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The Crystal Structure of Potassium Tetrachlorosulfatoborate, $K[B(SO_3Cl)_4]$

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$K[B(SO_3Cl)_4]$ crystallizes in the triclinic space group $P1$ with $a = 10{\cdot}513\,(9)$, $b = 10{\cdot}838\,(7)$, $c = 10{\cdot}965\,(11)$ Å, $\alpha = 99{\cdot}21\,(3)$, $\beta = 135{\cdot}48\,(3)$, $\gamma = 97{\cdot}15\,(3)°$, $Z = 2$. The structure was refined to $R = 0{\cdot}035$ and $R_w = 0{\cdot}045$ for 2107 counter reflexions. The $[B(SO_3Cl)_4]^-$ anions exist as optical images and the crystal is racemic. Each anion has lost the approximate T_d symmetry owing to the positional inversion of some Cl and O atoms. This seems to be due to steric hindrance in the crystal packing. If we neglect this inversion, the crystal structure is close to $I\bar{4}$ body-centered tetragonal, with a cell volume twice that of the actual triclinic cell. The anionic structure consists of a B atom tetracoordinated to four SO_3Cl moieties with one O atom involved per ligand. All the B—O_b (b = bridge) lengths are practically equal (average 1·465 Å) and the average B—O—S angle is 127·1°. The thermal motion of the SO_3Cl ligand is in keeping with the **TLS** rigid-body analysis. The average values of selected bond angles and corrected bond distances are: O_t—S—O_t (t = terminal) 119·5, Cl—S—O_b 100·9°, S—Cl 2·027, S—O_b 1·565, S—O_t 1·442 Å. The coordination of the K^+ cations is distorted octahedral with six O_t atoms, each belonging to a different anionic unit.

Introduction

We have recently synthesized new products with the empirical formula $M_IM_{III}O_{12}S_4Cl_4$, M_{III} being a Group III element (B, Al or Ga) and M_I an alkali metal. These compounds result from the reaction of sulfuric anhydride (SO_3) or chlorosulfuric acid (HSO_3Cl) on an alkaline tetrachlorometallate ($M_IM_{III}Cl_4$). Their preparative methods and preliminary characterization have been reported (Vandorpe & Drache, 1971; Vandorpe, Drache & Dubois, 1973; Drache, Vandorpe & Heubel, 1976). We have also synthesized the corresponding alkaline-earth salts $M_{II}Al_2O_{24}S_8Cl_8$ (with M_{II} = Ca, Sr and Ba) from $M_{II}(AlCl_4)_2$ (Mairesse, 1973).

The existence of such compounds raised an interesting structural problem. Preliminary investigations by infrared and Raman techniques enabled us to observe frequencies ascribed to the SO_3Cl moiety. To obtain additional information and particularly to ascertain the relative disposition of these SO_3Cl groups in the anion, we have determined the crystal structure of $K[B(SO_3Cl)_4]$.

Experimental

Single crystals were prepared by slow cooling of a supersaturated solution of the salt formed by the reaction of a solution of HSO_3Cl in $SOCl_2$ on $KBCl_4$. This procedure yielded needles, some of them several millimetres long. These crystals, very sensitive to moisture, were isolated in a dry box under nitrogen, washed in previously dried CCl_4, and mounted in sealed quartz capillaries.

The crystal used for X-ray diffraction was 0·25 × 0·20 × 0·20 mm. Weissenberg photographs revealed that $K[B(SO_3Cl)_4]$ crystallized in a nearly body-centered tetragonal system with $a' \simeq 14$ and $c' \simeq 8$ Å, this c' axis being the growing axis of the crystals. With such a unit cell, $d_m = 2{\cdot}07$ g cm^{-3} agrees with $Z = 4$ ($d_c = 2{\cdot}09$ g cm^{-3}). The determination of the actual symmetry was carried out on a four-circle Philips PW 1100 automatic diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å). The pseudotetragonal cell had the following parameters (non-refined): $a' = 14{\cdot}14$, $b' = 14{\cdot}13$, $c' = 8{\cdot}15$ Å, $\alpha' = \beta' = 92{\cdot}45$, $\gamma' = 90{\cdot}62°$. The real symmetry of the crystal is then triclinic with half the volume and $Z = 2$. Lattice parameters were determined by least squares from the setting angles of 25 independent reflexions centered on the diffractometer: $a = 10{\cdot}513\,(9)$, $b = 10{\cdot}838\,(7)$, $c = 10{\cdot}965\,(11)$ Å, $\alpha = 99{\cdot}21\,(3)$, $\beta = 135{\cdot}48\,(3)$, $\gamma = 97{\cdot}15\,(3)°$, $V = 813{\cdot}4$ Å^3, $Z = 2$. 6280 intensities within the $l > 0$ hemisphere (limited by $2° \leq \theta \leq 35°$) were measured by the ω-scan method with a scan speed of $0{\cdot}03°$ s^{-1}, a scan width of 1·40° and two background counts at each extremity of the scan for half the scan time. Three standard reflexions ($2\bar{2}0$, $40\bar{4}$ and $03\bar{2}$) were monitored every other hour. Only statistical variations were observed. The intensities were

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corrected for Lorentz and polarization effects; no correction for absorption ($\mu = 15$ cm^{-1}) was applied.

