Crystal Structures of New Alkali Metal-rich Oxometallates: Rubidium Aluminate Tetrahydroxide, $Rb_9(AlO_4)(OH)_4$, Rubidium Orthogallate, Rb_5GaO_4, Cesium *bis*-Chromate(IV) Oxide, $Cs_{10}(CrO_4)_2O$, and Cesium Diindate, $Cs_8In_2O_7$

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Several new alkali metal oxometallates with anions built up from tetrahedral $[MO_4]$ units were obtained in reactions aimed at the formation of alkali metal suboxometallates or by thermally decomposing the latter. Rubidium orthoaluminate tetrahydroxide $Rb_9(AlO_4)(OH)_4$ crystallizes with a new structure type (space group $P2_1/c$, $a = 13.116(1)$, $b = 6.9266(5)$, $c = 18.934(2)$ Å, $\beta = 92.05(1)^\circ$, $V = 1719.0(3)$ Å^3, $Z = 4$, $R1 = 0.0352$) and contains orthoaluminate anions $[AlO_4]^{5-}$ and isolated hydroxide anions. Rubidium orthogallate Rb_5GaO_4 crystallizes with the Na_5GaO_4 structure type (space group *Pbca*, $a = 6.9318(5)$, $b = 21.309(2)$, $c = 11.740(1)$ Å, $V = 1734.2(3)$ Å^3, $Z = 8$, $R1 = 0.0423$) with isolated orthogallate anions $[GaO_4]^{5-}$. Cesium chromate oxide $Cs_{10}(CrO_4)_2O$ adopts the $Cs_{10}(GeO_4)_2O$ structure type (space group $P2_1/c$, $a = 12.903(1)$, $b = 11.4523(8)$, $c = 19.074(3)$ Å, $\beta = 127.903(8)^\circ$, $V = 2223.9(4)$ Å^3, $Z = 4$, $R1 = 0.0326$) with orthochromate(IV) anions $[CrO_4]^{4-}$ and isolated oxide anions. In all orthometallates the anions $[MO_4]^{n-}$ deviate only slightly from ideal tetrahedral symmetry. Cesium diindate $Cs_8In_2O_7$ crystallizes with the $Cs_8Fe_2O_7$ structure type (space group $P2_1/c$, $a = 7.4307(6)$, $b = 18.6181(14)$, $c = 7.2639(6)$ Å, $\beta = 119.225(8)^\circ$, $V = 877.0(1)$ Å^3, $Z = 2$, $R1 = 0.0349$). A single-crystal structure investigation at r. t. has shown linear diindate units, but the temperature dependence of the libration angles from TLS studies for the bridging oxygen atom suggests a slightly bent and dynamically disordered diindate anion.

Key words: Oxometallates, Rubidium, Cesium, Aluminates, Gallates, Indates, Chromates, Dimetallates, TLS Analysis, Crystal Structure

Introduction

Orthometallates of the heavy alkali metals Rb and Cs are widely unknown. Pauling's second rule for ionic crystals [1] explains the low stability of orthometallates of large cations with regard to unsatisfying topological solutions of the problem of equilibrating the local Coulomb potentials between large cations of low charge density and small anions of high charge density. The stability in terms of the Madelung part of the lattice energy of the structures can be increased by inserting small additional anions, *e. g.* oxide or hydroxide anions, or by condensing the orthometallate units, *e. g.* to dimetallates.

All compounds presented here were the result of experiments aimed at the synthesis of new alkali metal (A) suboxometallates A_9MO_4 [2, 3]. In these novel compounds the orthometallate substructure is stabilized by insertion not of an additional small anion but of a metallic alkali metal atom, following the structural principles known from alkali metal suboxides and subnitrides [4 – 8]. The structural chemistry of the suboxometallates not only is an interesting topic for analysing the underlying bonding mechanisms, but these materials can also be utilized for further chemical preparations. They provide new access to oxometallates with lowest possible connectivity in the anionic substructure due to the high metal content present in the precursor materials, and allow exploring the frontiers set by Pauling's second rule for ionic crystals [1].

Reactions aimed at the formation of new alkali metal suboxometallates of *e. g.* Al, Ga, In, and Cr do not always work out right in the first attempt. In cases of a set of reaction conditions that do not lead to the desired products, the products are oxometallates immersed in excess alkali metal, alkali metal suboxides

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or intermetallic phases. However, this decomposition process can be carried out on purpose by thermally decomposing suboxometallates, or by thermally inducing redox reactions of the metallically bonded alkali metal with the oxometallate anion.

Here we present the crystal structures of several new alkali metal oxometallates which contain the smallest possible anionic subunits for the systems (Rb/Cs)–*M*–O (*M* = Al, Ga, In, Cr(IV)). Only one structure is a proper orthometallate, two structures show the presence of small anions (oxide or hydroxide) which is essential for the formation of a stable arrangement of the components, and a fourth structure is an example for the condensation to a dimetallate anion. These compounds represent the stability limits for minimal lattice energy.

Experimental Section

As the alkali metal oxometallates presented in this work were the result of experiments towards the formation of new alkali metal suboxometallates, the reaction mixtures were all rich in rubidium or cesium metal. All products were separated under a binocular from a metallic, liquid matrix of alkali metal or alkali metal suboxides. Alkali metal melts have in many cases been shown to enhance the crystallization of well developed single crystals in the function of a solvent, even for purely oxidic species [9, 10]. The reduction of the metal present in the oxometallate anion was observed only in the case of $Cs_{10}(Cr^{IV}O_4)_2O$, where $Cs_2Cr^{VI}O_4$ was used as the educt. All reactions were conducted in mechanically closed tantalum crucibles placed in small steel autoclaves to prevent distilling off of the alkali metal. The tantalum crucibles were not closed by arc-welding in order to prevent any local increase of the temperature to the range where the reactions already set in (*ca.* 473 – 573 K). The autoclaves were placed in argon-filled glass tubes in vertical furnaces. After the reactions the tantalum crucibles were opened in an argon-filled glove box, and a small portion of the product mixtures was brought in air under paraffin oil dried with potassium sand* for optical evaluation and separation of crystals suitable for single-crystal investigations. As all compounds are very hygroscopic, the crystals were sealed in thin-walled glass capillaries (∅ = 0.1 mm) filled with dried paraffin oil.

$Rb_9(AlO_4)(OH)_4$ was one of the products of the reaction of Rb metal (6.97 mmol), Rb_2O (4.35 mmol) (see below) and Al_2O_3 (0.87 mmol) in the molar ratio 8 : 5 : 1, according to the composition Rb_9AlO_4. The mixture was heated to 573 K within 5.5 h and allowed to react for two hours. After cooling to 473 K with a rate of 10 K/h the furnace was switched off. Rb_2O was prepared by reaction of a surplus of Rb metal with oxygen generated by slow thermal decomposition of HgO to the nominal composition of Rb_3O and subsequently distilling off the excess rubidium metal. The product contained some RbOH which lead to the formation of $Rb_9(AlO_4)(OH)_4$. Byproducts were structurally unidentified intermetallic Rb–Al compounds embedded in a bronze-colored liquid matrix of rubidium suboxides. $Rb_9(AlO_4)(OH)_4$ forms brittle transparent xenomorphic crystals.

