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High-Pressure Synthesis and Structure Determination of $K_6(SeO_4)(SeO_5)$, the First Potassium Orthoselenate(VI)

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We report on the first synthesis of a potassium orthoselenate(VI), $K_6(SeO_4)(SeO_5)$, and the structure determination from synchrotron powder diffraction data. The title compound crystallizes in the tetragonal space group $P4_12_12$ with $a = 8.1259(1)$ Å, $c = 17.4953(2)$ Å, $V = 1155.21(2)$ Å^3, and $Z = 4$. Selenium displays two different complex anions, tetrahedral SeO_4^{2-} and trigonal-bipyramidal SeO_5^{4-}. When the formula is reduced to A_3B, the spatial arrangement of the constituting building units can be derived from the Li_3Bi type of structure.

Introduction

Besides the preferred coordination, the highest possible coordination numbers (CNs) of an element constitute an important fingerprint, e.g., characterizing the span of its structural flexibility. In particular, variations in the CNs have significant consequences for the chemical bonds involved in terms of hybridization or ionicity, and they influence the electronic structures and mechanical properties of the respective materials. Historically, this issue has been addressed primarily in the context of main-group oxoanions. The option exercised has been to expand the coordination of the central nonmetal, mostly in its highest oxidation state, by adding one or more additional oxide ions, in an acid−base reaction. The resulting complex anions, which are richer in oxygen than the genuine anions, are commonly addressed as orthoanions. Prominent examples are Na_3NO_3 and Na_3NO_4, which were both understood to contain the orthoanions NO_3^{3-} and NO_4^{3-}.[1] However, more recent structure investigations have shown the nitrite family A_3NO_3 (A = Na, K, Rb, Cs) to be oxide nitrites, forming a perovskite type of structure, still containing the conventional NO_2^- anion in rotational disorder.[2] In contrast, the nitrates A_3NO_4 (A = Na, K, Rb, Cs) are true orthosalts with the exotic tetrahedral NO_4^{3-} anions as constitutive units.[3] Obvious candidates for extending this still small family would be the carbonates and borates. However, even upon application of elevated hydrostatic pressure during synthesis, which would favor the formation of a higher coordination, all of our attempts to synthesize the respective orthosalts have failed, so far. However, it has been possible, on the other hand, to attach a fluoride to carbonate, producing CO_3F^-, which is isoelectronic to the orthocarbonate anion.[4] In their oxoanions, the nonmetal elements of the third and fourth period prefer a tetrahedral coordination, which is thermodynamically as well as kinetically rather stable. Because the alacrity to expand the coordination sphere grows with the size of the central atom, we regarded nonmetals of the fourth period to be amenable to adding one or two oxide ions to their tetrahedral oxoanions. Indeed, recently first examples of penta- and hexaoxoselenates(VI) have been realized. With the present knowledge, it is difficult to classify or even understand the resulting compositions and structures: Li_4SeO_5 forms upon reacting Li_2O and Li_2SeO_4 at ambient pressure and contains selenium in trigonal-bipyramidal coordination,[5] while the synthesis of Na_4SeO_5[6] with selenium in a square-pyramidal coordination requires hydrostatic pressure of 2.5 GPa. Finally, $Na_{12}(SeO_6)(SeO_4)_3$ contains an octahedral oxoanion and is accessible at ambient pressure.[7] As a prerequisite for

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being able to rationalize the general underlying principles governing the synthesis conditions, the compositions, and the structures of the orthoselenates, the empirical knowledge needs to be broadened. Therefore, we have included the system K_2O/K_2SeO_4 in our investigations. In this paper, we report on a new potassium selenate, obtained through high-pressure synthesis.