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). Statistical intensity tests indicated that the structure was noncentrosymmetric:

		Theoretical	
	Experimental	Centrosymmetric	Noncentrosymmetric
E^2	0·9993	1·0000	1·0000
$\langle E^2 - 1\rangle$	0·7340	0·9680	0·7360
$\langle E\rangle$	0·8842	0·7980	0·8860.

The correct space group is then *P*1, which was confirmed in the subsequent structure refinement. The reflexions chosen in the starting set by the *CONVERGE* procedure were:

	h	*k*	*l*	*E*	
Origin-fixing reflexions	2	−17	3	2·47	
	6	1	−2	2·28	
	9	−8	−1	2·06	
Starting-set reflexions	11	−1	−1	2·92	← enantiomorph-fixing reflexion
	1	9	−5	2·19	
	7	4	−7	2·14	
	7	−4	−7	2·14.	

They led to the phases of the 499 strongest *E* values obtained by the weighted tangent formula. Thus, we obtained 128 sets of phases and the *E* map computed from the most reliable (PSI ZERO figure of merit minimum) enabled us to determine the positions of 32 of the 44 atoms in the cell: the two K$^+$ ions, the eight Cl, the eight S and 14 O atoms. The ten remaining O and the two B atoms were then located by least-squares refinement and difference maps. Limitations of core memory precluded full-matrix anisotropic refinement of the entire structure.

Therefore we used only the 2107 reflexions with $|F_o| > 470$ and refined separate blocks (with the scale factor common to all blocks) with a maximum of 122 parameters. In the last cycle, the variable parameters were the scale factor and the atomic coordinates of all the atoms except the two B atoms and the two K$^+$ ions. This gave $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0{\cdot}035$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2} = 0{\cdot}045$ with the weighting scheme $w = 1/\sigma^2(F_o)$, $\sigma(F_o)$ being deduced from counting statistics. $\sigma(I) = [\mathrm{CT} + (B_1 + B_2) + (pI)^2]^{1/2}$, where CT is the total integrated peak count obtained in scan time t_c, B_1 and B_2 are the background counts, each obtained during time $t_c/2$, and $I = \mathrm{CT} - (B_1 + B_2)$. A value of 0·04 was assigned to p. The largest parameter shift during the last cycle was $<0{\cdot}5\sigma$ (average parameter shift $<0{\cdot}06\sigma$), and the standard deviation of an observation of unit weight was 2·07. With the 3978 reflexions with $\theta \leq 30°$ out of the 4751 with $I > 3\sigma(I)$, R and R_w were respectively 0·049 and 0·064 with the same parameters.* Scattering factors were taken from Cromer & Waber (1965) for K$^+$, Cl, S, O and B. The effects of anomalous dispersion were ignored. For the refinement a version of *ORFLS* (Busing, Martin & Levy, 1962) was used. All computations were carried out on the CII 10070 computer of this university.

Description of the structure and discussion

Anionic conformations, cationic surroundings and lattice geometry

The atomic coordinates are listed in Table 1. The matrix transformation giving the x_i' coordinates of the body-centered pseudotetragonal cell from the x_i coordinates of the real triclinic one is

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} -0{\cdot}5 & -0{\cdot}5 & 0{\cdot}5 \\ -0{\cdot}5 & 0{\cdot}5 & 0{\cdot}5 \\ -0{\cdot}5 & 0{\cdot}5 & -0{\cdot}5 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}.$$

Table 1. *Atomic coordinates* ($\times 10^4$) *with standard deviations in parentheses*