Rb_5GaO_4 was the main product of the reaction of Rb metal (10.18 mmol), Rb_2O (6.36 mmol) and Ga_2O_3 (1.28 mmol) in the molar ratio 8 : 5 : 1, aiming at the formation of Rb_9GaO_4, one of the border phases of the solid solution $Rb_xCs_{9-x}GaO_4$ [3]. The reaction mixture was treated in the same way as described for $Rb_9(AlO_4)(OH)_4$. The crystals of Rb_5GaO_4 were transparent and light blue, probably due to the presence of color centers. For this experiment a new, RbOH-free Rb_2O was used. The crystals of Rb_5GaO_4 were separated machanically from a bronze-colored matrix of rubidium suboxides. Byproducts were structurally unidentified intermetallic Rb–Ga compounds.

$Cs_{10}(CrO_4)_2O$ could be obtained as xenomorphic, transparent light-brown crystals embedded in a liquid matrix of cesium suboxides by reacting cesium metal (8.00 mmol) and Cs_2CrO_4 (1.14 mmol) at 523 K for 2 h and cooling the reation mixture to r. t. with a rate of 20 K/h, Cs_2CrO_4 being prepared by cation exchange of aqueous solutions of K_2CrO_4 with CsCl. The reaction was aimed at the formation of $Cs_9Cr^{VI}O_4$. At lower temperatures no reaction took place between Cs metal and Cs_2CrO_4; the same holds for mixtures of Cs metal and CrO_3. Obviously, the reaction only sets in at a temperature high enough to induce the reduction of Cr(VI) to Cr(IV). First attempts to prepare phase-pure samples of $Cs_{10}(CrO_4)_2O$ starting from reaction mixtures of Cs_2O and CrO_2 in stoichiometric ratios yielded mixtures of cesium suboxides and crystals of $Cs_7Cr_2O_8 = Cs_7(Cr^{IV}O_4)(Cr^{V}O_4)$ which crystallizes with the $Cs_7Fe_2O_8$ structure type [11] (space group $P2_1/c$, a = 6.679(4), b = 10.964(7), c = 21.75(2) Å, β = 92.90(7)° [12]). It is remarkable that Cs_2O acts as oxidant in this reaction.

The first single crystals of $Cs_8In_2O_7$ appeared as the main product when mixtures of In_2O_3 and Cs_2O were reduced with metallic cesium (molar ratio $In_2O_3 : Cs_2O : Cs$ = 1 : 3 : 4, T_{max} = 673 K) as xenomorphic, yellow single crys-

*K metal lumps were cleaned from oxide layers with a knife and inserted into a Schlenk bottle filled with paraffin oil with a boiling range of 393 – 433 K under argon. The bottle was heated to 353 K while stirring vigorously with the aid of a magnetic stirrer. The stirring dissipated the liquid potassium into spherical droplets of several mm in diameter and was continued after switching off the heater until the temperature of the oil was lowered beneath the melting point of K. The solidified K spheres are a powerful drying agent and can easily be regenerated after oxidation of the surface by remelting, stirring and recooling. This procedure is much easier than the one used for preparing the commonly used sodium wire.

Table 1. Crystallographic data (r. t.) and details on data collection and refinement for $Rb_9(AlO_4)(OH)_4$, Rb_5GaO_4, $Cs_8In_2O_7$, and $Cs_{10}(CrO_4)_2O$. Standard deviations of the last digit are given in parentheses.

Empirical formula	$Rb_9(AlO_4)(OH)_4$	Rb_5GaO_4	$Cs_8In_2O_7$	$Cs_{10}(CrO_4)_2O$
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	*Pbca* (no. 61)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
Z	4	8	2	4
Lattice parameters				
a, Å	13.116(1)	6.9318(5)	7.4307(6)	12.903(1)
b, Å	6.9266(5)	21.309(2)	18.618(1)	11.4523(8)
c, Å	18.934(2)	11.740(1)	7.2639(6)	19.074(3)
β, deg	92.05(1)		119.225(8)	127.903(8)
V, Å^3	1719.0(3)	1734.2(3)	877.0(1)	2223.9(4)
Calc. density, g cm^{-3}	3.59	4.30	5.32	4.71
Crystal color	colorless	light blue	yellow	light brown
Crystal shape	fragment	cuboid	prism	fragment
Diffractometer	– IPDS1 –			
Radiation, wave length, Å	– Ag$K\alpha$, 0.56083 –			
Monochromator	– graphite –			
Data collection mode	– φ scans –			
Data collection range				
$h_{\min/\max}$	−16/16	−8/7	−10/10	−17/17
$k_{\min/\max}$	−8/8	−25/25	−25/25	−15/15
$l_{\min/\max}$	−24/24	−14/14	−9/9	−26/26
$2\vartheta_{\min/\max}$, deg	4.1/47.9	4.0/47.2	4.9/56.2	3.5/ 48.3
Corrections	— Lorentz, polarization, absorption (numerical) [14] —			
Structure solution	— Direct Methods [15] —			
Structure refinement	— full-matrix least-squares refinement on F_o^2 —			
No. of ls. parameters	177	92	80	194
R_{int}	0.1143	0.1639	0.0362	0.0800
R_σ	0.0743	0.0937	0.0261	0.0476
$R1$ [$F_o^2 \geq 2\sigma(F_o^2)$]/$R1$ (all data)	0.0637/0.0352	0.0824/0.0423	0.0449/0.0349	0.0434/0.0326
$wR2$ [$F_o^2 \geq 2\sigma(F_o^2)$]/$wR2$ (all data)	0.0712/0.0653	0.0878/0.0794	0.0898/0.0880	0.0678/0.0651
Absorption coeff., mm^{-1}	13.7	16.7	10.1	9.0
Min. transmission	0.1254	0.2084	0.3293	0.1640
Max. transmission	0.3497	0.3032	0.4211	0.2595
Min. res. el. density, e Å^{-3}	1.04	1.13	2.67	1.50
Max. res. el. density, e Å^{-3}	−1.47	−1.10	−2.43	−1.23

tals, with $Cs_6In_2O_6$ [13] as a byproduct. Samples that do not show impurities in X-ray powder diffractometry can be obtained by reacting finely ground stoichiometric mixtures of Cs_2O and In_2O_3 in tantalum crucibles under argon at 673 K for two weeks. At lower temperature ($T_{max} \approx 573$ K) reaction mixtures like the first one above yield the cesium suboxoindate Cs_9InO_4 [2] as the main product.

X-Ray structure determinations

The crystals were centered on a one-circle goniometer equipped with an image-plate detector using graphite-monochromatized Ag$K\alpha$ radiation (IPDS1, Stoe & Cie. Darmstadt, Germany). Data were collected in φ scans, and data reductions were performed with the diffractometer software packages [14]. The intensities were corrected for Lorentz, polarization and absorption effects (numerical absorption correction with optimized crystal shape [14]). The structures were solved by Direct Methods [15] after determining suitable space group candidates following the reflection statistics and absence conditions. Structure refinements were carried out with full-matrix least-squares techniques on F^2 [15] introducing anisotropic displacement factors for all non-H atoms. Information on data collection, crystallographic data and structure determination are compiled in Table 1. Standardized fractional atomic parameters [37], anisotropic and equivalent isotropic displacement parameters as well as selected interatomic distances and angles can be found in Tables 2 – 4.

Preliminary studies on single crystals of $Cs_8In_2O_7$ revealed that larger specimens showed polysynthetic twinning according to $\begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$. Therefore a small single-crystalline sample was selected under a polarization microscope and centerered on the goniometer. The temperature was controlled by a cooling system with a nitrogen gas stream. The crystal in use showed no significant twinning; after applying the twin law as above, the batch scale factors for the respective twin volumes refined to 1 and 0 within the error margin, respectively. TLS analyses were carried out using Schomaker's algorythm [16] as inplemented in the PLATON program package [17].

