Crystal structure of lithium disulfate, $Li_2[S_2O_7]$, $Li_2O_7S_2$

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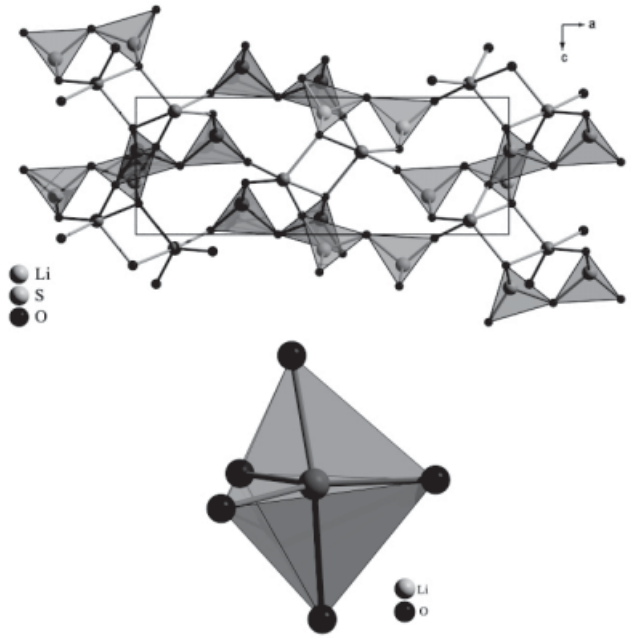
Received February 19, 2013, accepted February 20, 2013, available online March 01, 2013, CSD no. 710087



Abstract

$Li_2O_7S_2$, orthorhombic, *Pnma* (no. 62), $a = 13.177(2)$ Å, $b = 8.2516(7)$ Å, $c = 4.8547(4)$ Å, $V = 527.8$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0338$, $wR_{ref}(F^2) = 0.1054$, $T = 153$ K.

Table 1. Data collection and handling.

Crystal:	colourless plates, size 0.19×0.30×0.49 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	9.82 cm^{-1}
Diffractometer, scan mode:	IPDS, Stoe & Cie, φ
$2\theta_{max}$:	56.42°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6216, 656
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 592
$N(param)_{refined}$:	58
Programs:	SHELX [1], X-RED[2], X-SHAPE[3], DIAMOND [4]

Source of material

$Li_2[S_2O_7]$ has been prepared by reaction of Li_2SO_4 (98+ %, 30 mg) and Oleum (65 % SO_3, 1 ml) in CCl_4. 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 $Au_2(SO_4)_2$ [5], the oxidation of elemental platinum with H_2SO_4 yielding $Pt_2(HSO_4)_2(SO_4)_2$ [6] and the unique cluster anion $[Pt_{12}O_8(SO_4)_{12}]^{4-}$ [7]. Reactions with fuming sulfuric acid resulted in the first molecular disulfate $Re_2O_4Cl_2(S_2O_7)$ [8], the gold disulfates $M[Au(S_2O_7)_2]$ [9], and the trisulfate $Pb[S_3O_{10}]$ [10]. The application of neat SO_3 as a reactant resulted in $Pd(S_2O_7)$ [11] and $(NO_2)_2[S_4O_{13}]$, representing the first crystal structure of a tetrasulfate [12]. Crystallographic data of disulfates for a number of alkali sulfates has already been presented, namely $Na_2[S_2O_7]$ [13], $K_2[S_2O_7]$ [14], $Cs_2[S_2O_7]$ [15], and the ternary phase $NaK[S_2O_7]$ [13]. We were now able to prepare a new member of the alkali polysulfate family, $Li_2[S_2O_7]$. $Li_2[S_2O_7]$ 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 $[LiO_5]$ 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 Li_4SeO_5 [16]. Li_2SO_4 for example shows tetrahedral oxygen coordination with Li–O distances ranging from 191 to 198 pm [17].

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

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	4*c*	–0.21600(4)	–¾	–0.2787(1)	0.0137(4)	0.0143(5)	0.0164(4)	0	–0.0003(2)	0
S(2)	4*c*	0.99614(4)	¼	0.6139(1)	0.0138(4)	0.0136(5)	0.0133(4)	0	–0.0001(2)	0
O(11)	8*d*	–0.2061(1)	–0.6027(2)	–0.1231(3)	0.0189(7)	0.0186(9)	0.0218(7)	–0.0011(5)	0.0013(4)	–0.0054(5)
O(12)	4*c*	–0.3002(1)	–¾	–0.4715(4)	0.0155(8)	0.016(1)	0.0223(9)	0	–0.0035(7)	0
O(121)	4*c*	–0.1188(1)	–¾	–0.4986(3)	0.0140(8)	0.018(1)	0.0152(9)	0	–0.0003(7)	0
O(21)	8*d*	0.0079(1)	–0.6027(2)	–0.2254(3)	0.0172(6)	0.0149(9)	0.0171(6)	0.0005(5)	–0.0012(4)	–0.0017(5)
O(22)	4*c*	0.0546(1)	–¾	–0.6393(4)	0.0181(8)	0.018(1)	0.0160(8)	0	0.0026(7)	0
Li(1)	8*d*	0.8955(3)	0.5683(4)	0.8990(6)	0.020(2)	0.020(2)	0.022(2)	–0.001(1)	–0.000(1)	–0.001(1)

Acknowledgments. The author thank Dipl.-Chem. Wolfgang Saak for the collection of the X-ray Data.

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