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Lithium Tetrakis(chlorosulfato)borate

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Abstract. Li[B(SO$_3$Cl)$_4$], monoclinic, $P2_1/c$, $Z = 4$, $a = 8{\cdot}832\,(5)$, $b = 8{\cdot}388\,(4)$, $c = 20{\cdot}765\,(8)$ Å, $\beta = 91{\cdot}89\,(5)°$, $V = 1537$ Å^3, $R = 0{\cdot}040$ for 3538 observed reflections ($I > 3\sigma I$). The average values of the anionic bond distances and angles are similar to those observed in the K$^+$ salt but the conformation imposed by the Li$^+$ cation is very different. Li$^+$ has an octahedral coordination and three O atoms belonging to three SO$_3$Cl moieties of the same anion are involved in this octahedron.

Introduction. The tetrakis(chlorosulfato)borate salts are characterized by a [B(SO$_3$Cl)$_4$] anion formed by a central B atom tetracoordinated to four SO$_3$Cl moieties through one O atom per ligand (Mairesse & Drache, 1978). The anionic geometry of the K$^+$ salt was close to T_d symmetry except for the positional inversion of some Cl and O atoms. The crystal structure of the Li$^+$ salt was determined to analyze the counterion influence on the anionic geometry.

Single crystals were prepared and mounted as previously described for the K$^+$ salt. Preliminary photographs revealed that Li[B(SO$_3$Cl)$_4$] crystallized in a monoclinic system. The space-group extinctions ($0k0$ absent for $k = 2n + 1$ and $h0l$ absent for $l = 2n + 1$) led to the space group $P2_1/c$. The cell parameters and the intensities were measured with the automatic Philips PW 1100 four-circle diffractometer of this University [λ(Mo $K\alpha$) = 0·7107 Å, graphite monochromator]. Cell parameters were determined by least squares from 25 automatically centered reflections. 4492 independent reflections were measured within the $l > 0$ hemisphere ($2 \leq \theta \leq 30°$) with a fixed $\omega/2\theta$ scan rate of 0·035° s^{-1} and scan width of 1°. Two background counts at each extremity of the scan were made for half the scan time. The intensities of three standard reflexions, monitored every other hour, displayed no observable trend. Intensities were corrected for the Lorentz–polarization factor but not for absorption ($\mu = 1{\cdot}3$ mm^{-1}).

Table 1. *Atomic coordinates* ($\times 10^5$) *with e.s.d.'s in parentheses*

	x	y	z	B_{eq} (Å^2)
B	64878 (27)	74555 (32)	8898 (12)	1·88
S(1)	85183 (7)	87610 (8)	17427 (3)	2·58
Cl(1)	94171 (14)	75120 (16)	24621 (6)	6·65
O(1)	73476 (19)	75437 (22)	15015 (9)	2·57
O(2)	96663 (22)	89714 (26)	12844 (11)	3·77
O(3)	78199 (29)	101141 (27)	19920 (13)	4·64
S(2)	80970 (6)	47882 (7)	6141 (3)	2·11
Cl(2)	75328 (9)	32413 (10)	12787 (4)	4·22
O(4)	67422 (17)	59201 (20)	5737 (8)	2·15
O(5)	80900 (24)	39639 (26)	241 (10)	3·69
O(6)	94316 (20)	55537 (23)	8479 (10)	3·15
S(3)	39567 (6)	67860 (8)	15074 (3)	2·17
Cl(3)	42739 (13)	82245 (15)	22517 (5)	6·14
O(7)	48619 (18)	76098 (21)	9887 (8)	2·30
O(8)	24158 (20)	68907 (28)	13220 (10)	3·57
O(9)	45900 (25)	53008 (28)	16749 (12)	4·21
S(4)	77167 (6)	89470 (7)	−1394 (3)	2·22
Cl(4)	63542 (13)	79789 (14)	−8026 (5)	5·56
O(10)	68104 (20)	88234 (21)	4670 (9)	2·49
O(11)	78481 (23)	105803 (24)	−2844 (11)	3·56
O(12)	90314 (22)	79866 (25)	−1002 (10)	3·48
Li$^+$	8958 (50)	74882 (60)	6198 (24)	2·81

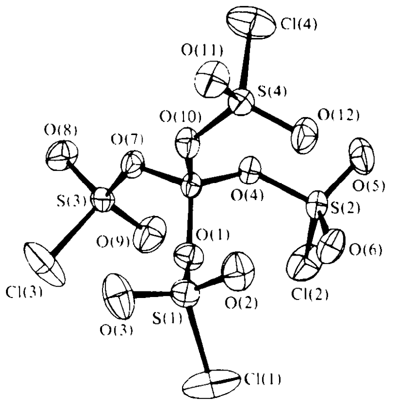

Fig. 1. Perspective drawing of the anion, showing the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). 350 E values ($>1{\cdot}75$) were used and 16 sets of phases computed. The most reliable set enabled us to determine the positions of 17 atoms out of 22 in the asymmetric unit: four Cl, four S and nine O. The remaining atoms were located by least-squares refinement and difference maps. The structure was refined by full-matrix least squares to $R = 0{\cdot}040$

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Table 2. *Interatomic distances* (Å) *and angles* (°) *in the* $|B(SO_3Cl)_4|$ *anion* (*with their e.s.d.'s*)