Further details of the structure investigations may be obtained from Fachinformationszentrum Karlsruhe,

Table 2. Fractional atomic coordinates in standardized setting [37] and equivalent isotropic displacement parameters (pm^2) for $Rb_9(AlO_4)(OH)_4$, Rb_5GaO_4, $Cs_8In_2O_7$, and $Cs_{10}(CrO_4)_2O$ at r. t. The H atoms in $Rb_9(AlO_4)(OH)_4$ were refined applying common values for the isotropic displacement factors. In $Rb_9(AlO_4)(OH)_4$, Rb_5GaO_4, and $Cs_{10}(CrO_4)_2O$ all atoms occupy the general positions with Wyckoff-No. 4*e* ($Rb_9(AlO_4)(OH)_4$ and $Cs_{10}(CrO_4)_2O$) *resp.* 8*c* (Rb_5GaO_4). In $Cs_8In_2O_7$ the bridging oxygen atom O1 is located on the inversion center at 0, 0, 0 with Wyckoff-No. 2*a*, while all other atoms occupy the general position with Wyckoff-No. 4*e*. Standard deviations of the last digit are given in parentheses.

Atom	*x*	*y*	*z*	U_{equiv}	Atom	*x*	*y*	*z*	U_{equiv}
		$Rb_9(AlO_4)(OH)_4$					$Cs_{10}(CrO_4)_2O$		
Rb1	0.03088(4)	0.2529(1)	0.49187(4)	272(2)	Cs1	0.06281(4)	0.82495(4)	0.41044(2)	252.7(9)
Rb2	0.05777(5)	0.3597(1)	0.31663(5)	344(2)	Cs2	0.07862(3)	0.72523(3)	0.22198(2)	213.5(8)
Rb3	0.23342(5)	0.6960(1)	0.19482(4)	274(2)	Cs3	0.13241(4)	0.09435(4)	0.01047(3)	268.4(9)
Rb4	0.25204(5)	0.6055(1)	0.01054(4)	236(2)	Cs4	0.21763(3)	0.42520(3)	0.32414(2)	190.6(8)
Rb5	0.27747(6)	0.1130(1)	0.08101(4)	354(2)	Cs5	0.25539(4)	0.13638(3)	0.45316(2)	235.4(8)
Rb6	0.33055(6)	0.2125(1)	0.28015(5)	385(2)	Cs6	0.30903(4)	0.47584(4)	0.16332(3)	278.1(9)
Rb7	0.47438(5)	0.2504(1)	0.46714(5)	343(2)	Cs7	0.36683(4)	0.16013(4)	0.25604(3)	236.2(8)
Rb8	0.56253(5)	0.2088(1)	0.16159(4)	291(2)	Cs8	0.61135(3)	0.37554(3)	0.49428(2)	199.1(8)
Rb9	0.86474(5)	0.3866(1)	0.14641(4)	283(2)	Cs9	0.62620(4)	0.39967(3)	0.12143(3)	247.0(9)
Al1	0.2467(1)	0.4776(3)	0.41590(10)	142(4)	Cs10	0.69379(4)	0.31624(3)	0.33623(3)	218.7(8)
O11	0.1359(3)	0.5763(7)	0.4541(3)	240(10)	Cr1	0.06873(8)	0.05247(7)	0.20882(5)	123(2)
O12	0.2435(4)	0.2183(7)	0.4203(3)	280(10)	O11	0.0770(4)	0.5299(4)	0.7906(3)	225(9)
O13	0.2456(3)	0.5517(7)	0.3242(3)	210(10)	O12	0.0986(4)	0.5787(4)	0.3838(3)	218(9)
O14	0.6432(3)	0.0717(7)	0.0386(3)	200(10)	O13	0.1457(4)	0.1895(4)	0.2563(3)	223(9)
O1	0.0710(4)	0.5136(10)	0.1142(3)	400(20)	O14	0.1528(4)	0.5244(4)	0.6765(3)	255(9)
H1	0.13(2)	0.46(6)	0.10(2)	400(120)	Cr2	0.48285(8)	0.14497(7)	0.12691(5)	118(2)
O2	0.1352(4)	0.0665(9)	0.2119(3)	360(10)	O21	0.4010(4)	0.1409(4)	0.0116(3)	212(8)
H2	0.15(3)	0.11(6)	0.258(10)	400(120)	O22	0.4341(4)	0.2756(4)	0.1514(3)	227(9)
O3	0.3931(4)	0.4554(10)	0.1133(4)	430(20)	O23	0.4410(4)	0.0198(4)	0.1607(3)	242(9)
H3	0.36(3)	0.49(6)	0.068(10)	400(120)	O24	0.6554(4)	0.1506(4)	0.1869(3)	262(10)
O4	0.5738(5)	0.4032(10)	0.3067(4)	490(20)	O1	0.0255(10)	0.1526(9)	0.4698(6)	590(20)
H4	0.52(2)	0.35(6)	0.27(2)	400(120)	O2	0.618(3)	0.105(2)	0.447(2)	590(20)
		Rb_5GaO_4					$Cs_8In_2O_7$		
Rb1	0.0737(2)	0.37004(6)	0.2034(1)	192(3)	Cs1	0.2332(1)	0.00436(4)	0.4669(1)	179(2)
Rb2	0.0771(2)	0.00375(6)	0.1391(1)	244(3)	Cs2	0.2400(1)	0.20861(4)	0.4636(1)	214(2)
Rb3	0.0846(2)	0.06608(5)	0.4280(1)	188(3)	Cs3	0.3595(1)	0.58444(4)	0.5062(1)	228(2)
Rb4	0.3799(2)	0.25538(6)	0.0880(1)	234(3)	Cs4	0.7775(1)	0.30660(4)	0.0425(1)	214(2)
Rb5	0.3886(2)	0.17814(5)	0.32859(9)	193(3)	In1	0.1453(1)	0.09775(3)	0.0011(1)	92(1)
Ga1	0.1778(2)	0.12479(6)	−0.0313(1)	78(3)	O1	0	0	0	190(20)
O1	0.248(1)	0.1300(4)	0.1225(6)	150(20)	O2	0.042(1)	0.6780(4)	0.490(1)	180(20)
O2	0.257(1)	0.3018(4)	0.3908(6)	130(20)	O3	0.157(1)	0.3940(5)	0.225(1)	240(20)
O3	0.289(1)	0.4453(4)	0.3996(7)	140(20)	O4	0.429(1)	0.0993(5)	0.266(1)	230(20)
O4	0.408(1)	0.3835(4)	0.0411(7)	140(20)					

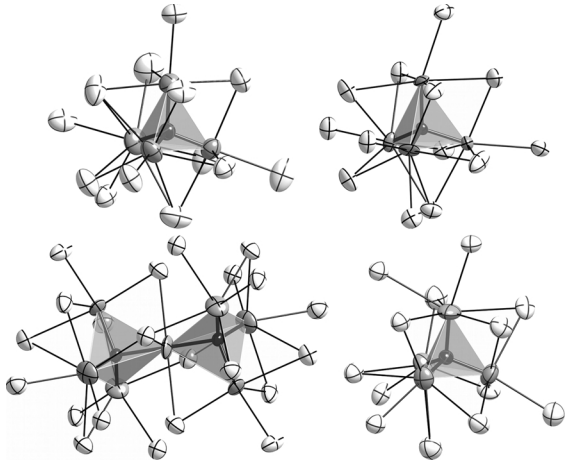
76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition numbers CSD-422148 ($Rb_9(AlO_4)(OH)_4$), CSD-420328 (Rb_5GaO_4), CSD-422147 ($Cs_{10}(CrO_4)_2O$), CSD-421564 ($Cs_8In_2O_7$, 293 K), CSD-421565 ($Cs_8In_2O_7$, 243 K), CSD-421566 ($Cs_8In_2O_7$, 193 K), CSD-421567 ($Cs_8In_2O_7$, 143 K), and CSD-421568 ($Cs_8In_2O_7$, 93 K).