	x	*y*	*z*
K$^+$(1)	7991 (3)	−710 (2)	3957 (3)
B(1)	0	0	0
S(1)	−1224 (3)	2084 (2)	−633 (3)
Cl(1)	−2187 (7)	2518 (5)	−2787 (6)
O(1)	−187 (7)	1172 (5)	−554 (7)
O(2)	166 (11)	3273 (6)	938 (12)
O(3)	−2787 (8)	1397 (7)	−1059 (9)
S(2)	3413 (3)	593 (2)	1291 (4)
Cl(2)	2699 (4)	1140 (3)	−738 (4)
O(4)	1473 (7)	−360 (5)	288 (8)
O(5)	4592 (11)	−168 (9)	1738 (14)
O(6)	4092 (8)	1757 (7)	2676 (9)
S(3)	−2800 (3)	−2009 (2)	−3323 (3)
Cl(3)	−1479 (4)	−3338 (3)	−2734 (4)
O(7)	−1797 (7)	−1158 (5)	−1415 (7)
O(8)	−4732 (9)	−2722 (7)	−4419 (9)
O(9)	−2385 (10)	−1247 (7)	−3997 (9)
S(4)	602 (3)	−563 (2)	2622 (3)
Cl(4)	2852 (6)	605 (4)	5212 (4)
O(10)	480 (9)	360 (5)	1657 (7)
O(11)	991 (16)	−1676 (8)	2253 (15)
O(12)	−955 (12)	−795 (10)	2319 (13)
K$^+$(2)	1319 (3)	5950 (2)	2286 (3)
B(2)	2617 (11)	5244 (8)	7611 (11)
S(5)	−689 (3)	3155 (2)	4900 (3)
Cl(5)	−2083 (4)	2721 (5)	2318 (4)
O(13)	1258 (7)	4067 (5)	5893 (7)
O(14)	−490 (12)	1970 (6)	5278 (12)
O(15)	−1557 (8)	3838 (7)	5167 (9)
S(6)	5443 (3)	4649 (2)	8322 (3)
Cl(6)	4176 (4)	4098 (3)	5739 (4)
O(16)	4455 (7)	5603 (5)	8268 (8)
O(17)	7384 (9)	5401 (9)	9532 (12)
O(18)	4954 (10)	3479 (7)	8535 (10)
S(7)	1829 (3)	7248 (2)	6304 (3)
Cl(7)	4479 (4)	8578 (3)	8222 (4)
O(19)	1980 (7)	6401 (5)	7368 (7)
O(20)	622 (11)	7967 (7)	5931 (11)
O(21)	1482 (11)	6499 (7)	4874 (9)
S(8)	3786 (3)	5804 (2)	10805 (3)
Cl(8)	4871 (8)	4634 (4)	12231 (5)
O(22)	2746 (8)	4882 (5)	8923 (7)
O(23)	5300 (12)	6918 (8)	11563 (12)
O(24)	2473 (13)	6043 (10)	10740 (13)

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33324 (47 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

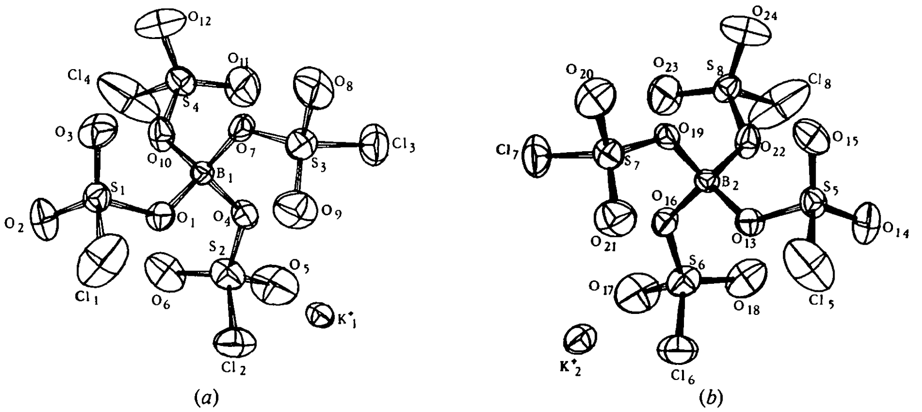

Fig. 1. Perspective drawing of K[B(SO_3Cl)$_4$], showing the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. (*a*) B(1) anion; (*b*) B(2) anion.

This matrix is derived from the orientation matrices of each cell with respect to the right-handed rectangular coordinate system of the diffractometer.

The crystal contains two crystallographically independent $[B(SO_3Cl)_4]^-$ anions and K^+ cations. The geometry of the anions is illustrated in Fig. 1 (Nowogroki, 1977). In each anion the B atom is tetrahedrally linked to four O atoms each belonging to one chlorosulfate group. The most striking feature is that these two independent anions are mirror images of each other (Fig. 1*a* and *b*). Thus, in these two anions we find approximately the same variations in bond distances and angles: the central S(1), S(2), S(3), S(4) of the chlorosulfate ligands in the B(1) anion correspond to S(5), S(6), S(7), S(8) in the second anion B(2) (Table 2). These two optical antipodes, in equal quantities in the solid, form a racemic crystal.

