Table 3. *The geometry of hydrogen bonds and other short* O(*W*)···O *contacts*

Listed are all *d*[O(*W*)···O] smaller than 3·0 Å. The estimated standard errors are 0·002 Å for *d*[O(*W*)···O], 0·03 Å for *d*[H(*a*/*b*)···O], and 2° for angle at H(*a*/*b*). Values characteristic for hydrogen bonds (two single from O(*W*1) and two bifurcated from O(*W*2)) are marked with an asterisk. All remaining O(*W*)···O contacts are edges of the $AlO_4(OH_2)_2$ octahedron.

I : $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
II: $1+x, y, z$
III: $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
IV: $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$
V: $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$

O(*W*)—H(*a*/*b*)·····O		*d*[O(*W*)···O]	*d*[*H*(*a*/*b*)···O]		Angle at H	
			a	*b*	*a*	*b*
O(*W*1)-H(11/12)···	O(1)	2·605 Å	3·35 Å	2·68 Å	25°	76°
	O(1,III)	2·598*	1·81*	3·16	154*	41
	O(2,I)	2·741	3·36	3·14	38	54
	O(4,IV)	2·623*	2·77	1·88*	71	153*
	O(4,III)	2·607	2·52	3·41	87	7
	O(*W*2)	2·672	2·75	3·20	76	43
O(*W*2)-H(21/22)···	O(1)	2·686 Å	2·62 Å	3·38 Å	85°	31°
	O(1,V)	2·972*	2·95	2·28*	83	139*
	O(2,II)	2·993*	3·46	2·39*	51	128*
	O(2)	2·961*	2·20*	3·50	146*	45
	O(3,II)	2·696	3·28	2·79	42	75
	O(3,V)	2·827*	2·12*	2·82	138*	82
	O(4,III)	2·639	3·44	2·84	20	68
	O(*W*1)	2·672	2·87	3·44	68	22

species (H_2O, OH^- and possibly H_3O^+) along with the same recurrent building units of cation and anion polyhedra.

Bond lengths and bond angles are listed in Table 2. Table 3 gives the geometry of hydrogen bonds and other short O(*W*)···O contacts. Fig. 1 shows the asymmetric unit plus some more symmetry-equivalent atoms, necessary to generate a complete $AlO_4(H_2O)_2$ octahedron besides the PO_4 tetrahedron. Fig. 2 shows the repetition of this unit of structure into a three-dimensional framework.

Despite the highly significant difference of the two Al···O(*W*) distances of 1·892 and 1·953 Å, both water molecules of the structure are true H_2O species. Their hydrogen bonding can be described in terms of two single (*W*1) and two bifurcated (*W*2) hydrogen bonds, none of which is to an oxygen atom of the same $AlO_4(OH_2)_2$ octahedron.

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Li_2ZrF_6

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Abstract. Hexagonal, $P\bar{3}1m$, $a_o=4{\cdot}9733$ (9), $c_o=4{\cdot}658$ (1) Å, 24·5°C, $Z=1$, $\varrho_x=3{\cdot}646$ g cm^{-3}. Six (Zr–F) at 2·016 (1) Å; 6(Li–F) at 2·0246 (9) Å. Each ZrF_6^{2-} ion is coordinated by $12Li^+$ ions; Zr–Li = 3·6971 (5) Å. Automated diffractometer data, 2θ scan, Si–Li detector, Mo $K\alpha$ radiation.

Introduction. The crystal structure of Li_2ZrF_6 was partially determined by Hoppe & Dahne (1960) with some ambiguity as to the position of the Li ions. This structural determination resolves that ambiguity and presents more precise structural parameters.

A crystal of Li_2ZrF_6 grown from a melt of the stoichiometric composition was ground to an ellipsoid (0·277 × 0·585 × 0·255 mm) for data collection on an automated four-circle Picker goniostat equipped with a Si–Li detector. A 400 eV detector window eliminated Mo $K\beta$ radiation and Zr fluorescence.

Lattice parameters were determined by the least-squares adjustment of 29 Mo $K\alpha_1$ reflections; a_o = 4·9733 (9) and c_o = 4·658 (1) Å at 24·5 °C, λ = 0·70926 Å. The Laue symmetry is $\bar{3}m$ and there are no extinction conditions. The mirror plane was parallel to [110] and the preceding conditions are consistent with space groups $P\bar{3}1m$, $P3m1$ and $P321$.

