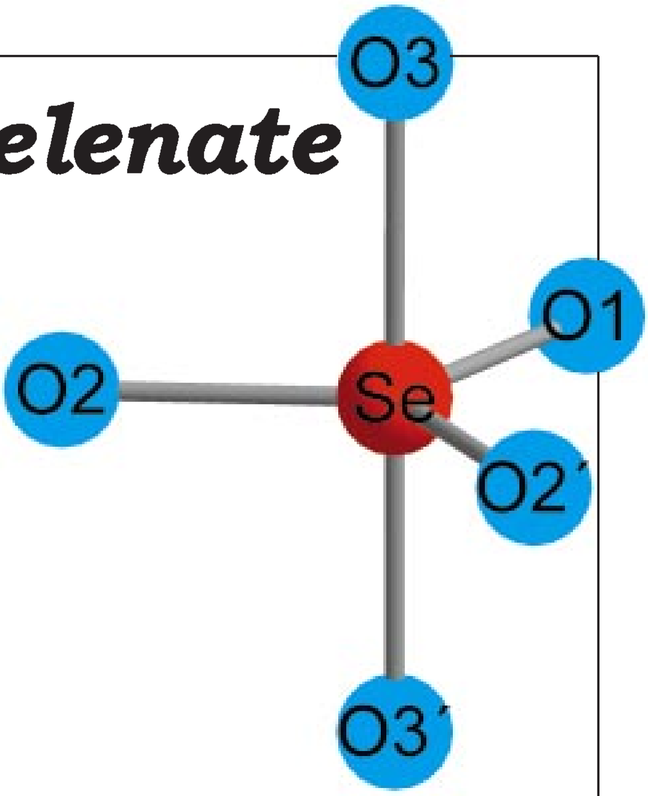
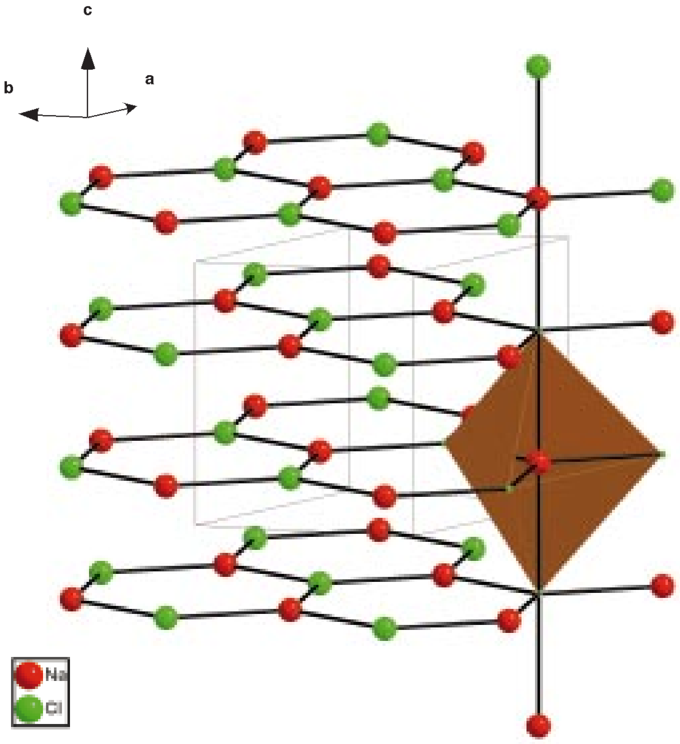
Lithium orthoselenate

The first orthoselenate contains novel trigonal-bipyramidal complex anions.