In each anion, the S atom and two O atoms of the SO_3Cl ligands are disposed about the central B atom in such a way as to roughly correspond to each other through a $\bar{4}$ axis, as follows: S(1), S(2), S(3), S(4); O(1), O(4), O(7), O(10); O(3), O(6), O(9), O(11) in the B(1) anion (Fig. 1*a*); S(5), S(6), S(7), S(8); O(13), O(16), O(19), O(22); O(15), O(18), O(21), O(23) in the B(2) anion (Fig. 1*b*). But this tetrahedral symmetry is destroyed by the relative disposition of the third O atom and of the Cl atom of each group, in which we observe positional inversions from S(1) to S(2), then from S(3) to S(4) in the B(1) unit. The same holds from S(5) to S(6) and from S(7) to S(8) in the B(2) unit.

This inversion seems to be due to steric crowding. Indeed, in each anion, two Cl atoms [Cl(1) and Cl(4) in B(1), and Cl(5) and Cl(8) in B(2)] are at about 4·02 (2) Å from the central B atom while the other two [Cl(2), Cl(3) and Cl(6), Cl(7) respectively] are at 3·60 Å. Furthermore the most distant Cl atoms have thermal parameters significantly higher than the others. If we build hypothetical anions from ligands S(1) and S(5) so that each atom of these ions is symmetrically related by a $\bar{4}$ axis, each Cl atom is 4·02 Å from the B atom in each anion. Keeping the same sites for the B(1) and

Table 2. *Interatomic distances* (Å) *and angles* (°) *in both* $[B(SO_3Cl)_4]^-$ *anions with standard deviations in parentheses*

	Measured	Corrected		Measured	Corrected
B(1)–O(1)	1·469 (11)		B(2)–O(13)	1·469 (10)	
B(1)–O(4)	1·464 (17)		B(2)–O(16)	1·463 (17)	
B(1)–O(7)	1·469 (11)		B(2)–O(19)	1·467 (12)	
B(1)–O(10)	1·458 (13)		B(2)–O(22)	1·468 (13)	
S(1)–Cl(1)	1·972 (6)	2·021	S(5)–Cl(5)	1·968 (4)	2·016
S(1)–O(1)	1·527 (9)	1·565	S(5)–O(13)	1·525 (8)	1·562
S(1)–O(2)	1·413 (9)	1·448	S(5)–O(14)	1·407 (8)	1·441
S(1)–O(3)	1·401 (11)	1·436	S(5)–O(15)	1·395 (11)	1·429
S(2)–Cl(2)	2·004 (5)	2·037	S(6)–Cl(6)	2·008 (5)	2·040
S(2)–O(4)	1·533 (9)	1·558	S(6)–O(16)	1·534 (9)	1·558
S(2)–O(5)	1·405 (14)	1·428	S(6)–O(17)	1·403 (12)	1·425
S(2)–O(6)	1·422 (8)	1·445	S(6)–O(18)	1·424 (9)	1·447
S(3)–Cl(3)	1·985 (5)	2·021	S(7)–Cl(7)	1·984 (5)	2·019
S(3)–O(7)	1·528 (6)	1·555	S(7)–O(19)	1·531 (7)	1·558