Experimental Details

Synthesis. $K_6Se_2O_9$ was synthesized by solid-state reaction of a molar mixture (1:1) of K_2O and K_2SeO_4 in welded gold ampules ($\varnothing = 4$ mm), applying an elevated hydrostatic pressure. The starting material of K_2SeO_4 was dried before use under vacuum at a temperature of $T = 200$ °C for 2 days and was handled in a glovebox with an atmosphere of dry argon. K_2O was prepared as described elsewhere.[8] The sealed gold ampules with the starting mixture were placed in a modified piston−cylinder press[9] and were subjected to a pressure of 2 GPa and a temperature of 625 °C for 3 days. After the reaction time, the samples were quenched to room temperature by switching off the power, followed by pressure release. The reaction product is a pallid-colored crystalline powder that is very sensitive to air and moisture.

X-ray Powder Diffraction and Crystal Structure Determination. High-resolution X-ray powder diffraction data of $K_6Se_2O_9$ were collected at ambient conditions on the beamline X3B1 of the Brookhaven National Synchrotron Light Source (NSLS) in transmission geometry with the sample sealed in a lithium borate glass capillary of 0.3-mm diameter (Hilgenberg glass no. 50). X-rays of wavelength 0.65 Å were selected by a double Si(111) monochromator. Wavelengths and the zero point were determined from eight well-defined reflections of the NBS1976 flat-plate alumina standard. The diffracted beam was analyzed with a Ge(111) crystal and detected with a Na(Tl)I scintillation counter employing a pulse height discriminator in the counting chain. The incoming beam was monitored by an ion chamber for normalization purposes in order to take the decay of the primary beam into account. In this parallel-beam configuration, the resolution is determined by the analyzer crystal instead of slits.[10] Data were taken in steps of 0.003° 2Θ from 4.0 to 44.0° 2Θ for 3.0 s (Table 1). The sample was spun during measurement for better particle statistics. The powder pattern of $K_6Se_2O_9$ exhibits several peaks of very small amounts ($<0.5\%$) of an unknown impurity phase.

Indexing with ITO[11] and TREOR[12] led to a tetragonal unit cell for $K_6Se_2O_9$. A list of probable space groups was determined by the algorithm of Markvardsen et al.,[13] using a probabilistic approach as implemented in the global optimization program DASH.[14] The correct space group $P4_12_12$, which was later confirmed during the structure determination process, was ranked no. 5 in the list given by DASH. The lattice parameters, along with all relevant crystallographic data of $K_6Se_2O_9$, are given in Table 1. The number of formula units per unit cell were determined to be $Z = 4$ from volume increments. The peak profiles and precise lattice parameters were determined by LeBail-type fits[15] using the programs *GSAS* and *EXPGUI*.[16,17] The background was picked manually using *EXPGUI*.[17] The peak profile was described by a pseudo-Voigt function in combination with a special function that accounts for the asymmetry due to axial divergence.[18,19] A small anisotropy of the peak widths was observed that could be modeled by the phenomenological microstrain model from Stephens[20] as implemented in *GSAS*.

Table 1. Crystallographic Data for $K_6Se_2O_9$

empirical formula	$K_6Se_2O_9$
space group	$P4_12_12$ (No. 92)
cell parameters [Å]	$a = 8.1259(1)$ $c = 17.4953(2)$
cell volume V [Å^3]	1155.21(2)
Z	4
T [K]	295
fw [g/mol]	536.504
ρ_{calc} [g/cm^3]	3.085
wavelength/λ [Å]	0.648 95
measured range [deg], step width [deg 2θ]	$4 \leq 2\theta \leq 44$, 0.003
capillary diameter [mm]	0.3
absorption [cm^{-1}]	65.5
no. of reflections	567
no. of refined parameters	41
R_p [%]^a	7.51
R_{wp} [%]^a	9.72
$R(F^2)$ [%]^a	7.96

^{a} R_p, R_{wp}, and $R(F^2)$ as defined in *GSAS*.[24]

Crystal structure determination of $K_6Se_2O_9$ using the DASH program in different space groups did not converge to a successful solution. Therefore, the peak intensity versus 2Θ data as obtained from the LeBail fit using *GSAS* were subjected to the structure determination program ENDEAVOUR,[21] combining global optimization of the difference between the calculated and measured diffraction patterns and of the potential energy of the system. A promising solution was exclusively found in space group $P4_12_12$. Typical run times for each space group were on the order of 24 h on a standard personal computer.

