Crystal structure of lithium disulfate, Li₂[S₂O₇], Li₂O₇S₂

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Abstract
Li₂O₇S₂, orthorhombic, Pnma (no. 62), a = 13.177(2) Å, b = 8.2516(7) Å, c = 4.8547(4) Å, V = 527.8 Å³, Z = 4, Rgt(F) = 0.0338, wRref(F²) = 0.1054, T = 153 K.

Source of material
Li₂[S₂O₇] has been prepared by reaction of Li₂SO₄ (98+ %, 30 mg) and Oleum (65 % SO₃, 1 ml) in CCl₄. The reaction was performed in a thick-walled glass ampoule. The tube was loaded with the reactants, torch-sealed under vacuum and placed in a resistance furnace. The ampoule was held at a temperature of 250 °C for 24 h and cooled down to room temperature at a rate of 1.8 °C·h⁻¹. After that a number of colourless single crystals could be obtained.

Experimental details
The structure could be successfully solved using Direct Methods of SHELXS [1]. The structure was expanded using Fourier techniques. Refinement of the structure with anisotropic displacement parameters for all atoms was performed after the data were corrected for absorption effects. All calculations were performed with the SHELX program [1] and the data were processed with the programs X-RED [2] and X-Shape [3].

Discussion
One of the main research projects of our working group is the investigation of the reactivity of sulfuric acid and its derivatives under harsh conditions. Milestones of this research were the preparation of gold(II)sulfate Au₂(SO₄)₂ [5], the oxidation of elemental platinum with H₂SO₄ yielding Pt₂(HSO₄)₂(SO₄)₂ [6] and the unique cluster anion [Pt₉O₄(SO₄)₄]²⁻ [7]. Reactions with fuming sulfuric acid resulted in the first molecular disulfate Re₂O₄Cl₂(S₂O₇) [8], the gold disulfates M[Au(S₂O₇)₂] [9], and the trisulfate Pb[S₃O₁₀] [10]. The application of neat SO₃ as a reactant resulted in Pd(S₂O₇) [11] and (NO₂)₂[S₄O₁₃], representing the first crystal structure of a tetrasulfate [12]. Crystallographic data of disulfates for a number of alkali sulfates has already been presented, namely Na₂[S₂O₇] [13], K₂[S₂O₇] [14], Cs₂[S₂O₇] [15], and the ternary phase NaK[S₂O₇] [13]. We were now able to prepare a new member of the alkali polysulfate family, Li₂[S₂O₇]. Li₂[S₂O₇] crystallizes in the orthorhombic space group Pnma with 4 formula units per unit cell. In this compound the lithium cations are coordinated by disulfate anions to form a complex three-dimensional structure (Fig. top). The disulfate anion shows perfect ecliptic conformation with an O–S–S–O torsion angle of 0° and terminal S–O bond lengths ranging from 143.7(2) to 145.2(2) pm. The bridging S–O–S bonds show asymmetric behaviour with bond lengths of 161.0(2) and 166.7(2) pm. The lithium ion is in an unusual coordination of five oxygen atoms, forming a [LiO₅] trigonal bipyramide with Li–O distances ranging from 194.7(4) to 213.3(4) pm (Fig. bottom). This kind of coordination has also been described by Jansen et al. for Li₄SeO₅ [16]. Li₂SO₄ for example shows tetrahedral oxygen coordination with Li–O distances ranging from 191 to 198 pm [17].
Acknowledgments. The author thanks Dipl.-Chem. Wolfgang Saak for the collection of the X-ray Data.

References


Table 2. Atomic coordinates and anisotropic displacement parameters (in Å²).

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