S(3)–O(8)	1·413 (11)	1·438	S(7)–O(20)	1·411 (13)	1·436
S(3)–O(9)	1·409 (11)	1·434	S(7)–O(21)	1·398 (11)	1·422
S(4)–Cl(4)	1·946 (4)	2·027	S(8)–Cl(8)	1·951 (5)	2·031
S(4)–O(10)	1·521 (7)	1·584	S(8)–O(22)	1·518 (7)	1·580
S(4)–O(11)	1·410 (15)	1·469	S(8)–O(23)	1·413 (12)	1·471
S(4)–O(12)	1·396 (16)	1·454	S(8)–O(24)	1·388 (17)	1·445
O(1)–B(1)–O(4)	107·1 (8)		O(13)–B(2)–O(16)	107·4 (8)	
O(1)–B(1)–O(7)	113·3 (8)		O(13)–B(2)–O(19)	113·8 (8)	
O(1)–B(1)–O(10)	107·3 (8)		O(13)–B(2)–O(22)	106·9 (8)	
O(4)–B(1)–O(7)	108·2 (8)		O(16)–B(2)–O(19)	108·6 (8)	
O(4)–B(1)–O(10)	114·2 (8)		O(16)–B(2)–O(22)	113·7 (8)	
O(7)–B(1)–O(10)	106·9 (8)		O(19)–B(2)–O(22)	106·5 (8)	
B(1)–O(1)–S(1)	127·0 (7)		B(2)–O(13)–S(5)	127·3 (6)	
Cl(1)–S(1)–O(1)	98·5 (4)		Cl(5)–S(5)–O(13)	98·6 (3)	
Cl(1)–S(1)–O(2)	106·7 (5)		Cl(5)–S(5)–O(14)	106·6 (5)	
Cl(1)–S(1)–O(3)	109·7 (4)		Cl(5)–S(5)–O(15)	110·0 (4)	
O(1)–S(1)–O(2)	109·0 (6)		O(13)–S(5)–O(14)	109·0 (6)	
O(1)–S(1)–O(3)	111·8 (5)		O(13)–S(5)–O(15)	111·8 (5)	
O(2)–S(1)–O(3)	119·0 (6)		O(14)–S(5)–O(15)	118·9 (6)	
B(1)–O(4)–S(2)	126·8 (7)		B(2)–O(16)–S(6)	126·9 (6)	
Cl(2)–S(2)–O(4)	102·6 (3)		Cl(6)–S(6)–O(16)	102·4 (3)	
Cl(2)–S(2)–O(5)	106·3 (6)		Cl(6)–S(6)–O(17)	106·5 (5)	
Cl(2)–S(2)–O(6)	107·3 (4)		Cl(6)–S(6)–O(18)	107·0 (4)	
O(4)–S(2)–O(5)	107·4 (6)		O(16)–S(6)–O(17)	107·8 (6)	
O(4)–S(2)–O(6)	110·9 (5)		O(16)–S(6)–O(18)	111·2 (5)	
O(5)–S(2)–O(6)	120·8 (7)		O(17)–S(6)–O(18)	120·5 (6)	
B(1)–O(7)–S(3)	127·9 (6)		B(2)–O(19)–S(7)	127·2 (6)	
Cl(3)–S(3)–O(7)	102·5 (3)		Cl(7)–S(7)–O(19)	102·4 (3)	
Cl(3)–S(3)–O(8)	106·3 (4)		Cl(7)–S(7)–O(20)	105·9 (5)	
Cl(3)–S(3)–O(9)	107·7 (5)		Cl(7)–S(7)–O(21)	107·6 (5)	
O(7)–S(3)–O(8)	107·9 (5)		O(19)–S(7)–O(20)	107·8 (6)	
O(7)–S(3)–O(9)	110·3 (5)		O(19)–S(7)–O(21)	110·9 (5)	
O(8)–S(3)–O(9)	120·6 (6)		O(20)–S(7)–O(21)	120·6 (6)	
B(1)–O(10)–S(4)	126·9 (7)		B(2)–O(22)–S(8)	127·0 (7)	
Cl(4)–S(4)–O(10)	100·0 (4)		Cl(8)–S(8)–O(22)	99·9 (4)	
Cl(4)–S(4)–O(11)	109·9 (6)		Cl(8)–S(8)–O(23)	109·5 (5)	
Cl(4)–S(4)–O(12)	105·9 (6)		Cl(8)–S(8)–O(24)	106·1 (6)	
O(10)–S(4)–O(11)	111·0 (7)		O(22)–S(8)–O(23)	111·2 (6)	
O(10)–S(4)–O(12)	110·5 (6)		O(22)–S(8)–O(24)	110·9 (6)	
O(11)–S(4)–O(12)	117·9 (8)		O(23)–S(8)–O(24)	117·6 (8)	