A Rietveld refinement[22] using the program package *GSAS* (Figure 1) converged quickly using the atomic coordinates given by ENDEAVOUR as starting parameters. Slack soft constraints for the Se−O distances were introduced to stabilize the refinements. Agreement factors (R values) are given in Table 1 and the atomic coordinates in Table 2. A selection of intra- and intermolecular distances and angles is given in Table 3.

Results

$K_6Se_2O_9$, the first potassium orthoselenate(VI), was obtained by reacting K_2O and K_2SeO_4 in a sealed gold ampule,

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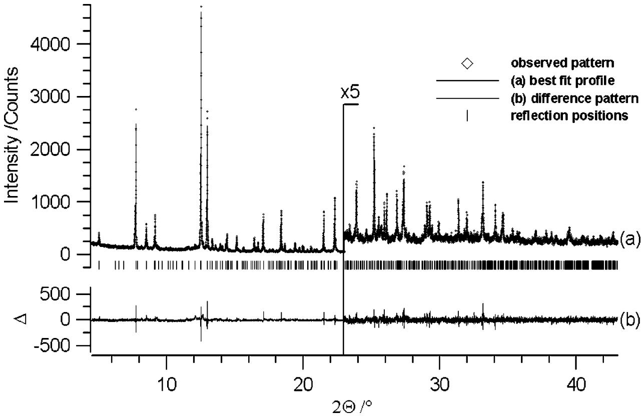

Figure 1. Scattered X-ray intensities for the high-pressure phase of $K_6Se_2O_9$ at ambient conditions as a function of diffraction angle 2Θ. Shown are the observed patterns (diamonds), the best Rietveld-fit profiles (line), and the enlarged difference curve between observed and calculated profiles (below in an additional window). The high-angle part starting a 23° 2Θ is enlarged for clarity.

Table 2. Atomic Positions and Thermal Parameters of $K_6Se_2O_9$

atom	Wyckoff	*x*/*a*	*y*/*b*	*z*/*c*	*U* [Å^2]
Se(1)	4a	0.2381(3)	0.2381(3)	0	0.002(1)
Se(2)	4a	0.2530(3)	0.2530(3)	$^1/_2$	0.002(1)
K(1)	8b	−0.0032(9)	0.4760(9)	0.3731(7)	0.017(1)
K(2)	8b	0.2225(6)	0.2120(6)	0.2455(3)	0.022(1)
K(3)	8b	−0.0013(6)	0.0419(8)	0.3957(2)	0.012(2)
O(1)	8b	0.2597(2)	0.0384(6)	0.0132(9)	0.028(4)
O(2)	8b	0.2973(2)	0.3349(2)	0.0771(5)	0.065(6)
O(3)	8b	0.2558(2)	0.2556(2)	0.3993(2)	0.009(3)
O(4)	8b	0.0581(5)	0.3069(1)	0.4985(1)	0.011(4)
O(5)	4a	0.6047(6)	0.6047(6)	0	0.022(5)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $K_6Se_2O_9$