The θ–2θ scan technique was used to measure 368 independent reflections to 90° in 2θ. Each reflection was step-scanned at intervals of 0·05° 2θ with a 3 sec count at each step for a total of 2·4° 2θ. The background was counted for 30 sec on each side of the reflection. Lorentz, polarization and absorption corrections were made for each reflection (μ = 27·601 cm^{-1}, absorption correction range 0·50–0·59). The total count range of the 004 standard reflection is 12173 to 19103.

Initial parameters for Zr^{4+} and F^- in $P\bar{3}1m$ were taken from Hoppe & Dahne (1960). The scattering factors for the ions are from Cromer & Waber (1965) and

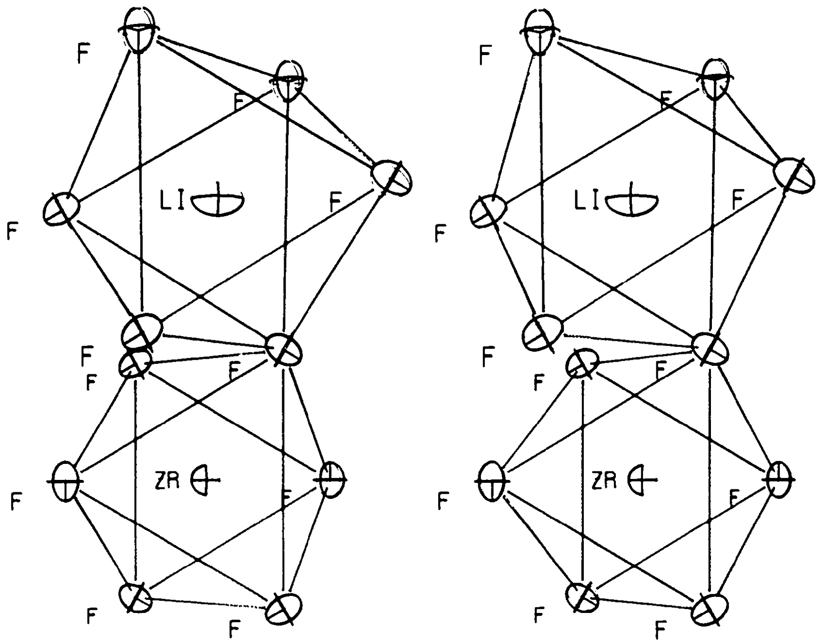

Fig. 1. One asymmetric unit of Li$_2$ZrF$_6$. View parallel to $\mathbf{c}_0$.

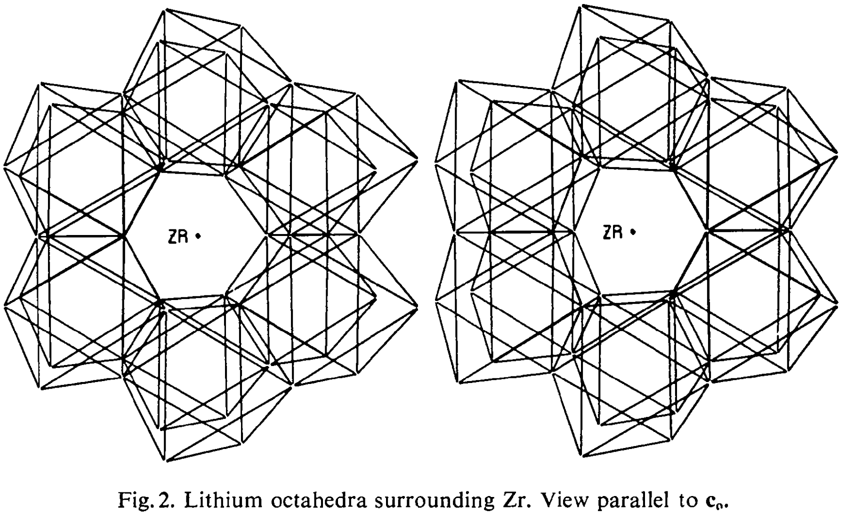

Fig. 2. Lithium octahedra surrounding Zr. View parallel to $\mathbf{c}_0$.

the anomalous dispersion scattering factor for Zr is from Cromer (1965). The structure was determined by iterative least-square adjustment with a modification of *ORFLS* (Busing, Martin & Levy, 1962). The position of the Li ion was easily determined from a difference map.

