, the resulting AB_4 structure types have not yet been described in binary phases, rendering this approach spurious.

Summary

Cesium suboxometallates offer a new preparative access to new metal-rich oxometallates. Three examples of the small class of structures with trigonal-planar anions are shown here. Their crystal structures exhibit metrical *pseudo*-symmetries which can be understood with topological considerations of underlying packing of spheres. The spheres consist of clusters $[Cs_xMO_3]$ and offer a much more convenient access to a more rational understanding of the structures than packing analyses of the heavy atoms only. The reverse case was found for the structures of similarly prepared metal-rich oxometallates with tetrahedral $[MO_4]$ anions [3]. Oddly enough, one would consider the $[Cs_xMO_4]$ clusters present in their crystal structures much more adequate for a description as spherical entities than the coordination clusters $[Cs_xMO_3]$ around the trigonal-planar anions in the crystal structures described here.

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[1] L. Pauling, *J. Am. Chem. Soc.* **1929**, *51*, 1010–1026.

[2] a) C. Hoch, J. Bender, A. Simon, *Angew. Chem.* **2009**, *121*, 2451–2453; *Angew. Chem. Int. Ed.* **2009**, *48*, 2415–2417; b) C. Hoch, J. Bender, A. Wohlfarth, A. Simon, *Z. Anorg. Allg. Chem.* **2009**, *635*, 1777–1782.

[3] J. Bender, A. Wohlfarth, C. Hoch, *Z. Naturforsch.* **2010**, *65b*, 1416–1426.

[4] a) F. Stewner, *Acta Crystallogr.* **1971**, *B27*, 904–910; b) Y. Piffard, R. Marchand, M. Tournoux, *Rev. Chim. Minér.* **1975**, *12*, 210–217; c) H. König, R. Hoppe, *Z. Anorg. Allg. Chem.* **1977**, *434*, 225–232; d) H. Rieck, R. Hoppe, *Z. Anorg. Allg. Chem.* **1977**, *437*, 95–104; e) W. Burow, R. Hoppe, *Z. Anorg. Allg. Chem.* **1979**, *459*, 59–71; f) M. G. Barker, G. A. Fairhall, *J. Chem. Res.* **1979**, *1979*, 371; g) M. Jansen, W. Scheld, *Z. Anorg. Allg. Chem.* **1981**, *477*, 85–89; h) M. Jansen, G. Brachtel, *Z. Anorg. Allg. Chem.* **1982**, *489*, 42–46; i) R. Baier, R. Hoppe, *Z. Anorg. Allg. Chem.* **1987**, *546*, 122–136; j) A. Möller, *Chem. Mater.* **1998**, *10*, 3196–3201; k) G. Frisch, *Dissertation* **2006**, Universität Freiburg im Breisgau (Germany).

[5] a) H. D. Stöver, R. Hoppe, *Z. Anorg. Allg. Chem.* **1980**, *468*, 137–147; b) B. Nowitzki, R. Hoppe, *Z. Anorg. Allg. Chem.* **1984**, *515*, 114–126; c) H. Stoll, B. Brazel, R. Hoppe, *Z. Anorg. Allg. Chem.* **1988**, *564*, 45–60; d) R. Hübenthal, R. Hoppe, *Z. Anorg. Allg. Chem.* **1989**, *576*, 169–178; e) R. Brandes, R. Hoppe, *Z. Anorg. Allg. Chem.* **1994**, *620*, 1549–1558; f) C. Röhr, *Z. Anorg. Allg. Chem.* **1995**, *621*, 757–760; g) N. Zoche, M. Jansen, *Z. Anorg. Allg. Chem.* **1997**, *623*, 832–836; h) N. Zoche, M. Jansen, *Z. Naturforsch.* **1997**, *52b*, 1031–1036; i) P. Zönnchen, C. Röhr, *Z. Anorg. Allg. Chem.* **1998**, *624*, 797–801; j) F. Emmerling, C. Röhr, *Acta Crystallogr.* **2001**, *C57*, 1127–1128; k) B. M. Sobotka, A. Möller, *Z. Anorg. Allg. Chem.* **2003**, *629*, 2063–2065.