Results and Discussion

$Rb_9(AlO_4)(OH)_4$ crystallizes in a new monoclinic structure type which contains orthoaluminate anions $[AlO_4]^{5-}$ and isolated hydroxide anions. Alkali metal orthoaluminates A_5AlO_4 are only known for the smallest alkali metal cations A = Li and Na [18, 19]. It can be assumed that in accordance with the above-mentioned limits given by Pauling's electroneutrality rule the orthoaluminates of the larger alkali metal cations are not stable unless further anions are inserted into the structure, *e. g.* hydroxide anions. The insertion of further metal atoms may also stabilize the structure, as is shown in the suboxoaluminates Cs_9AlO_4 and $Cs_{9-x}Rb_xAlO_4$ [3]. In these compounds the orthoaluminate anion is coordinated by 12 cesium atoms in a rather regular way (all oxygen atoms have a coordination number of 5 + 1) and has higher point symmetry (point group $\bar{4}2m$, Wyckoff position 4*b* in space

Table 3. Anisotropic displacement parameters (pm^2) for $Rb_9(AlO_4)(OH)_4$, Rb_5GaO_4, $Cs_8In_2O_7$, and $Cs_{10}(CrO_4)_2O$ 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}	Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
			$Rb_9(AlO_4)(OH)_4$							$Cs_{10}(CrO_4)_2O$			
Rb1	244(3)	189(4)	389(4)	13(3)	107(3)	1(2)	Cs1	289(2)	252(2)	214(2)	−1(1)	153(2)	−12(1)
Rb2	257(3)	319(5)	449(5)	−2(4)	−89(3)	−37(3)	Cs2	156(2)	225(2)	248(2)	21(1)	118(1)	3(1)
Rb3	309(3)	322(4)	189(3)	25(3)	−2(2)	−20(3)	Cs3	259(2)	256(2)	241(2)	7(1)	129(2)	−0(1)
Rb4	281(3)	184(4)	241(3)	25(3)	−20(2)	−1(2)	Cs4	190(2)	173(2)	196(2)	−24(1)	112(1)	−9(1)
Rb5	474(4)	329(5)	264(4)	−33(3)	90(3)	−57(3)	Cs5	219(2)	208(2)	212(2)	−8(1)	98(1)	16(1)
Rb6	413(4)	323(5)	422(5)	−139(4)	79(3)	55(3)	Cs6	304(2)	243(2)	291(2)	−10(2)	184(2)	7(2)
Rb7	262(3)	264(4)	497(5)	−106(4)	−69(3)	73(3)	Cs7	216(2)	297(2)	251(2)	−18(2)	171(2)	−44(1)
Rb8	221(3)	351(4)	300(4)	−38(3)	24(3)	83(3)	Cs8	204(2)	184(2)	214(2)	−9(1)	131(1)	−1(1)
Rb9	356(3)	237(4)	257(4)	−26(3)	12(3)	−89(3)	Cs9	241(2)	229(2)	244(2)	23(1)	136(2)	−21(1)
Al1	120(8)	160(10)	140(10)	−8(8)	9(7)	1(7)	Cs10	274(2)	189(2)	252(2)	−15(1)	191(2)	−37(1)
O11	210(20)	260(30)	260(30)	0(20)	90(20)	−1(2)	Cr1	104(3)	114(4)	147(4)	−9(3)	75(3)	0(3)
O12	330(20)	150(30)	350(30)	−10(20)	30(20)	10(20)	O11	250(20)	240(20)	210(20)	−30(20)	130(20)	30(20)
O13	200(20)	260(30)	180(30)	0(20)	−100(20)	−10(20)	O12	130(20)	210(20)	220(20)	−10(20)	60(20)	−10(10)
O14	190(20)	210(30)	200(30)	40(20)	0(20)	−10(2	O13	180(20)	200(20)	280(20)	−60(20)	130(20)	−30(20)
O1	350(30)	450(40)	380(40)	10(30)	−90(30)	−70(30)	O14	270(20)	240(20)	330(20)	60(20)	220(20)	−30(20)
O2	350(30)	350(40)	380(30)	0(30)	0(20)	−10(20)	Cr2	111(3)	112(4)	132(4)	−8(3)	77(3)	−12(3)
O3	420(30)	350(40)	510(40)	60(30)	−70(30)	60(20)	O21	270(20)	230(20)	150(20)	0(20)	130(20)	−1(20)
O4	500(30)	430(40)	530(40)	−40(30)	90(30)	130(30)	O22	250(20)	210(20)	260(20)	−20(20)	180(20)	50(20)
							O23	270(20)	230(20)	250(20)	0(20)	170(20)	−70(20)
							O24	130(20)	280(20)	340(20)	−30(20)	170(20)	−20(20)
							O1	840(60)	570(50)	590(50)	−40(40)	560(50)	−40(50)
							O2	840(60)	570(50)	590(50)	−40(40)	560(50)	−40(50)
			Rb_5GaO_4							$Cs_8In_2O_7$			
Rb1	150(6)	237(6)	188(6)	13(5)	−35(5)	−14(5)	Cs1	199(3)	183(3)	139(3)	0(2)	69(2)	0(3)
Rb2	227(7)	199(6)	306(6)	−56(5)	−6(5)	−64(5)	Cs2	225(4)	220(3)	210(3)	1(3)	117(3)	30(3)
Rb3	116(6)	156(5)	292(6)	−24(5)	−4(5)	14(5)	Cs3	182(3)	241(3)	291(4)	4(3)	139(3)	26(3)
Rb4	298(8)	195(6)	210(6)	43(5)	−45(5)	−116(5)	Cs4	173(3)	181(3)	222(3)	−36(3)	46(3)	39(3)
Rb5	224(7)	201(6)	153(6)	2(5)	−41(5)	55(5)	In1	98(3)	78(3)	94(3)	−4(2)	42(2)	−6(2)
Ga1	67(6)	77(6)	91(6)	−8(5)	−6(4)	−8(5)	O1	270(60)	60(40)	200(50)	30(40)	90(50)	−70(40)
O1	200(50)	170(40)	70(40)	60(30)	−40(30)	−80(40)	O2	210(40)	80(30)	290(40)	20(30)	150(30)	−10(30)
O2	180(50)	90(40)	120(40)	0(30)	−30(30)	20(30)	O3	250(40)	360(50)	150(40)	−50(30)	140(30)	−30(40)
O3	100(50)	110(40)	200(50)	−30(40)	20(30)	−30(30)	O4	140(40)	330(50)	150(40)	0(30)	0(30)	−40(30)
O4	70(40)	210(50)	140(40)	−30(30)	80(30)	−50(30)							



← Fig. 1. Synopsis of the oxometallate anions and their coordinations by alkali metal cations in $Rb_9(AlO_4)(OH)_4$ (upper left), Rb_5GaO_5 (upper right), $Cs_8In_2O_7$ (lower left), and $Cs_{10}(CrO_4)_2O$ (lower right). All ellipsoids are drawn at a probability level of 95 %. Metal cations centering the oxometallate anion are drawn in dark grey, oxygen atoms in grey and alkali metal atoms in light grey.

group *I*4/*mcm*, in comparison to Wyckoff position 4*e* with point symmetry 1 in $Rb_9(AlO_4)(OH)_4$. However, the orthoaluminate anion in $Rb_9(AlO_4)(OH)_4$ deviates only slightly from the ideal tetrahedral geometry (angles O–Al–O range from 107.6(2) to 111.3°, bond lengths Al–O from 1.778(5) to 181.0(5) Å, see Tables 4). The interatomic distances found for the orthoaluminate anion in $Rb_9(AlO_4)(OH)_4$ are in good agreement with those found for Cs_9AlO_4 (1.82 Å [3]), α-Li_5AlO_4 (1.81 – 1.82 Å [18]), β-Li_5AlO_4 (1.75 – 1.78 Å [18]) and Na_5AlO_4 (1.76 – 1.79 Å [19]).