Discussion. The structure proposed by Hoppe & Dahne (1960) is essentially correct and the Li ions are on positions 2(*d*); $\frac{1}{3},\frac{2}{3},\frac{1}{2}$. The atomic parameters are listed in Table 1.† Figs. 1 and 2 are respectively one asymmetrical unit and the lithium coordination polyhedra surrounding one Zr ion, both views parallel to **c**. Each Zr^{4+} is coordinated by $6F^-$ at the corners of a regular octahedron; Zr–F = 2·016 (1) Å. Similarly each Li^+ is coordinated by $6F^-$ at 2·0246 (9) Å. Each corner of the ZrF_6^{2-} ion is shared by two Li^+ octahedra that each share edges with one another, as illustrated by Fig. 3, with a total of $12Li^+$ ions coordinating each ZrF_6^{2-} ion; Li–Zr = 3·6971 (5) Å.

Table 1. *Atomic and thermal parameters* (× 10^4)

$\varrho_x = 3{\cdot}646$ g cm^{-3}, $R(F_o^2) = 0{\cdot}0605$

Coefficients in the temperature factor:

$$\exp\,[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]\,.$$

The number in parentheses is the standard error in terms of the last significant digit as derived from the variance-covariance matrix.

	Li	Zr	F
Wyckoff notation	2(*d*)	1(*a*)	6(*k*)
x	$\frac{1}{3}$	0	0·6724 (3)
y	$\frac{2}{3}$	0	0
z	$\frac{1}{2}$	0	0·2550 (3)
β_{11}	206 (20)	121 (1)	180 (3)
β_{22}	β_{11}	β_{11}	195 (5)
β_{33}	200 (24)	95 (1)	163 (3)
β_{12}	$\frac{1}{2}\beta_{11}$	$\frac{1}{2}\beta_{11}$	$\frac{1}{2}\beta_{22}$
β_{13}	0	0	30 (3)
β_{23}	0	0	0

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† A table of structure factors has been deposited with the National Lending Library, England, as Supplementary Publication No. SUP 30154. Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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Thioxanthene

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Abstract. $C_{13}H_{10}S$, orthorhombic, $P2_12_12_1$, $a = 21{\cdot}096$ (4), $b = 7{\cdot}804$ (1), $c = 6{\cdot}049$ (1) Å, $Z = 4$, $D_c = 1{\cdot}326$, $D_x = 1{\cdot}33$ g cm^{-3} (by suspension). The C–S bond lengths are 1·781 (6) and 1·759 (6) Å, the CSC angle is 99·2 (3)°, and the angle between the phenylene planes is 135·3 (1)°.

Introduction. Slow evaporation of thioxanthene–methylene chloride–octane solution yielded colorless crystals. The crystal selected for data collection was bounded by the faces {100}, {110}, {$\bar{1}$10}, and {001}. Distances from the center of mass to these face planes were 0·36, 0·22, 0·27, and 0·36 mm (all ±0·01 mm), respectively. The crystal was mounted with **c** parallel to the φ axis of the diffractometer. Unit-cell parameters and intensity data were obtained on a G. E. XRD-5 manually operated quarter-circle diffractometer with Zr-filtered Mo $K\alpha$ ($\lambda = 0{\cdot}71069$ Å) radiation and a scintillation detection system. Systematic absences of *h*00 with *h* odd, 0*k*0 with *k* odd, 00*l* with *l* odd indicated space group $P2_12_12_1$ (No. 19). No absorption or extinction corrections were made. The linear absorption coefficient is 2·72 cm^{-1}; calculated transmission coefficients for *F* varied from 0·97 to 0·94.

Data collection involved θ–2θ scans of 2° at 2°/min, with 10-sec stationary backgrounds at each end of the scans. All 1062 unique reflections with $0° < 2\theta < 50°$ were examined; 768 had $I \geq 2\sigma(I)$ and these were used for the refinement. Four reflections measured periodically during the two days of data collection varied by less than 2σ and thereby indicated crystal and electronic stability.

The standard deviations for *I* were calculated by $\sigma(I) = (S + 9B + 0{\cdot}0016I^2)^{1/2}$ (where S = scan count, B = sum of the background counts, and $I = S - 3B$), except for a small number of reflections for which the two background readings differed by more than twice the calculated σ owing to tailing of the reflection peak. For