[6] a) H. Riek, R. Hoppe, *Angew. Chem* **1973**, *85*, 589–590; b) A. Bon, C. Gleitzer, A. Courtois, J. Protas, *Compt. Rend. Hebd. Séances Acad. Sci.* **1974**, *C278*, 785–788; c) R. Hoppe, F. Griesfeller, *Z. Anorg. Allg. Chem.* **1978**, *440*, 74–80; d) G. Brachtel, R. Hoppe, *Z. Anorg. Allg. Chem.* **1978**, *446*, 64–76; e) R. Hoppe, G. Wagner, H. Glaum, *Z. Anorg. Allg. Chem.* **1987**, *547*, 188–198; f) R. Hoppe, H. P. Müller, *Solid State Ionics* **1990**, *43*, 23–30; g) M. Schläger, R. Hoppe, *Z. Anorg. Allg. Chem.* **1994**, *620*, 882–887; h) M. Sofin, M. Jansen, *J. Solid State Chem.* **2004**, *177*, 2550–2556; i) G. Frisch, C. Röhr, *Z. Kristallogr.* **2005**, *220*, 135–141; j) G. Frisch, C. Röhr, *Z. Naturforsch.* **2005**, *60b*, 732–740; k) S. Pfeiffer, D. Fischer, M. Jansen, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1673–1676.

[7] M. Bortz, M. Jansen, *Z. Anorg. Allg. Chem.* **1993**, *619*, 1446–1454.

[8] a) H. D. Wasel-Nielen, R. Hoppe, *Z. Anorg. Allg. Chem.* **1970**, *375*, 43–51; b) H. N. Migeon, A. Courtois, M. Zanne, C. Gleitzer, J. Aubry, *Rev. Chim. Minér.* **1975**, *12*, 203–209; c) N. Bukovec, I. Leban, R. Hoppe, *Z. Anorg. Allg. Chem.* **1988**, *563*, 79–86.

[9] F. Stewner, R. Hoppe, *Z. Anorg. Allg. Chem.* **1970**, *374*, 239–258.

[10] M. Sofin, M. Jansen, *Solid State Sci.* **2006**, *8*, 19–23.

[11] L. Hackspill, *Compt. Rend.* **1905**, *141*, 106–107.

[12] C. Hoch, I. Schellenberg, R. Pöttgen, *Z. Naturforsch.* **2011**, *66b*, 441–443.

[13] a) Stoe & Cie. GmbH X-SHAPE 2.07 Crystal optimization for numerical absorption correction, Darmstadt (Germany) **2005**. b) Stoe & Cie. GmbH X-RED 1.31, Stoe data reduction program, Darmstadt (Germany) **2005**.

[14] a) G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick *Acta Crystallogr.* **1990**, *A46*, 467–473; b) G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122.

[15] M. Gelato, E. Parthé, *J. Appl. Crystallogr.* **1987**, *20*, 139–143.

[16] R. D. Shannon, *Acta Crystallogr.* **1976**, *A32*, 751–767.

[17] a) M. G. Barker, P. G. Gadd, M. J. Begley, *J. Chem. Soc.* **1981**, *1981*, 379–381; b) N. Z. Ali, J. Nuss, D. Sheptyakov, M. Jansen, *J. Solid State Chem.* **2010**, *183*, 752–759; c) M. Schläger, R. Hoppe, *Z. Anorg. Allg. Chem.* **1994**, *620*, 1867–1871; d) K. R. Warmbach, R. Hoppe, *Z. Anorg. Allg. Chem.* **1978**, *444*, 30–46.

[18] H. Kohlmann, *Z. Anorg. Allg. Chem.* **2010**, *183*, 367–372.