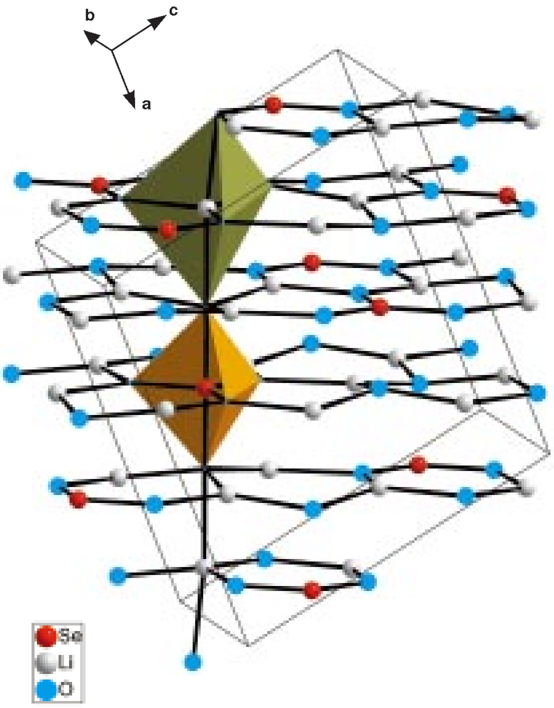
It crystallizes as an order variant of a theoretically predicted AB structure ...



theoretically predicted AB structure

More about this on the following pages.

... in which the cations and anions are equally coordinated as $A^{[5]}B^{[5]}$.



lithium orthoselenate

Li_4SeO_5, the First Orthoselenate, Crystallizes as an Order Variant of a Theoretically Predicted $A^{[5]}B^{[5]}$ Structure Type**

Helmut Haas and Martin Jansen*

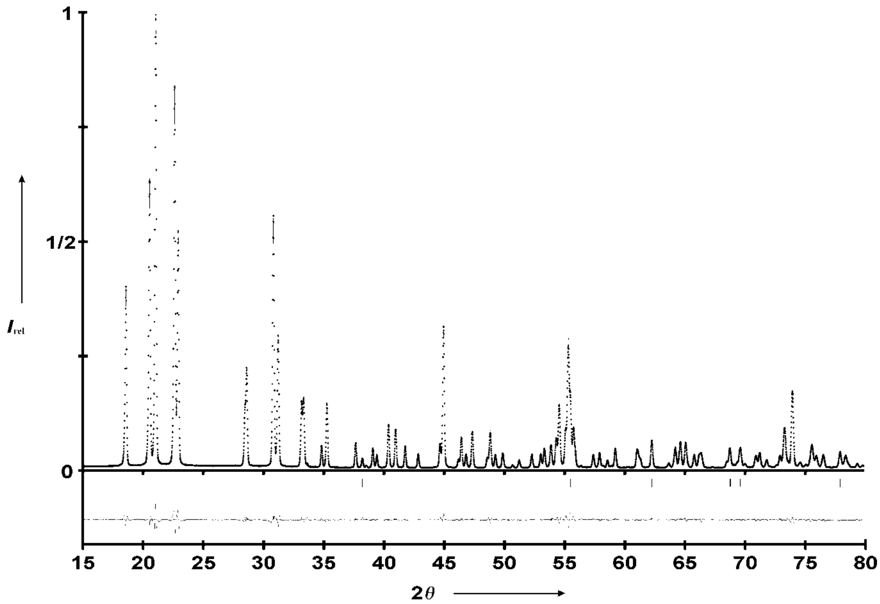


Figure 1. Powder diffraction diagram of Li_4SeO_5. Top: measured (data points) and calculated intensities (solid line), bottom: difference plot.

Addition of water to nonmetal oxides results in the formation of oxoacids. The most water-rich form of an oxoacid and the anion derived from it are described by the prefix *ortho*. The maximum possible number of constituent water molecules is only found in the case of boron and tellurium, however. Even H_4CO_4 or H_4SiO_4 are unstable to intra- or intermolecular cleavage of water. In the case of fully deprotonated oxoanions, solid-state reaction with strong oxide bases provides access to further orthoanions, which are then only stable in the crystalline state. The most well known examples are the alkali metal orthonitrates.[1] Although the existence of orthoesters does not guarantee that the corresponding orthoanions can also be prepared—the $C(OR)_4/CO_4^{4-}$ pair confirms this—we have taken the existence of esters[2] of the hypothetical orthoselenium acid, H_6SeO_6, as an incentive to attempt the synthesis of an orthoselenate. With this goal, we have systematically worked through the quasi-binary system Li_2O/Li_2SeO_4, initially under high isotactic pressures (piston-cylinder press).[3] We discovered that a new phase is indeed formed, however, with the surprising Li_2O:Li_2SeO_4 ratio of 1:1 instead of the initially sought 2:1 product ("Li_6SeO_6"). We subsequently established that, under suitable temperature conditions, the new phase can also be formed under normal pressure. The colorless samples are only slightly sensitive to moisture and CO_2.

