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Crystal Structure of $Li_2Cu_3(SeO_3)_2(SeO_4)_2$

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Summary. Single crystal X-ray data of the hydrothermally grown new phase $Li_2Cu_3(SeO_3)_2(SeO_4)_2$ were measured with a four-circle diffractometer up to $\sin\theta/\lambda = 0.81\,\text{Å}^{-1}$ [I2/a, $Z = 4$, $V = 1\,175.5\,\text{Å}^3$, $a = 16.293(6)$, $b = 5.007(2)$, $c = 14.448(6)\,\text{Å}$, $\beta = 94.21(1)°$]. The structure was determined by direct and Fourier methods and refined to $R = 0.034$, $R_w = 0.027$ for 2086 independent reflections.

$Cu(1)^{[4+1]}O_5$ forms a tetragonal pyramid, $Cu(2)^{[4+2]}O_6$ is a strongly elongated octahedron. The Li atom is surrounded by four O atoms forming a distorted tetrahedron. $Se(IV)O_3$ and $Se(VI)O_4$ groups are in accordance to literature, mean Se—O bond lengths are 1.714 and 1.644 Å.

Keywords. $Li_2Cu_3(SeO_3)_2(SeO_4)_2$; Lithium-copper-selenite-selenate; Hydrothermal synthesis; Crystal structure.

Die Kristallstruktur von $Li_2Cu_3(SeO_3)_2(SeO_4)_2$

Zusammenfassung. Einkristall-Röntgendaten der hydrothermal gezüchteten neuen Phase $Li_2Cu_3(SeO_3)_2(SeO_4)_2$ wurden mit einem Vierkreisdiffraktometer im Bereich bis zu $\sin\theta/\lambda = 0.81\,\text{Å}^{-1}$ gemessen [I2/a, $Z = 4$, $V = 1\,175.5\,\text{Å}^3$, $a = 16.293(6)$, $b = 5.007(2)$, $c = 14.448(6)\,\text{Å}$, $\beta = 94.21(1)°$]. Die Kristallstruktur wurde mittels direkter und Fourier-Methoden bestimmt und für 2086 unabhängige Reflexe zu $R = 0.034$, $R_w = 0.027$ verfeinert.

$Cu(1)^{[4+1]}O_5$ bildet eine tetragonale Pyramide, $Cu(2)^{[4+2]}O_6$ ist ein stark verlängertes Oktaeder. Das Li-Atom ist von vier O-Atomen in Gestalt eines verzerrten Tetraeders umgeben. Die $Se(IV)O_3$- und $Se(VI)O_4$-Gruppen entsprechen der Literatur, die mittleren Se—O-Abstände betragen 1.714 und 1.644 Å.

Introduction

The occurrence of both selenite and selenate groups within a compound has up to now only been described for the rare mineral schmiederite [1]. The crystal structures of schmiederite $Pb_2Cu_2(OH)_4(SeO_3)(SeO_4)$ and of $Li_2Cu_3(SeO_3)_2(SeO_4)_2$ are not related.

Experimental

Crystals of $Li_2Cu_3(SeO_3)_2(SeO_4)_2$ were prepared under hydrothermal conditions. "Teflon"-lined steel vessels of ~ 6 cm³ capacity were filled with each ~ 0.5 g Li_2CO_3 and $Cu(OH)_2$; H_2SeO_4 conc. was added up to ~ 30 vol%. After a heating period of one week at 500(5) K the vessels were cooled to room temperature. Among various phases, light green crystals of the title compound in sizes up to some few tenths of a mm had formed.

Setting:	C2/c	I2/a
	$a =$ 20.968(6) Å	$a =$ 16.293(6) Å
	$b =$ 5.007(2) Å	$b =$ 5.007(2) Å
	$c =$ 16.293(6) Å	$c =$ 14.448(6) Å
	$\beta =$ 136.59(1)°	$\beta =$ 94.21(1)°
$Z = 4$; $V = 1\,175.5$ Å^3		

Preliminary X-ray investigations were done with a Weissenberg diffractometer (film methods), for measurements a STOE four-circle diffractometer AED 2 (graphite monochromatized MoKα radiation) was used. Lattice parameters were calculated from 46 2θ angle measurements in the range $35° < 2\theta < 50°$. 5 926 intensity data (2 593 unique reflections) were collected up to $\sin\theta/\lambda = 0.81$ Å^{-1} using 2θ-ω scans [43 steps/reflection, increased for α_1-α_2 splitting; 7 steps at each side for background measurement; step width 0.03°; step time 0.5–1.5 sec; 3 standard reflections]. The intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied (μMoKα = 173.85 cm^{-1}). The positions of the heavy atoms (Cu, Se) were established by direct methods. Subsequent Fourier summations revealed the positions of the O atoms, the Li atom was located by a final difference Fourier summation. Complex scattering curves for neutral atoms were taken from the International Tables for X-ray Crystallography [2]. 2 086 reflections with $F_o > 3\sigma(F_o)$ were used for the least-squares refinement ($R = 0.034$, $R_w = 0.027$, $w = [\sigma(F_o)]^{-2}$, 107 parameters), the secondary isotropic extinction according to Zachariasen [3] was taken into consideration [$g = 2.8(1)\cdot 10^{-6}$].