There are four crystallographic positions fully occupied by the hydroxide anions present in the

Table 4a. Selected interatomic distances (Å) for $Rb_9(AlO_4)(OH)_4$ and Rb_5GaO_4 at r. t. Standard deviations of the last digit are given in parentheses.

Atoms		Distance	Atoms		Distance	Atoms		Distance	Atoms		Distance
$Rb_9(AlO_4)(OH)_4$											
Al1	– O11	1.784(5)	Rb8	– O13	2.746(4)	O11	– Al1	1.784(5)	O12	– Rb9	2.960(5)
	– O12	1.798(6)		– O14	2.760(5)		– Rb1	2.718(5)	O13	– Al1	1.810(5)
	– O13	1.810(5)		– O3	2.924(6)		– Rb1	2.738(5)		– Rb2	2.799(4)
	– O14	1.778(5)		– O4	2.849(6)		– Rb2	3.145(5)		– Rb3	2.646(5)
Rb1	– O11	2.718(5)		– O4	3.059(7)		– Rb4	2.864(5)		– Rb6	2.743(5)
	– O11	2.738(5)	Rb9	– O11	2.871(5)		– Rb5	3.259(5)		– Rb8	2.746(4)
	– O12	3.153(5)		– O12	2.960(5)		– Rb9	2.871(5)		– Rb9	2.780(5)
	– O1	2.894(6)		– O13	2.800(5)	O12	– Al1	1.798(6)	O14	– Al1	1.778(5)
	– O1	2.993(6)		– O1	2.930(6)		– Rb1	3.153(5)		– Rb4	2.801(5)
Rb2	– O11	3.145(5)		– O2	2.958(6)		– Rb2	3.226(5)		– Rb5	2.832(5)
	– O12	3.226(5)	O1	– H1	0.95(2)		– Rb4	2.819(5)		– Rb7	2.708(5)
	– O13	2.800(4)		– Rb1	2.894(6)		– Rb5	3.275(6)		– Rb7	2.835(4)
	– O1	3.237(7)		– Rb1	2.993(6)		– Rb6	2.927(6)		– Rb8	2.760(5)
	– O2	2.942(5)		– Rb2	3.237(7)		– Rb7	3.133(5)			
	– O2	3.038(6)		– Rb2	3.988(7)	Rb_5GaO_4					
Rb3	– O13	2.646(5)		– Rb3	2.869(5)	Ga1	– O1	1.874(8)	Rb2	– O4	2.810(8)
	– O1	2.869(5)		– Rb4	3.198(6)		– O2	1.894(8)		– O4	3.410(8)
	– O2	2.895(6)		– Rb5	3.943(7)		– O3	1.866(8)	Rb3	– O1	2.766(9)
	– O3	3.127(7)		– Rb9	2.930(6)		– O4	1.884(8)		– O3	2.740(8)
	– O4	2.908(6)	O2	– H2	0.95(2)	Rb1	– O2	2.855(9)		– O3	2.891(8)
Rb4	– O11	2.864(5)		– Rb2	2.942(5)		– O2	2.928(8)		– O4	2.817(9)
	– O12	2.819(5)		– Rb2	3.038(6)		– O3	2.816(8)	Rb4	– O1	2.854(8)
	– O14	2.801(5)		– Rb3	2.895(6)		– O3	3.178(8)		– O2	2.751(8)
	– O1	3.198(6)		– Rb5	3.172(6)		– O4	3.013(8)		– O2	2.807(9)
	– O3	2.834(6)		– Rb6	3.003(5)		– O4	3.225(8)		– O4	2.793(8)
Rb5	– O11	3.259(5)		– Rb9	2.958(6)	Rb2	– O1	2.945(8)	Rb5	– O1	2.755(9)
	– O12	3.275(6)		– Rb9	4.327(6)		– O3	2.863(8)		– O1	2.803(8)
	– O14	2.832(5)	O3	– H3	0.95(2)		– O3	3.353(8)		– O2	2.882(8)
	– O2	3.172(6)		– Rb3	3.127(7)		– O3	3.430(8)		– O4	2.823(8)
	– O3	2.869(7)		– Rb4	2.834(6)	O1	– Ga1	1.874(8)	O2	– Ga1	1.894(8)
	– O4	3.184(7)		– Rb5	2.869(7)		– Rb2	2.945(8)		– Rb1	2.855(9)
Rb6	– O12	2.927(6)		– Rb6	3.697(7)		– Rb3	2.766(9)		– Rb1	2.928(8)
	– O13	2.743(5)		– Rb7	3.116(7)		– Rb4	2.854(8)		– Rb4	2.751(8)
	– O2	3.003(5)		– Rb7	3.322(7)		– Rb5	2.755(9)		– Rb4	2.807(9)
	– O4	3.003(7)		– Rb8	2.924(6)		– Rb5	2.803(8)		– Rb5	2.882(8)
	– O4	3.473(7)	O4	– H4	0.95(2)	O3	– Ga1	1.866(8)	O4	– Ga1	1.884(8)
Rb7	– O12	3.133(5)		– Rb3	2.908(6)		– Rb1	2.816(8)		– Rb1	3.013(8)
	– O14	2.708(5)		– Rb5	3.184(7)		– Rb1	3.178(8)		– Rb1	3.225(8)
	– O14	2.835(4)		– Rb6	3.003(7)		– Rb2	2.863(8)		– Rb2	2.810(8)
	– O3	3.116(7)		– Rb6	3.473(7)		– Rb2	3.353(8)		– Rb2	3.410(8)
	– O3	3.322(7)		– Rb7	3.511(7)		– Rb2	3.430(8)		– Rb3	2.817(8)
	– O4	3.511(7)		– Rb8	2.849(6)		– Rb3	2.740(8)		– Rb4	2.793(8)
				– Rb8	3.059(7)		– Rb3	2.891(8)		– Rb5	2.823(8)

$Rb_9(AlO_4)(OH)_4$ structure. These anions are accommodated in large polyhedra with coordination numbers of 6+2, 6+1, 6+2, and 5+2 for O1, O2, O3, and O4, respectively (see Table 4a and Fig. 3). Together with the $[AlO_4]^{4-}$ anions, the hydroxide anions are packed in slightly puckered hexagonal layers perpendicular to $[50\bar{1}]$ (see Fig. 2) with the rubidium cations situated between them. The layers are stacked according to a …ABA′B′… pattern, where A and A′ *resp.* B and B′ are related *via* inversion centers.