Since all attempts to grow single crystals failed, the ab initio crystal structure was determined from powder intensities and refined by profile fitting of the powder diffraction diagram[4, 5] (Figure 1). The structure analysis revealed that the compound was indeed an orthoselenate,[6] with the composition Li_4SeO_5. The selenium atom is coordinated in a trigonal-bipyramidal fashion by oxygen atoms (Figure 2). Since the bonding arrangement is without precedence, there are no comparable data to assess the Se–O bond lengths. It is clear, however, that the increase in the mean Se–O bond length of 6.7 %, which results from the increase in the coordination number from four (SeO_4^{2-}) to five, lies within the expected range. Despite integration into the crystal structure and the low site symmetry 2, the dimensions of the SeO_5^{4-} anion are remarkably regular. It displays, within the margins of error of the structure determination, the point symmetry $\bar{6}2m$ (D_{3h}). The trigonal bipyramid is one of the coordination polyhedra in which the ligands cannot form bonds of equal length to the central atom and to each other. The compromise between these mutually exclusive requirements results, in this case, in an increase in the distance to the axial ligands (+4.9 %, for comparison, in PF_5:[7] +3.8 %). The lithium and oxygen atoms also show trigonal-bipyramidal coordination (Figures 2 and 3). The mean Li–O distances of 204.6 (Li1) and 200.5 pm (Li2) lie between the typical values for tetrahedral and octahedrally coordinated lithium (196.3 and 212.5 pm, respectively). The coordination polyhedra around lithium are very distorted with respect to bond angles and distances (Figure 2; maximum deviation from the mean value and the ideal value: 12.8 pm and 12.9°). In the case of oxygen, the bond distances and angles (Figure 2) are dispersed over a

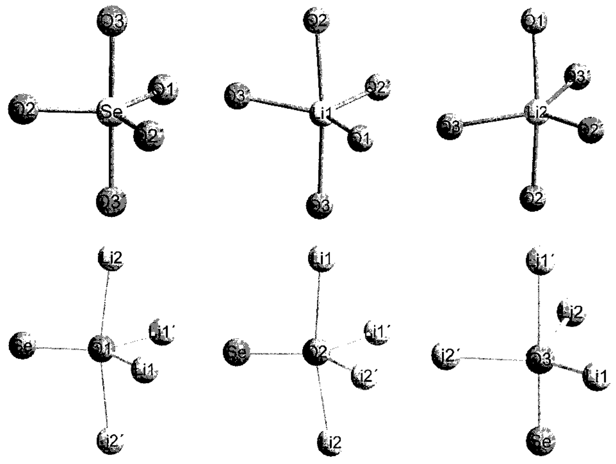


Figure 2. Coordination polyhedra in the crystal structureof Li_4SeO_5. Selected bond lengths [pm] and angles [°]: Se–O1 172.0(2), Se–O2 170.6(1) 2 ×, Se–O3 179.5(1) 2 ×; O1-Se-O2 120.4(2) 2 ×, O1-Se-O3 89.9(1), O2-Se-O2′ 119.1(1), O2-Se-O3 90.1(1), O2′-Se-O3′ 90.1(1), O2-Se-O3′ 90.0(1), O2′-Se-O3 90.0(1), O3-Se-O3′ 179.8(1).

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comparable range. All deformations can be explained by the strong variation in the cation valences. The corresponding compensation in the bond distances can be quantitatively understood on the basis of bond length/bond strength relationships.[8] The valence sums determined (Li1: 1.07, Li2: 1.19, Se: 5.65, O1: 2.07, O2: 2.06, O3: 1.98) lie within the acceptable tolerances of the expected values of 1, 6, and 2.

From the empirical formula and the coordination environments described above, it is clear that this is an order variant of an AB structure, in which the cations and anions are equally coordinated as $A^{[5]}B^{[5]}$ (Figure 3). The aristotype[9, 10] of Li_4SeO_5 can be regarded as a counterpart to the conventional sodium chloride structure ($A^{[6]}B^{[6]}$). This new structure type was first discovered as one of the viable modifications during an investigation of the energy landscape of NaCl (Figure 4).[11] To our knowledge, this is the first example of a virtually ab initio predicted structure type, which was then experimentally realized.