Final atomic coordinates and anisotropic thermal parameters are listed in Table 1 (based on the setting I2/a).

Results and Discussion

Selected interatomic bond distances, bond angles and bond strengths according to Brown [4] are given in Table 2. Figure 1 shows the crystal structure of the title compound in a projection parallel to [010]. With the exception of Cu(2) [site symmetry $\bar{1}$] all atoms occupy the general site.

Two crystallographically different Cu(II) atom positions exist; the coordination polyhedra of these atoms are distorted due to the Jahn-Teller effect. The resulting distortions are considered to be quite common for Cu(II) ions: The Cu(1) atom is coordinated to four O atoms (bond distances range from 1.953 Å to 1.999 Å within the "square") and one O atom [Cu—O(3): 2.305 Å] to form a "tetragonal pyramid" Cu(1)$^{[4+1]}$O$_5$. Additionally one very weak bond to an O atom [Cu—O(1): 2.794 Å] should be taken into consideration. The Cu(2) atom is [4 + 2] coordinated by oxygen atoms forming a strongly elongated "octahedron" [Cu—O: 1.896 Å, 2.025 Å, 2.606 Å (each 2 ×)].

The Li atom is bonded to 4 O atoms with distances ranging from 1.976 Å to 2.051 Å to form a distorted tetrahedron, next neighbours have Li—O distances $\geqslant 2.9$ Å.

The Se(VI) atom is tetrahedrally coordinated to O atoms, the bond angles O—Se(1)—O differ only slightly from the ideal value. The Se(2)O$_3$ group forms a trigonal pyramid with bond lengths and bond angles as characteristic for selenite groups. Mean bond lengths of the selenate and the selenite groups are 1.644 Å and 1.714 Å, respectively.

Table 1. Structural parameters of $Li_2Cu_3(SeO_3)_2(SeO_4)_2$, e.s.d.'s in parentheses.

$$\mathrm{ATF} = \exp\left[-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} h_i h_j a^*_i a^*_j\right].$$

U_{ij} are given in pm^2

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Li	0.4309(4)	0.2458(15)	0.0549(5)	261(31)	208(35)	165(32)	− 50(27)	− 14(24)	27(29)
Cu(1)	0.86307(2)	0.24980(9)	0.39451(3)	114(2)	101(2)	168(2)	− 5(1)	− 3(1)	− 21(2)
Cu(2)	1/4	1/4	1/4	112(2)	128(3)	138(3)	− 3(2)	− 16(2)	46(2)
Se(1)	0.66654(2)	0.22760(7)	0.37410(2)	109(1)	115(1)	97(1)	− 4(1)	15(1)	− 11(1)
Se(2)	0.43474(2)	0.21697(7)	0.33628(2)	111(1)	105(1)	113(1)	− 1(1)	4(1)	10(1)
O(1)	0.6668(2)	0.0291(5)	0.2823(2)	165(11)	145(11)	122(12)	10(8)	− 15(9)	− 47(10)
O(2)	0.7527(1)	0.4047(5)	0.3852(2)	114(10)	140(11)	189(14)	− 1(8)	20(9)	− 6(10)
O(3)	0.6546(2)	0.0445(5)	0.4655(2)	208(12)	174(12)	108(12)	− 30(9)	15(10)	25(10)
O(4)	0.5914(1)	0.4415(5)	0.3576(2)	143(11)	166(12)	165(14)	30(8)	0(10)	− 16(10)
O(5)	0.4713(2)	− 0.0644(5)	0.3893(2)	149(11)	123(11)	198(14)	23(8)	− 14(9)	48(10)
O(6)	0.4218(1)	0.4204(5)	0.4286(2)	191(11)	110(11)	106(12)	33(8)	− 22(9)	− 1(9)
O(7)	0.3358(1)	0.0798(5)	0.3236(2)	112(10)	129(11)	144(13)	− 2(8)	− 13(9)	35(9)

Table 2. Interatomic distances (Å), bond angles (°) and bond valences [4] (v.u.) of Li$_2$Cu$_3$(SeO$_3$)$_2$(SeO$_4$)$_2$ with e.s.d.'s in parentheses; intrapolyhedral O—O bond distances are given in brackets