Se(1)−O(2)	1.634(4) (2×)	K(1)−O(4)	2.636(23)
Se(1)−O(1)	1.649(4) (2×)	K(1)−O(4)	2.685(22)
		K(1)−O(3)	2.744(20)
Se(2)−O(5)	1.636(6)	K(1)−O(3)	2.801(20)
Se(2)−O(4)	1.643(4) (2×)	K(1)−O(1)	2.940(15)
Se(2)−O(3)	1.763(5) (2×)	K(1)−O(2)	3.055(19)
		K(1)−O(1)	3.141(20)
O(2)−Se(1)−O(2)	113.5(5)	K(1)−O(2)	3.379(20)
O(2)−Se(1)−O(1)	109.0(6)		
O(2)−Se(1)−O(1)	110.8(6)	K(2)−O(1)	2.661(7)
O(2)−Se(1)−O(1)	110.8(7)	K(2)−O(3)	2.727(8)
O(2)−Se(1)−O(1)	109.0(8)	K(2)−O(4)	2.733(7)
O(1)−Se(1)−O(1)	103.3(5)	K(2)−O(5)	2.799(7)
		K(2)−O(2)	3.170(12)
O(5)−Se(2)−O(4)	119.5(3)	K(2)−O(2)	3.321(16)
O(5)−Se(2)−O(4)	119.5(2)		
O(5)−Se(2)−O(3)	89.0(6) (2×)	K(3)−O(2)	2.687(17)
O(4)−Se(2)−O(4)	121.0(3)	K(3)−O(3)	2.687(18)
O(4)−Se(2)−O(3)	91.4(10) (2×)	K(3)−O(3)	2.717(19)
O(4)−Se(2)−O(3)	89.6(10) (2×)	K(3)−O(5)	2.732(41)
O(3)−Se(2)−O(3)	177.9(2)	K(3)−O(4)	2.847(17)
		K(3)−O(1)	2.938(11)
		K(3)−O(1)	3.011(18)
		K(3)−O(4)	3.117(15)

applying an elevated hydrostatic pressure. According to the formula $K_6(SeO_4)(SeO_5)$, the constituting building units are potassium cations and two different types of complex oxoselenate(VI) anions. SeO_4^{2-} is the anion normally encountered in selenates, and the averages of bond lengths and bond angles correspond well with the literature data.[23] In $K_6(SeO_4)(SeO_5)$, there is the second realization of a pentaoxoselenate anion SeO_5^{4-} in the shape of a trigonal bipyramid (see Figure 2). In comparison with Li_4SeO_5, the SeO_5^{4-} anion in $K_6Se_2O_9$ has virtually the same intrinsic geometry. It contains slightly shorter bonds in apical as well as axial directions, and this results also in a shorter mean Se−O bond distance of 1.69(1) Å compared to 1.74(1) Å in the corresponding lithium compound. The bond length difference between the apical and axial Se−O bonds is about 7.0%, while it is 4.9% in Li_4SeO_5. Also the bond angles in the title compound show a slightly larger deviation from an ideal trigonal bipyramid than those in the lithium oxoselenate(VI). Within the margins of plus/minus estimated standard deviations, these differences in the bond lengths are regarded as significant. We attribute them to the stronger polarization as effected by the lithium cation in comparison to the potassium cation and to the well-balanced $A^{[5]}B^{[5]}$ structure variant[5] adopted by Li_4SeO_5. The CN for the potassium atom K(2) is 6, and for K(1) and K(3), it is 8. The K−O bond lengths are in the range between 2.64(2) and 3.38(2) Å.

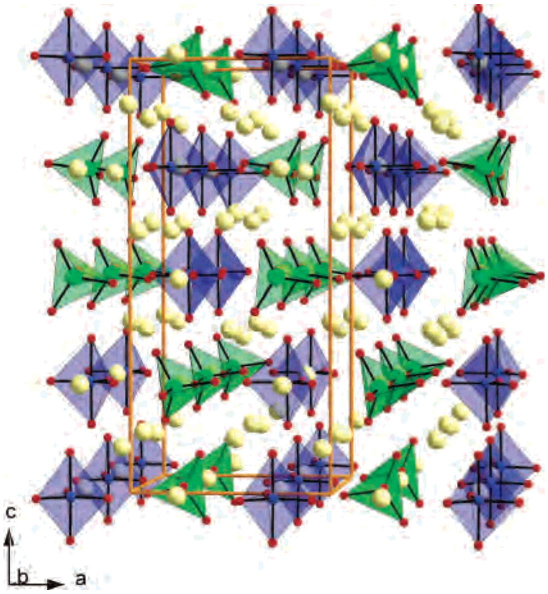

Figure 2. Crystal structure of $K_6Se_2O_9$ viewed along [010]. The trigonal-bipyramidal coordination around selenium(6+) is shown in blue, and the tetrahedral coordination for selenium(6+) is in green. Potassium atoms are shown in light yellow.