		Corrected			Corrected
B(1) O(1)	1·460 (3)		S(2) O(5)	1·407 (2)	1·425
B(1) O(4)	1·466 (3)		S(2) O(6)	1·414 (2)	1·432
B(1) O(7)	1·463 (3)		S(3) Cl(3)	1·973 (1)	2·011
B(1) O(10)	1·478 (3)		S(3) O(7)	1·528 (2)	1·557
S(1) Cl(1)	1·970 (1)	2·008	S(3) O(8)	1·405 (2)	1·432
S(1) O(1)	1·526 (2)	1·555	S(3) O(9)	1·405 (2)	1·432
S(1) O(2)	1·424 (2)	1·451	S(4) Cl(4)	1·974 (1)	2·006
S(1) O(3)	1·399 (3)	1·426	S(4) O(10)	1·518 (2)	1·543
S(2) Cl(2)	1·970 (1)	1·995	S(4) O(11)	1·408 (2)	1·431
S(2) O(4)	1·528 (2)	1·547	S(4) O(12)	1·413 (2)	1·436

O(1) B O(4)	110·5 (2)	O(4) S(2) O(5)	106·1 (1)
O(1) B O(7)	111·0 (2)	O(4)–S(2) O(6)	112·3 (1)
O(1) B O(10)	111·9 (2)	O(5) S(2)–O(6)	120·1 (1)
O(4) B O(7)	107·8 (2)	B O(7)–S(3)	126·7 (2)
O(4) B O(10)	112·4 (2)	Cl(3) S(3) O(7)	102·21 (8)
O(7) B O(10)	102·9 (2)	Cl(3) S(3) O(8)	106·7 (1)
B O(1) S(1)	130·3 (2)	Cl(3) S(3)–O(9)	107·6 (1)
Cl(1) S(1) O(1)	98·32 (8)	O(7)–S(3) O(8)	107·7 (1)
Cl(1) S(1) O(2)	107·1 (1)	O(7) S(3)–O(9)	111·2 (1)
Cl(1) S(1) O(3)	108·8 (1)	O(8) S(3) O(9)	119·8 (1)
O(1) S(1) O(2)	110·7 (1)	B O(10) S(4)	131·5 (2)
O(1) S(1) O(3)	111·2 (1)	Cl(4) S(4) O(10)	102·95 (8)
O(2) S(1) O(3)	118·6 (1)	Cl(4) S(4) O(11)	107·7 (1)
B O(4) S(2)	130·7 (2)	Cl(4) S(4) O(12)	106·7 (1)
Cl(2) S(2) O(4)	103·42 (7)	O(10) S(4)–O(11)	107·0 (1)
Cl(2) S(2) O(5)	107·0 (1)	O(10) S(4)–O(12)	111·6 (1)
Cl(2) S(2) O(6)	106·6 (9)	O(11) S(4)–O(12)	119·6 (1)

and $R_w = 0.052$ $[w = 1/\sigma^2(F_o)]$ using the 3538 reflections with $I > 3\sigma I$. Scattering factors were taken from Cromer & Waber (1965) for Li^+, Cl, S, O and B: the imaginary component of dispersion (Cromer & Liberman, 1970) was included for Cl and S. The calculations were performed on the CII–Honeywell Bull Iris 80 computer of this University.

The final atomic coordinates are presented in Table 1, intra-anionic distances and angles in Table 2. The anion is illustrated in Fig. 1. The thermal motion of the SO_3Cl ligands can be described by a rigid-body model (Schomaker & Trueblood, 1968) which enabled us to assess the bond-length corrections resulting from librational motion.*

Table 3. *Interionic distances* (Å) *and angles* (°) *about the* Li^+ *cation*

Coding: (1) x,y,z; (1) $\bar{x},\bar{y},\bar{z}$. O(5) $\bar{1}$/110 means that O(5) is in position $\bar{1}$ translated by $1a$, $1b$, $0c$.

Li^+···O(8) 1/000	2·013 (5)	Li^+···O(6) 1/$\bar{1}$00	2·138 (5)
···O(5) $\bar{1}$/110	2·038 (5)	···O(2) 1/100	2·175 (5)
···O(11) 1/120	2·096 (5)	···O(12) 1/$\bar{1}$00	2·227 (6)
O(8)···Li···O(5)	91·7 (2)	O(5)···Li···O(12)	90·2 (2)
O(8)···Li···O(11)	94·9 (2)	O(11)···Li···O(6)	172·4 (3)
O(8)···Li···O(6)	92·5 (2)	O(11)···Li···O(2)	92·8 (2)
O(8)···Li···O(2)	91·0 (2)	O(11)···Li···O(12)	91·1 (2)
O(8)···Li···O(12)	173·7 (3)	O(6)···Li···O(2)	88·6 (2)
O(5)···Li···O(11)	89·7 (2)	O(6)···Li···O(12)	81·5 (2)
O(5)···Li···O(6)	88·5 (2)	O(2)···Li···O(12)	86·8 (2)
O(5)···Li···O(2)	176·1 (3)		

Discussion. Bond lengths and angles in the anion are similar when associated with Li^+ or K^+, but the conformation is considerably affected: whereas the anion has approximate T_d symmetry in the K^+ salt, no internal symmetry element is present in the Li^+ salt. This is due to the electrostatic interactions between the cation and the O atoms (Table 3). Each Li^+ is surrounded by six O atoms forming a distorted octahedron. Three of these belong to the same anion and the others to a different anion. The three O atoms of the same anion each belong to one SO_3Cl ligand, which implies the anionic conformation. Therefore the anion–cation coordination is 4/4 whereas it is 6/6 with the same octahedral surrounding of the cation in the K^+ salt.

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* Lists of structure factors, anisotropic thermal parameters and rigid-body motion parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35390 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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