	[Å]	[v.u.]		[°]	[Å]
Li—O(3)	2.051(7)	0.199	O(3)—Li—O(4)	119.1(3)	[3.517(4)]
Li—O(4)	2.030(7)	0.207	O(3)—Li—O(5)	103.1(3)	[3.155(4)]
Li—O(5)	1.976(7)	0.231	O(3)—Li—O(6)	99.7(3)	[3.096(4)]
Li—O(6)	2.001(8)	0.219	O(4)—Li—O(5)	106.4(3)	[3.208(4)]
			O(4)—Li—O(6)	104.6(3)	[3.188(4)]
⟨Li$^{[4]}$—O⟩	2.015		O(5)—Li—O(6)	125.2(3)	[3.531(4)]
Li—O(5′)	2.988(8)	0.043	⟨O—Li—O⟩	109.68	[3.283]
Li—O(6′)	2.896(7)	0.049			
Li—O(1)	3.261(7)	0.030			
		$\sum$ 0.978			
Se(1)—O(1)	1.657(2) Å	1.410	O(1)—Se(1)—O(2)	110.3(1)	[2.719(4)]
Se(1)—O(2)	1.658(2) Å	1.406	O(1)—Se(1)—O(3)	108.6(1)	[2.669(4)]
Se(1)—O(3)	1.631(2) Å	1.527	O(1)—Se(1)—O(4)	108.9(1)	[2.674(4)]
Se(1)—O(4)	1.631(2) Å	1.527	O(2)—Se(1)—O(3)	111.9(1)	[2.724(4)]
			O(2)—Se(1)—O(4)	106.5(1)	[2.635(3)]
⟨Se(1)$^{[4]}$—O⟩	1.644	$\sum$ 5.870	O(3)—Se(1)—O(4)	110.8(1)	[2.685(4)]
			⟨O—Se(1)—O⟩	109.47	[2.684]
Se(2)—O(5)	1.690(2) Å	1.275	O(5)—Se(2)—O(6)	101.7(1)	[2.633(4)]
Se(2)—O(6)	1.704(2) Å	1.234	O(5)—Se(2)—O(7)	90.7(1)	[2.447(3)]
Se(2)—O(7)	1.749(2) Å	1.112	O(6)—Se(2)—O(7)	98.7(1)	[2.619(4)]
⟨Se(2)$^{[3]}$—O⟩	1.714		⟨O—Se(2)—O⟩	97.02	[2.566]
Se(2)—O(1)	2.775(2) Å	0.176			
Se(2)—O(4)	2.786(2) Å	0.173			
		$\sum$ 3.970			
Cu(1)—O(2)	1.955(2) Å	0.461	O(2)—Cu(1)—O(3)	93.7(1)	[3.116(4)]
Cu(1)—O(3)	2.305(2) Å	0.171	O(2)—Cu(1)—O(5)	172.6(8)	[3.945(3)]
Cu(1)—O(5)	1.999(2) Å	0.403	O(2)—Cu(1)—O(6)	96.5(1)	[2.915(3)]
Cu(1)—O(6)	1.953(2) Å	0.463	O(2)—Cu(1)—O(7)	97.2(1)	[2.948(4)]
Cu(1)—O(7)	1.976(2) Å	0.432	O(3)—Cu(1)—O(5)	89.6(1)	[3.042(4)]
Cu(1)—O(1)	2.794(2) Å	0.054	O(3)—Cu(1)—O(6)	104.3(1)	[3.369(4)]
			O(3)—Cu(1)—O(7)	92.6(1)	[3.103(4)]
⟨Cu(1)$^{[5]}$—O⟩	2.038		O(5)—Cu(1)—O(6)	89.2(1)	[2.774(4)]
			O(5)—Cu(1)—O(7)	76.0(1)	[2.447(3)]
⟨Cu(1)$^{[4]}$—O⟩	1.971	$\sum$ 1.984	O(6)—Cu(1)—O(7)	157.6(3)	[3.854(4)]

Table 2 (continued)

	[Å]		[v.u.]		[°]		[Å]
Cu(2)—O(1)	2.025(2) Å	2×	0.373	O(1)—Cu(2)—O(7)	87.8(1)	2×	[2.720(4)]
Cu(2)—O(2)	2.606(2) Å	2×	0.082	O(1)—Cu(2)—O(7′)	92.2(1)	2×	[2.827(3)]
Cu(2)—O(7)	1.896(2) Å	2×	0.554	O(1)—Cu(2)—O(2)	105.0(1)	2×	[3.692(4)]
				O(1)—Cu(2)—O(2′)	75.0(1)	2×	[2.856(4)]
$\langle$Cu(2)$^{[6]}$—O$\rangle$	2.176	$\sum$	2.017	O(7)—Cu(2)—O(2)	95.4(1)	2×	[3.363(4)]
				O(7)—Cu(2)—O(2′)	84.6(1)	2×	[3.077(4)]
$\langle$Cu(2)$^{[4]}$—O$\rangle$	1.961						