The crystal structure of Rb_5GaO_4 is isotypical to Na_5GaO_4 [20] and shows isolated $[GaO_4]^{5-}$ anions (Fig. 1) deviating only slightly from ideal tetrahedral symmetry despite their low point symmetry (Wyckoff position 8*c* for Ga1 with point symmetry 1, angles O–Ga–O ranging from 108.0(3)° to 111.0(4)°, distances Ga–O from 1.866(8) to 1.894(8) Å, see Tables 4). The coordination of two of the oxygen atoms is 5+1 (5 Rb + 1 Ga) forming a distorted octahedron. The coordination spheres around the other two oxy-

Table 4b. Selected interatomic distances (Å) for $Cs_{10}(CrO_4)_2O$ and $Cs_8In_2O_7$ at r. t. Standard deviations of the last digit are given in parentheses.

Atoms		Distance	Atoms		Distance	Atoms		Distance	Atoms		Distance
$Cs_{10}(CrO_4)_2O$											
Cr1	– O11	1.770(4)	Cs7	– O13	2.875(4)	O12	– Cs3	2.943(5)	O21	– Cs9	3.760(4)
	– O12	1.785(4)		– O14	3.041(5)		– Cs4	2.982(5)	O22	– Cr2	1.793(4)
	– O13	1.779(4)		– O22	2.934(5)		– Cs8	2.999(4)		– Cs3	3.719(4)
	– O14	1.775(4)		– O23	2.989(5)	O13	– Cr1	1.779(4)		– Cs5	3.150(5)
Cr2	– O21	1.760(4)		– O2	3.111(3)		– Cs1	3.041(4)		– Cs6	2.892(4)
	– O22	1.793(4)	Cs8	– O12	2.999(4)		– Cs2	3.193(4)		– Cs7	2.934(5)
	– O23	1.786(4)		– O21	2.936(4)		– Cs4	2.889(4)		– Cs9	3.199(5)
	– O24	1.772(4)		– O21	3.041(4)		– Cs5	3.154(5)		– Cs10	3.059(4)
Cs1	– O11	2.921(4)		– O23	3.079(5)		– Cs7	2.875(4)	O23	– Cr2	1.786(4)
	– O12	2.952(4)		– O24	3.369(5)	O14	– Cr1	1.775(4)		– Cs3	3.282(4)
	– O13	3.041(4)		– O2	3.246(3)		– Cs2	3.303(5)		– Cs6	2.936(4)
	– O1	3.127(9)	Cs9	– O11	3.199(4)		– Cs3	3.283(5)		– Cs7	2.989(5)
	– O1	4.033(10)		– O14	3.199(5)		– Cs3	3.305(5)		– Cs8	3.079(5)
	– O2	3.352(3)		– O22	3.200(5)		– Cs7	3.041(5)		– Cs10	2.930(4)
Cs2	– O11	3.100(5)		– O24	3.043(5)		– Cs9	3.299(5)	O24	– Cr2	1.772(4)
	– O11	3.469(5)		– O2	3.262(3)		– Cs10	2.811(4)		– Cs2	2.863(4)
	– O12	3.381(5)		– O2	3.478(3)	O21	– Cr2	1.760(4)		– Cs4	3.133(5)
	– O13	3.193(4)	Cs10	– O14	2.811(4)		– Cs3	3.492(4)		– Cs6	3.281(5)
	– O14	3.303(5)		– O22	3.059(4)		– Cs4	2.926(4)		– Cs8	3.369(5)
	– O24	2.863(4)		– O23	2.930(4)		– Cs5	2.951(4)		– Cs9	3.043(5)
	– O1	3.137(9)		– O24	3.197(5)		– Cs8	2.936(4)		– Cs10	3.197(5)
Cs3	– O12	2.943(5)		– O1	3.863(11)		– Cs8	3.041(4)			
	– O14	3.283(5)		– O2	3.720(3)	$Cs_8In_2O_7$					
	– O14	3.305(5)	O1	– Cs1	3.127(9)	In1	– O1	2.1139(7)	O1	– In1	2.1139(7)
	– O21	3.492(4)		– Cs2	3.137(9)		– O2	2.0640(7)		– Cs1	2.9616(7)
	– O22	3.719(4)		– Cs3	3.096(10)		– O3	2.0527(8)		– Cs3	3.0811(8)
	– O23	3.282(4)		– Cs5	3.177(10)		– O4	2.0456(8)	O2	– In1	2.064(7)
	– O1	3.096(10)		– Cs6	3.547(10)	Cs1	– O1	2.9616(7)		– Cs2	2.973(9)
Cs4	– O11	3.047(4)	O2	– Cs1	3.352(3)		– O3	2.910(9)		– Cs2	3.105(8)
	– O12	2.982(5)		– Cs5	3.176(3)		– O3	3.257(9)		– Cs3	2.890(8)
	– O13	2.889(4)		– Cs6	3.151(3)		– O4	3.006(9)		– Cs4	2.810(7)
	– O21	2.926(4)		– Cs7	3.111(3)		– O4	3.074(9)		– Cs4	2.992(9)
	– O24	3.133(5)		– Cs8	3.246(3)	Cs2	– O2	2.973(9)	O3	– In1	2.053(8)
Cs5	– O11	3.125(4)		– Cs9	3.262(3)		– O2	3.105(8)		– Cs1	2.910(9)
	– O13	3.154(5)		– Cs9	3.478(3)		– O3	2.966(8)		– Cs1	3.257(9)
	– O21	2.951(4)	O11	– Cr1	1.770(4)		– O3	3.776(9)		– Cs2	2.966(8)
	– O22	3.150(4)		– Cs1	2.921(4)		– O4	3.186(9)		– Cs2	3.776(9)
	– O1	3.177(10)		– Cs2	3.100(5)	Cs3	– O1	3.0811(8)		– Cs3	3.170(9)
	– O2	3.176(3)		– Cs2	3.469(5)		– O2	2.890(8)		– Cs4	2.949(9)
Cs6	– O22	2.892(4)		– Cs4	3.047(4)		– O3	3.170(9)	O4	– In1	2.046(8)
	– O23	2.936(4)		– Cs5	3.125(4)		– O4	3.079(9)		– Cs1	3.006(9)
	– O24	3.281(5)		– Cs9	3.199(4)	Cs4	– O2	2.810(7)		– Cs1	3.074(9)
	– O1	3.547(10)	O12	– Cr1	1.785(4)		– O2	2.992(9)		– Cs2	3.186(9)
	– O1	3.963(10)		– Cs1	2.952(4)		– O3	2.949(9)		– Cs3	3.079(9)
	– O2	3.151(3)		– Cs2	3.381(5)		– O4	2.955(8)		– Cs4	2.955(8)

gen atoms are enlarged including two longer O – Rb contacts (see Table 4a). The orthogallate anions are arranged in hexagonal nets forming a slightly distorted α-U packing [21] along the *b* axis of the orthorhombic unit cell (Fig. 5). This underlying topological relation of the anion packing is the reason for the ratio $c/a = 1.6937$ which deviates only 2 % from the ideal value of $\sqrt{3}$ expected for a packing of ideal hexagonal nets in the α-U structure type in orthohexagonal setting.

$Cs_8In_2O_7$ crystallizes with the $Cs_8Fe_2O_7$ structure type [22] and contains cesium cations and oxoindate(III) groups $[InO_4]$ which form dinuclear $[In_2O_7]^{8-}$ anions *via* sharing a common vertex. As one would expect, the interatomic In–O distances are longer to the bridging oxygen atom than to the ter-

Table 4c. Selected interatomic angles (deg) for the anions in $Rb_9(AlO_4)(OH)_4$, Rb_5GaO_4, $Cs_{10}(CrO_4)_2O$, and $Cs_8In_2O_7$ at r. t. Standard deviations of the last digit are given in parentheses.