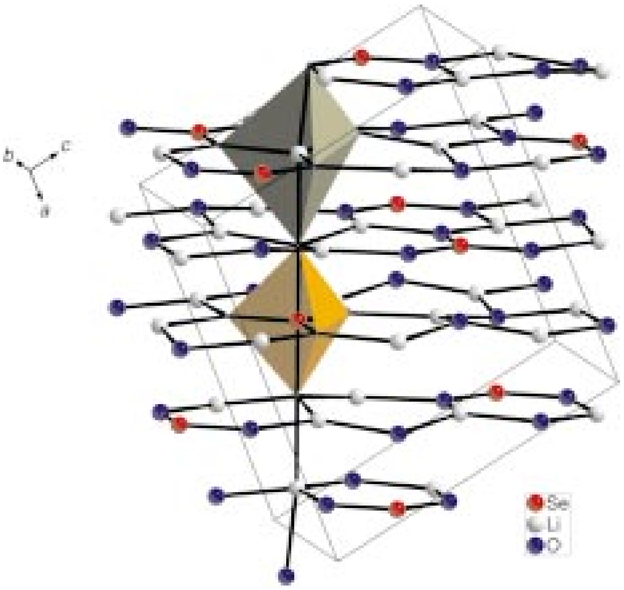

Figure 3. Crystal structure of Li_4SeO_5 (the layer motif is repeated after every tenth layer).

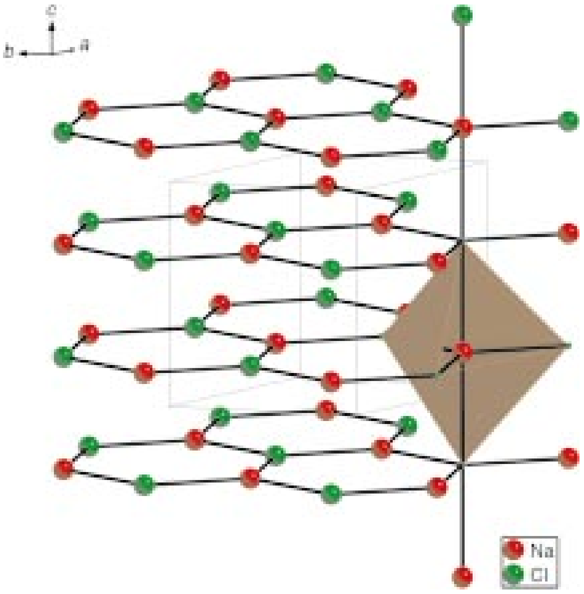

Figure 4. Hypothetical structure of $Na^{[5]}Cl^{[5]}$.

Experimental Section

Li_4SeO_5 was prepared from the solid-state reaction of Li_2O and Li_2SeO_4 in closed silver crucibles which were sealed in glass ampoules. The reaction time was two days, and the reaction temperature was 500 °C. Li_2O was produced by dehydration of LiOH, and Li_2SeO_4[12] by the reaction of Li_2CO_3 with H_2SeO_4. H_2SeO_4 was obtained by oxidation of SeO_2 with H_2O_2 under an oxygen atmosphere.[13]

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[5] X-ray crystal structure analysis of Li_4SeO_5: space group *C*2/*c*; $a = 873.29(10)$, $b = 572.49(10)$, $c = 783.57(10)$ pm, $\beta = 98.29(1)°$, $V = 387.65(9) \times 10^6\ pm^3$; $Z = 4$, $\rho_{calcd} = 3.199\ g\,cm^{-3}$; Stoe-Stadi-P transmission powder diffractometer, $Cu_{K\alpha 1}$ radiation, germanium monochromator, linear position-sensitive detector (Stoe-Mini-PSD), capillary measurement, 7500 data points, measurement range: $5 < 2\theta < 90°$, total measurement time: 15 h, 120 observed reflections, 14 refined positional parameters, 6 temperature parameters, Rietveld refinement: $R_{wp} = 6.60$, $R_i = 1.79$, GOF = 3.0. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-410714.

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