The structure of $Li_2Cu_3(SeO_3)_2(SeO_4)_2$ is geometrically characterized by chains along [0 1 0] as illustrated in Fig. 2. These chains are built up by corner-sharing Cu(1)O_5 and Cu(2)O_6 polyhedra and the selenite group. The SeO_3 pyramid has each a common edge [O(5)—O(7)] and a common corner O(6) with the CuO_4 square of two Cu(1)$^{[4+1]}$$O_5$ groups. This common edge is the shortest intrapolyhedral O—O distance [2.447 Å] in the structure. Each such chain is connected with six adjoining

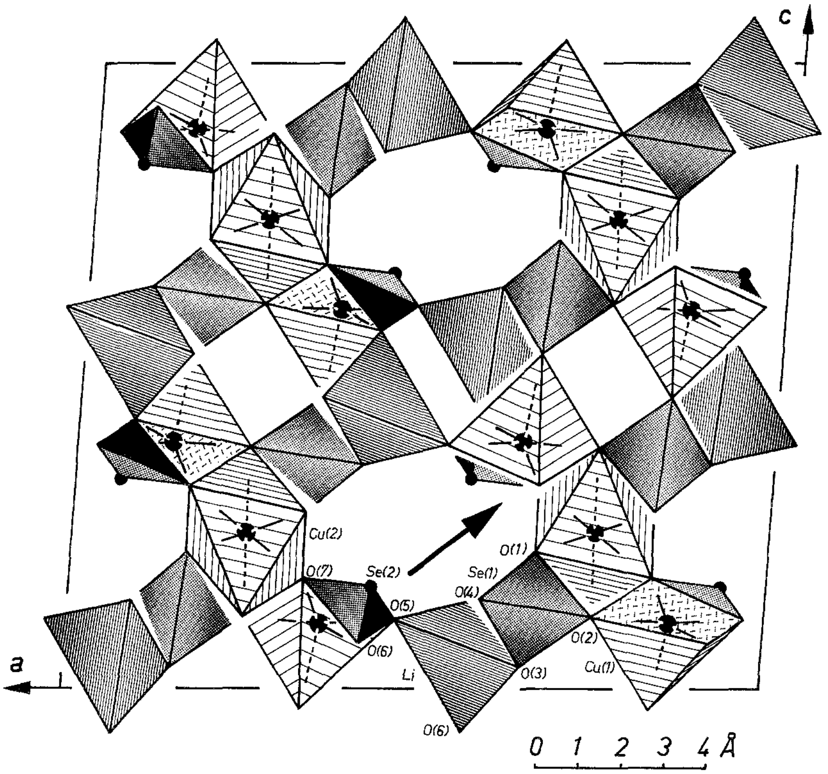

Fig. 1. Crystal structure of $Li_2Cu_3(SeO_3)_2(SeO_4)_2$ in a projection parallel to [0 1 0]. Strong Cu—O bonds are drawn with full lines, intermediate to weak Cu—O bonds are indicated by broken lines. The arrow gives the direction of the projection used in Fig. 2

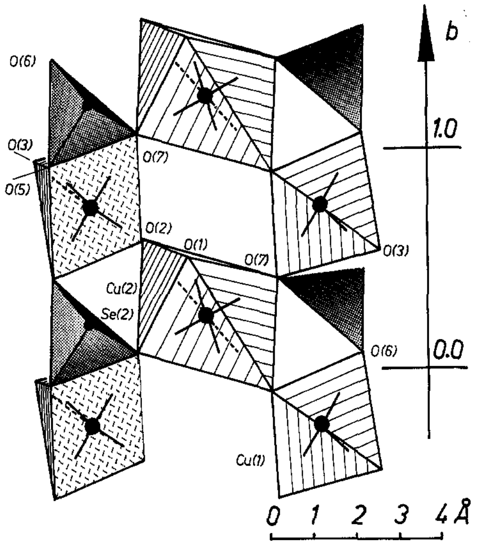

Fig. 2. Part of the crystal structure of $Li_2Cu_3(SeO_3)_2(SeO_4)_2$, illustrating the chains //*b*. Polyhedra around Li and Se(1) are not shown. The projection is parallel to the arrow given in Fig. 1

chains via the SeO_4 and LiO_4 tetrahedra to a characteristic framework illustrated in Fig. 1. Channels ca. 3.5 × 5 Å in diameter run parallel to [0 1 0]. The apices of the selenite groups (at $y/b \sim 0.25$ and 0.75) with the lone-pair electron region of the Se atom point into the channels. Such a configuration of selenite groups, their apices being adjusted to each other, is known for various selenite compounds.

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