B(2) atoms, we then obtain a hypothetical cell in which, as in the actual structure (Table 3), there is no interionic Cl···Cl or Cl···O contact significantly less than the sum of the van der Waals radii (1·40 for O, and 1·80 Å for Cl; Pauling, 1960). On the other hand, if we take another hypothetical cell built as previously but, this time, from S(2) and S(6) ligands, with each Cl atom 3·60 Å from the B atom, we then obtain a 2·80 Å Cl···Cl distance, much shorter than the sum of the van der Waals radii. This steric crowding can account for the positional inversion. The particular geometry of each anion seems to be due to a compromise between the maximum anionic compactness on the one hand, and crystal-packing effects, hence ionic interactions, on the other. Among these interactions occur the anion–anion interactions already described (they approach a molecular type because of the weak electric charge distributed among atoms of the anion), and also the electrostatic anion–cation interactions.

Table 3. *Shortest interanionic contacts* (Å) *with standard deviations in parentheses*

O(6)/$\bar{1}0\bar{1}$ means that O(6) belongs to the anion translated by $-1\mathbf{a},0\mathbf{b},-1\mathbf{c}$.

Cl(1)···O(6)/$\bar{1}0\bar{1}$	3·297 (8)	Cl(5)···O(18)/$\bar{1}0\bar{1}$	3·300 (8)
Cl(1)···Cl(6)/$\bar{1}0\bar{1}$	3·723 (9)	Cl(5)···Cl(2)/100	3·723 (9)
Cl(1)···O(15)/$00\bar{1}$	3·229 (11)	Cl(5)···O(3)/000	3·232 (10)
O(3)···Cl(5)/000	3·232 (10)	O(15)···Cl(1)/001	3·229 (11)
O(3)···Cl(4)/$\bar{1}0\bar{1}$	3·105 (9)	O(15)···Cl(8)/$\bar{1}0\bar{1}$	3·109 (10)
Cl(2)···Cl(8)/$00\bar{1}$	3·668 (5)	Cl(6)···Cl(4)/000	3·666 (6)
Cl(2)···Cl(5)/100	3·723 (7)	Cl(6)···Cl(1)/101	3·723 (9)
O(6)···Cl(8)/$00\bar{1}$	3·324 (9)	O(18)···Cl(4)/000	3·321 (9)
Cl(3)···O(24)/$0\bar{1}\bar{1}$	3·341 (12)	Cl(7)···O(12)/111	3·338 (12)
Cl(4)···Cl(6)/000	3·666 (6)	Cl(7)···Cl(4)/010	3·721 (5)
Cl(4)···O(18)/000	3·321 (9)	Cl(8)···O(6)/001	3·324 (9)
Cl(4)···Cl(7)/$0\bar{1}0$	3·721 (5)	Cl(8)···Cl(2)/001	3·668 (6)
O(12)···Cl(7)/$\bar{1}\bar{1}\bar{1}$	3·338 (12)	O(24)···Cl(3)/011	3·341 (12)

Table 4. *Interionic distances* (Å) *and angles* (°) *about the* K^+ *cations*

O(23)/$0\bar{1}\bar{1}$ means than O(23) is translated by $0\mathbf{a},-1\mathbf{b},-1\mathbf{c}$.

K^+(1)···	O(23)/$0\bar{1}\bar{1}$	2·635 (10)	K^+(2)···	O(11)/010	2·641 (10)
	O(9)/101	2·674 (11)		O(21)/000	2·680 (11)
	O(12)/100	2·697 (16)		O(2)/000	2·695 (8)
	O(14)/100	2·699 (8)		O(24)/$00\bar{1}$	2·705 (16)
	O(5)/000	2·760 (14)		O(17)/$\bar{1}0\bar{1}$	2·754 (12)
	O(20)/$\bar{1}\bar{1}0$	2·799 (11)		O(8)/111	2·796 (8)

O(23)–K^+(1)–	O(9)	83·0 (3)	O(11)–K^+(2)–	O(21)	82·9 (4)
O(23)	O(12)	91·5 (4)	O(11)	O(2)	156·6 (4)
O(23)	O(14)	156·6 (4)	O(11)	O(24)	91·4 (4)
O(23)	O(5)	76·5 (4)	O(11)	O(17)	76·5 (4)
O(23)	O(20)	87·0 (4)	O(11)	O(8)	87·0 (4)
O(9)	O(12)	159·4 (4)	O(21)	O(2)	105·1 (4)
O(9)	O(14)	105·0 (3)	O(21)	O(24)	159·1 (4)
O(9)	O(5)	90·2 (4)	O(21)	O(17)	90·1 (3)
O(9)	O(20)	77·4 (3)	O(21)	O(8)	77·3 (3)
O(12)	O(14)	87·8 (4)	O(2)	O(24)	88·1 (4)
O(12)	O(5)	107·9 (4)	O(2)	O(17)	81·4 (3)
O(12)	O(20)	82·5 (4)	O(2)	O(8)	116·1 (3)
O(14)	O(5)	81·5 (4)	O(24)	O(17)	108·1 (4)
O(14)	O(20)	116·1 (3)	O(24)	O(8)	82·3 (4)
O(5)	O(20)	160·5 (4)	O(17)	O(8)	160·4 (3)

Each K^+ cation is surrounded by six O atoms, each belonging to only one anion. The coordination is distorted octahedral (Table 4) in which the K^+···O contacts range from 2·63 to 2·80 Å. These distances are similar to those in $K_2S_5O_{16}$ (De Vries & Mijlhoff, 1969), $K[B(OAc)_4]$ (Dal Negro, Rossi & Perotti, 1974) and $KHSO_4$ (Payan & Haser, 1976). The nearest Cl atom is at 3·89 Å [K^+(1)···Cl(2), and K^+(2)···Cl(6)]; the other K^+···Cl distances are >4·2 Å. The anion–cation interactions essentially involve O atoms, *i.e.* the negative charge of the anion is preferentially distributed on the terminal O atoms.

The $K[B(SO_3Cl)_4]$ racemic crystal of pseudo-tetragonal symmetry is shown in projection in Fig. 2. If we do not take into account the real anionic symmetry (*i.e.* the T_d symmetry is not kept for the whole anion), we can roughly describe the structure in $I\bar{4}$ with one enantiomer B(1) at the origin (multiplicity 2), and the other, B(2), at $0,\frac{1}{2},\frac{1}{4}$ (multiplicity 2 also). The cation size seems to play a leading part in the lattice geometry of this salt family. Thus, for example, attempts to crystallize the Na salt have, up to now, always led to twinned crystals formed by four individual crystals having nearly square, common base cells. This phenomenon suggests the simultaneous existence of several possible anionic conformations and work is in progress to try to clear up these questions.