With regards to the overall arrangement of potassium, tetraoxoselenate, and pentaoxoselenate, $K_6Se_2O_9$ belongs to the rather extended family of inorganic A_3B-type structures for which Li_3Bi[24] may be considered the aristotype. Typical representatives are Na_3PO_4,[25] Na_3AlF_6,[26] and Na_3OsO_5.[27] All of these compounds are based on a cubic closed packing (ccp) of the complex anions with all tetrahedral and octahedral voids occupied by the alkali ions. The space group

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of highest possible symmetry, $Fm\bar{3}m$, has been found for Li_3Bi. Symmetry reduction occurs for several reasons: in the case of $K_6(SeO_4)(SeO_5)$ because two types of anions are present, among others. An analogous structural arrangement is found in the compound $Rb_6(TeO_4)(TeO_5)$,[28] which crystallizes in the monoclinic space group $C2/c$ (No. 15). It can also be described as a ccp-type packing of the anions with all tetrahedral and octahedral voids filled with rubidium but with the TeO_4 and TeO_5 polyhedra having orientations different from the ones found in $K_6Se_2O_9$. Because of this feature, the two structures cannot be related to each other by any group–subgroup relation. However, if the oxygen atoms are disregarded and only the alkali-metal, selenium, and tellurium atoms, respectively, are taken into account, it is possible to relate the structures to each other. Nevertheless, no direct group–subgroup relation between the tetragonal space group $P4_12_12$ for the potassium selenate and the monoclinic group $C2/c$ for the rubidium tellurate does exist. The most likely transition path between these space groups is through the common supergroup of $I4_1/amd$. The possible transition path with minimal non-isomorphic supergroups would be $P4_12_12 \rightarrow I4_122 \rightarrow I4_1/amd \leftarrow I4_1/a$, $Imma \leftarrow C2/c$.

Calculations of the Madelung part of lattice energy (MAPLE)[29] are for identical ions of comparable magnitude and in the expected range (Table 4). The overall Coulomb part of the lattice energy for $K_6Se_2O_9$ (63 859 kJ/mol) matches very well with the sum (63 079 kJ/mol) of the lattice energies for the educts K_2O (2511 kJ/mol) and K_2SeO_4 (2 × 30 284 kJ/mol).

Discussion

Considering the small number of alkali orthoselenates(VI) known to date, the richness in compositional and topological variety is amazing. Three different types of oxoselenate anions with CNs exceeding 4 have been observed: SeO_5^{4-} with trigonal-bipyramidal as well as square-pyramidal coordination geometries and octahedral SeO_6^{6-}. In terms of our energy landscape concept of chemical compounds,[30] the many structural and compositional degrees of freedom are corresponding to a great multitude of local minima for the class of alkali-metal orthoselenates, i.e., a rich variety of possible compounds. In a qualitative sense, the compositions, structures, and synthesis conditions of the thus far realized orthoselenates seem to mainly depend on whether some overriding structural principles are contributing to the stability of the phases obtained. The latter might apply to Li_4SeO_5, related to a binary $A^{[5]}B^{[5]}$ structure type[5] and to $Na_{12}(SeO_6)(SeO_4)_3$,[6] which can be derived from the Mo_6Cl_{12} structure. The synthesis of neither of these selenates(VI) requires high-pressure conditions.

Table 4. Madelung Part of the Lattice Energy for $K_6Se_2O_9$

	charge	PMF	MAPLE
Se(1)	+6	20.84	4228.6
Se(2)	+6	22.54	4572.5
K(1)	+1	0.603	122.4
K(2)	+1	0.625	126.9
K(3)	+1	0.628	127.4
O(1)	−2	3.304	669.8
O(2)	−2	3.353	681.0
O(3)	−2	2.737	555.1
O(4)	−2	3.110	631.1
O(5)	−2	3.085	627.0
			$\Sigma = 63\,859$ kJ/mol

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Supporting Information Available: X-ray crystallographic data and figure of coordination of the crystallographically independent potassium ions. This material is available free of charge via the Internet at http://pubs.acs.org.

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