Atoms	Angle	Atoms	Angle
$Rb_9(AlO_4)(OH)_4$			
O11 – Al1 – O12	110.1(3)	O12 – Al1 – O13	109.2(3)
O11 – Al1 – O13	107.6(2)	O12 – Al1 – O14	111.3(2)
O11 – Al1 – O14	108.8(2)	O13 – Al1 – O14	109.8(2)
Rb_5GaO_4			
O1 – Ga1 – O2	109.9(3)	O2 – Ga1 – O3	109.4(3)
O1 – Ga1 – O3	111.0(4)	O2 – Ga1 – O4	109.7(4)
O1 – Ga1 – O4	108.8(3)	O3 – Ga1 – O4	108.0(3)
$Cs_{10}(CrO_4)_2O$			
O11 – Cr1 – O12	110.1(2)	O12 – Cr1 – O13	108.2(2)
O11 – Cr1 – O13	108.0(2)	O12 – Cr1 – O14	111.4(2)
O11 – Cr1 – O14	108.8(2)	O13 – Cr1 – O14	110.2(2)
O21 – Cr2 – O22	108.1(2)	O22 – Cr2 – O23	110.0(2)
O21 – Cr2 – O23	110.3(2)	O22 – Cr2 – O24	107.7(2)
O21 – Cr2 – O24	111.1(2)	O23 – Cr2 – O24	109.6(2)
$Cs_8In_2O_7$			
O1 – In1 – O2	105.9(2)	O2 – In1 – O3	109.0(3)
O1 – In1 – O3	109.0(3)	O2 – In1 – O4	111.2(4)
O1 – In1 – O4	107.8(3)	O3 – In1 – O4	113.7(4)
In1 – O1 – In1	180		

minal oxygen atoms (211.39(7) pm *vs.* 204.56(8)–206.40(7) pm, see Table 4b). The terminal oxygen atoms of the diindate anion have a staggered conformation and are coordinated by one indium and five cesium atoms in a distorted octahedron. The bridging oxygen atom has two indium atoms and four cesium atoms as next neighbors (see Table 4b and Fig. 1). The cesium and indium atoms form slightly distorted hexagonal layers which are stacked in a triple hexagonal sequence …ABA′B′A″B″… (Fig. 4). The stacking direction of the layers is parallel to $[03\bar{5}]$ and [035]. This packing of the metal atoms results in *a* and *c* axes similar in their respective values and β close to 120°.

From single-crystal X-ray investigations at r. t. the diindate anions appear to be centrosymmetric with a linear In–O1–In arrangement and staggered terminal oxygen atoms O2, O3 and O4. This description is valid as far as it concerns the spatiotemporal average as observed by X-ray diffraction. However, a close observation of the structure at low temperatures shows that the diindate anion has to be described in a slightly bent configuration which at r. t. is averaged by either statistical disorder or vibrational motion around a central position. This can be derived from TLS analyses [16] in which the respective fractions of librational, rotational and translational motions of the anion are fitted against the thermal displacement parameters derived from sin-

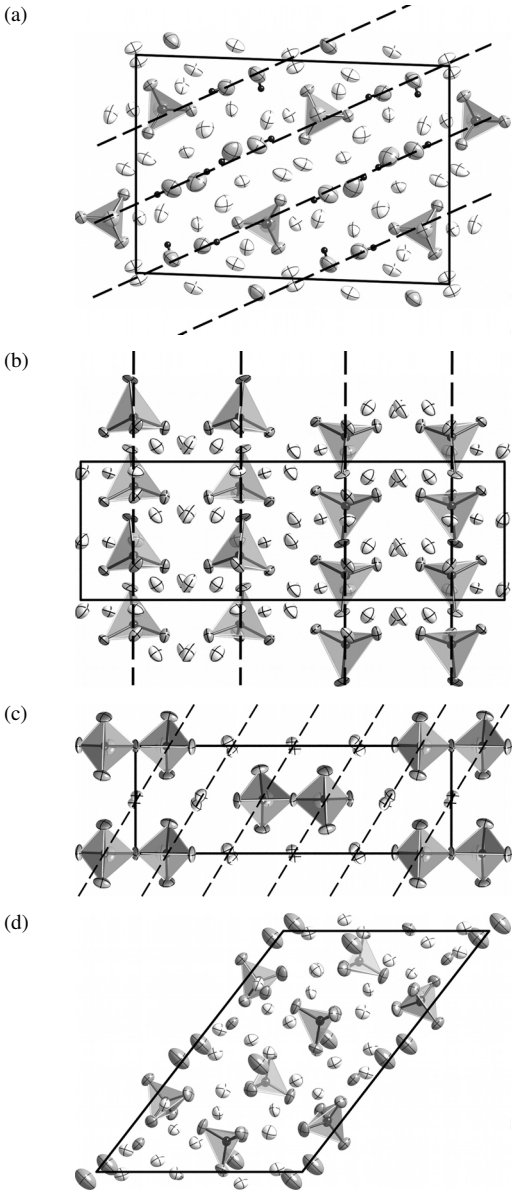


Fig. 2. (a) Projection of the unit cell of $Rb_9(AlO_4)(OH)_4$ along [100]. Dashed lines indicate the layers in which the orthoaluminate and the hydroxide anions are arranged. (b) The unit cell of Rb_5GaO_4 in a projection along [100] indicating the hexagonal layers formed by the $[GaO_4]^{5-}$ anions. (c) Projection of the unit cell of $Cs_8In_2O_7$ along [001]. The hexagonal close-packed layers of cesium and indium atoms are marked by dashed lines. (d) Projection of the unit cell of $Cs_{10}(CrO_4)_2O$ along [010]. For all figures the same encoding has been used: small black spheres depict hydrogen atoms in (a), dark-grey ellipsoids depict the metal atoms centering the $[MO_4]$ units, middle-gray ellipsoids represent oxygen atoms, and light-grey ellipsoids represent the alkali metal atoms. All ellipsoids are drawn at a 95 % probability level.

Table 5. Lattice parameters and R values for $Cs_8In_2O_7$ at different temperatures. Standard deviations of the last digit are given in parentheses.

Temperature, K	293.0(2)	243.0(2)	193.0(2)	143.0(2)	93.0(2)
a, Å	7.4287(6)	7.4221(6)	7.4102(6)	7.3994(6)	7.3911(6)
b, Å	18.6205(15)	18.6066(14)	18.6087(14)	18.6060(14)	18.6001(15)
c, Å	7.2620(6)	7.2514(6)	7.2380(6)	7.2257(6)	7.2153(6)
β, deg	119.228(8)	119.177(8)	119.150(8)	119.104(8)	119.081(8)
V, Å^3	876.63(12)	874.36(12)	871.67(12)	869.18(12)	866.88(12)
R_{int}	0.0467	0.0437	0.0334	0.0366	0.0319
R_σ	0.0309	0.0290	0.0237	0.0245	0.0210
$R1$ [$F_o^2 \geq 2\sigma(F_o^2)$]/$R1$ (all data)	0.0365/0.0448	0.0374/0.0448	0.0342/0.0405	0.0346/0.0397	0.0334/0.0373
$wR2$ [$F_o^2 \geq 2\sigma(F_o^2)$]/$wR2$ (all data)	0.0948/0.0963	0.0914/0.0927	0.0901/0.0911	0.0916/0.0925	0.0909/0.0916