Intra-anionic distances and angles

The bond distances and angles are reported in Table 2. In each BO_4 tetrahedron, the bond lengths are identical, the differences being less than the e.s.d.'s. The average B–O length of 1·465 Å is similar to those in other tetracoordinated B compounds, *e.g.* 1·472 Å in $K[B(OAc)_4]$ (Dal Negro, Rossi & Perotti, 1974), 1·48 Å in $Ca[B(OH)_4]_2$ (Simonov, Kazanskaya, Egorov-Tismenko, Gelezin & Belov, 1976), 1·485 Å in

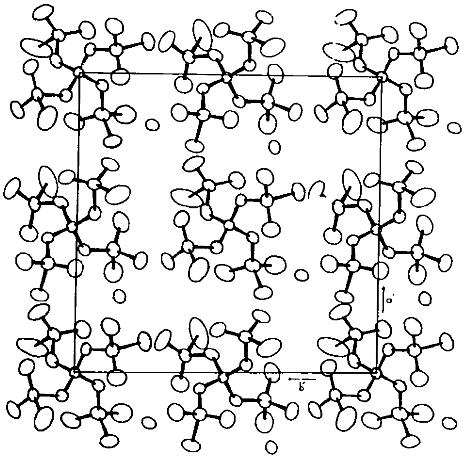

Fig. 2. Projection of the crystal structure down **c**′ of the $I\bar{4}$ pseudocell.

$Ca_2B_6O_{11}$ (Zayakina & Brovkin, 1976), and 1·465 and 1·450 Å in a molecule containing a BO_2NC tetrahedron (Rettig, Trotter, Kliegel & Becker, 1976). The O—B—O angles range from 106·5° for O(19)—B(2)—O(22) to 114·2° for O(4)—B(1)—O(10). These deviations from ideal tetrahedral symmetry are probably due to the steric crowding of the four ligands.

Each SO_3Cl group is linked to the B atom by an O atom so as to form a B—O—S bridge with an average angle of 127·1°; the maximum deviation is 0·8° [for B(1)—O(7)—S(3): 127·9°]. This bridge angle is slightly larger than those in S—O—S and B—O—C bridges: 124·2° in $K_2S_2O_7$ (Lynton & Truter, 1960); 121 and 124° in $(NO_2)_2S_3O_{10}$ (Cruickshank, 1964); 122·8 and 123·9° in $K_2S_5O_{16}$ (De Vries & Mijlhoff, 1969); 121·4° in $B(OCH_3)_3$ (Gundersen, 1976); and 125·13° in $K[B(OAc)_4]$ (Dal Negro, Rossi & Perotti, 1974). It is, on the other hand, much higher than the S—O—C bridge angle: 115·3° in $KSO_4C_2H_5$ (Truter, 1958).

In each anion, we can define two least-squares planes which are almost exactly perpendicular. Each plane contains two S atoms, an O atom and a Cl atom. These two planes intersect along the pseudoaxis $\bar{4}$ (Table 5).

The observed atomic thermal motion of the SO_3Cl ligands agrees well with values resulting from a rigid-body analysis by the **TLS** method (Schomaker & Trueblood, 1968). All the average differences in the U_{ij} range from 0·0012 [S(2) group] to 0·0026 Å² [S(6) group], every r.m.s. ΔU_{ij} value being less than $0{\cdot}6\sigma U_{ij}$ (e.s.d.). This enabled us to correct the bond lengths for librational motion. The correction reduced deviations among the different S—Cl lengths (Table 3) and gave a corrected average value of 2·027 instead of 1·977 Å. This distance is similar to those found in the chlorosulfate anion SO_3Cl^- (2·05 Å in $NOSO_3Cl$; Höhle & Mijlhoff, 1967), or in the SO_3Cl moiety linked by a bridge O atom in the chlorodisulfate anion $S_2O_6Cl^-$ (1·98 Å in $S_3N_2S_2O_6Cl$; Banister, Clarke, Rayment & Shearer, 1974).