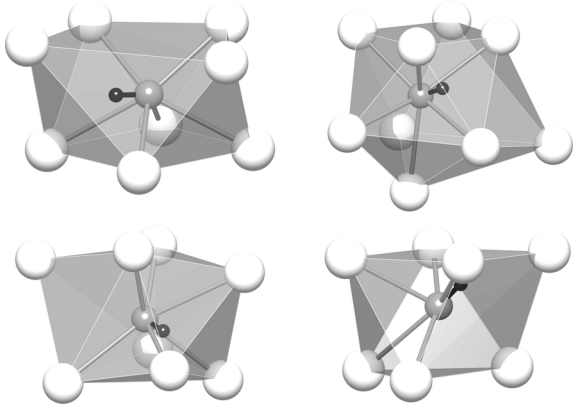


Fig. 3. Coordination of the four crystallographically independent hydroxide anions by Rb cations in $Rb_9(AlO_4)(OH)_4$ (upper left: O1, upper right O2, lower left: O3, lower right: O4). Hydrogen atoms are depicted by small black spheres, oxygen atoms by grey spheres and rubidium atoms by light-grey spheres. Rubidium atoms completing the coordination polyhedron with a long O–Rb distance (see also Table 4a) are not drawn connected to the oxygen atom.

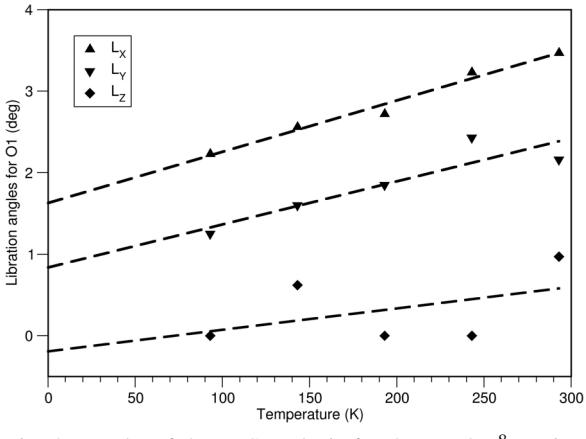


Fig. 4. Results of the TLS analysis for the $[In_2O_7]^{8-}$ anion in $Cs_8In_2O_7$ for various temperatures. The librational angle components L_x, L_y and L_z are shown *versus* the temperature of data collection.

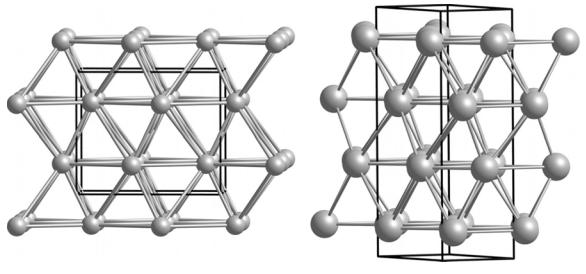


Fig. 5. Comparison of the structures of α-U (left) and the packing of the $[GaO_4]^{5-}$ anions in Rb_5GaO_4 (the spheres depict the positions of the Ga atoms).

gle crystal structure investigations at different temperatures (Fig. 4). The analysis of the librational angles of the motions of the anion shows that the contributions perpendicular to the In–O1–In axis (L_x and L_y) are significantly larger than the one parallel to it (L_z). At 0 K, L_x and L_y show a significant residual angle. Its maximum of about 1.6° at 0 K can be regarded as the "true" bonding angle of the anion.

No diindates $A_8In_2O_7$ are known for A = Li, Na, K or Rb. The only known digallate $Na_8Ga_2O_7$ shows clearly bent $[Ga_2O_7]^{8-}$ anions [23], as does the ferrate $Na_8Fe_2O_7$ [24]. The structures with larger cations all show linear anions. The linearity of the $[M_2O_7]^{n-}$ anion is an effect of cation size, as also can be observed in the structures of disilicates: $Li_6Si_2O_7$ [25] and $Ag_6Si_2O_7$ [26] show bent anions, whereas $A_6Si_2O_7$ with A = K, Rb, Cs [27, 28], $Hg_6Si_2O_7$ [29] and $Tl_6Si_2O_7$ [30] show linear disilicate groups. Many other examples can be found for this behavior throughout the structural chemistry of dimetallates $[M_2O_7]^{n-}$.

The new orthochromate(IV) $Cs_{10}(CrO_4)_2O$ crystallizes with the $Cs_{10}(GeO_4)_2O$ structure type [28]. Since Na_4CrO_4, Sr_2CrO_4 and Ba_2CrO_4 are the only simple orthochromates(IV) known so far [31 – 33], further in-

vestigations on the promising magnetic properties of the new compound are planned. The anion substructure consists of two crystallographically independent orthochromate anions $[CrO_4]^{4-}$ which deviate only slightly from ideal tetrahedral symmetry, and two isolated oxide anions. The $[CrO_4]^{4-}$ anions have the point symmetry 1 and exhibit Cr–O distances ranging from 1.760(4) to 1.793(4) Å with O–Cr–O angles in between 108.1(2) and 111.4(2)°. There is a small but significant difference between the structures of $Cs_{10}(CrO_4)_2O$ and $Cs_{10}(GeO_4)_2O$; all positions of the Cs and Cr *resp.* Ge atoms are identical within small error margins, and this also applies to the oxygen atoms common to the orthometallate anions. However, in $Cs_{10}(GeO_4)_2O$ the isolated oxygen atom fully occupies a special position, while in $Cs_{10}(CrO_4)_2O$ two underoccupied positions are found for its isolated oxygen atoms O1 and O2. The initially independent refinement of the occupation factors resulted in a sum of 1 within error margins for the occupation of both positions. Therefore they were coupled and restrained to give a chemically reasonable formula. The respective occupation factors were 0.73(1) for O1 and 0.27(1) for O2.

An underlying system of hexagonal close packed layers can be used neither for the cations nor for the anions in describing the structure of $Cs_{10}(CrO_4)_2O$. Although a layerwise arrangement of chromate anions together with the isolated oxide anions seems to be present (Fig. 2d), those layers do not correspond to the hexagonal arrangements described for the other structures.

The structural principle of an anionic substructure consisting of orthometallate and oxide anions is known from other oxide metallates, as for example $Ba_3(CrO_4)O$ [33], $Ba_3(FeO_4)O$ [34] or $Ba_3(SiO_4)O$ [35]. All of them represent combinations of large cations and small orthometallate anions. Formal substitution of Ba^{2+} by Cs^+ would lead to the hypothetical orthometallates Cs_4GeO_4 and Cs_4CrO_4 which are unknown, most likely due to a further decrease of the lattice energy. In the systems Li–Ge–O, and Ba–*M*–O with *M* = Si, Fe, Cr(IV) both the orthogermanate Li_4GeO_4 [36] *resp.* the orthometallates Ba_2MO_4 as well as the germanate oxide $Li_8(GeO_4)O_2$ [36] *resp.* the above-mentioned orthometallate oxides, have been described. Here the insertion of additional oxide anions is obviously unnecessary for generating a stable ionic structure, but probably favorable in order to increase the lattice energy.

Summary

The synthesis of alkali metal oxometallates starting from suboxometallates is a promising new route towards crystalline materials with high metal content and low-dimensional anionic substructures. Here we have presented only structures based on tetrahedral $[MO_4]$ building units. However, we have also encountered a series of other structures, *e. g.* examples of oxometallates containing trigonal planar $[MO_3]^{n-}$ anions (Cs_3BO_3, Cs_4ZnO_3, Cs_4FeO_3). Their crystal structures will be presented in a future publication.

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