In each ligand, the S—O_b length is significantly longer than the S—O_t lengths (respectively 1·565 and 1·442 Å for the average corrected values), a phenomenon explained by Cruickshank's (1961) theory or by EHMO (Extended Hückel Molecular Orbitals) calculations (Bartell, Su & Hsiukang Yow, 1970). The S—O_t lengths are as expected for such a compound. The S—O_b distances are similar to those observed in $HOSO_3^-$ (1·574 and 1·566 Å in $KHSO_4$; Payan & Haser, 1976), and slightly shorter than those reported in $H_3COSO_3^-$ (1·597 and 1·627 Å in $C_{14}H_{22}O_7N_2S$; Simon & Sasvári, 1975), and $H_5C_2OSO_3^-$ (1·603 Å in $KSO_4C_2H_5$; Truter, 1958).

The SO_3Cl tetrahedra also appear to suffer considerable angular distortion, the main feature being the increase of the O_t—S—O_t angles (average 119·5°), whereas the Cl—S—O_b angles are considerably decreased: 100·9° (average). These deformations are important compared with the C_{3v} point symmetry of the same unlinked SO_3Cl group in the ionic $NOSO_3Cl$ (Höhle & Mijlhoff, 1967).

Table 5. *Selected least-squares planes*

Equations have the form $AX + BY + CZ + D = 0$, where X, Y and Z are Cartesian axes lying along **a***, **a*** × **c** and **c** respectively.

	A	*B*	*C*	*D*
Plane 1	−0·2583	−0·1878	0·9476	0·3731
Plane 2	−0·3435	−0·8914	−0·2956	0·2273
Plane 3	−0·4147	−0·8714	0·2622	3·5382
Plane 4	0·2104	−0·3748	−0·9029	6·2592

Deviations from the planes (Å) and selected dihedral angles (°)

Plane 1		Plane 2		Plane 3	
Cl(3)	−0·0046	Cl(2)	0·0051	Cl(6)	0·0874
S(3)	0·0105	S(2)	−0·0084	S(6)	−0·0412
B(1)	0·3731	B(1)	0·2273	B(2)	−0·0868
S(1)	−0·0167	S(4)	0·0124	S(8)	−0·0225
O(2)	0·0124	O(12)	−0·0077	O(24)	0·0694

Plane 4		Angles	
Cl(7)	0·1338	(1)–(2)	88·63
S(7)	−0·0751	(3)–(4)	89·85
B(2)	−0·1562	(1)–(3)	58·72
S(5)	0·0045	(1)–(4)	32·90
O(14)	0·1024		

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The Crystal Structure of Li_3ThF_7

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The crystal structure Li_3ThF_7 has been solved by the Patterson method. Crystal data are: space group $P4/ncc$, $Z = 4$, $a = 6{\cdot}206$, $c = 12{\cdot}940$ Å. The final R value is 0·031 for 507 observed reflexions. The Th coordination polyhedron is unusual for complex fluoride actinides in that it is a square antiprism with a pyramid on one of the square faces.

Introduction

In connexion with a more general study of mixed fluorides of the actinides and of the fluorides of the monovalent elements, we felt it appropriate to undertake a complete crystal structure analysis of Li_3ThF_7. The space group and the number of formula units per cell both suggested that the Th atom would occupy a single site and that the compound might show interesting optical properties.

Experimental

Single crystals have been obtained using the flux growth method (Cousson, Pagès, Cousseins & Vedrine, 1977) and appear in the form of colourless rods and plates.

Lattice parameters and systematic absences were determined by a preliminary study first of single crystals with Weissenberg-camera and precession photographs, then of powder on a focusing goniometer: $a = 6{\cdot}206 \pm 0{\cdot}002$, $c = 12{\cdot}940 \pm 0{\cdot}005$ Å; $hk0$, $h + k = 2n + 1$; $0kl$, $l = 2n + 1$; hhl, $l = 2n + 1$. Cu $K\bar{\alpha}$ and Mo $K\bar{\alpha}$ radiations were used.

The density of the crystals was measured by pycnometry in *o*-xylene, and the value obtained combined with the calculated density leads to $Z = 4$.

The 3/7 stoichiometric ratio for Li/F was confirmed by Borderie, Pinault & Barrandon (1977) using fast γ-ray spectrometry.

A single crystal, 0·002 × 0·0052 × 0·0276 cm, was used for measuring the diffracted intensities with the Nonius CAD-4 four-circle diffractometer of the Centre de Mesures Physiques de Clermont-Ferrand. Data-collection conditions were: Mo $K\bar{\alpha}$ radiation with graphite monochromator, ω–2θ scan, $\theta_{\max} = 50°$, scanning range: $(1 + 0{\cdot}35 \tan \theta)°$, variable scan rate: from 5 to 1·54° min^{-1} for more accurate measurements of intensities. We used the sub-program *FLAT*, which optimizes the measurements in the case of plate-shaped crystals. The row normal to this plate is [001]. All 1411 reflexions out to $2\theta = 100°$ were recorded, 880 of which were unobserved. The intensity of three standard reflexions was checked hourly and the orientation every 100 reflexions (standard reflexions: