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The Crystal Structure of $Rb_5Zr_4F_{21}$

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The complex fluoride $Rb_5Zr_4F_{21}$ crystallizes with space group $P2_1$; $a_0=11{\cdot}520$ (5), $b_0=11{\cdot}222$ (5), $c_0=7{\cdot}868$ (2) Å and cos $\beta=-0{\cdot}1445$ (3). Calculated density $=3{\cdot}930$ g.cm^{-3} and $Z=2$. The structure was solved by a tangent-formula procedure and was refined by Fourier and least-squares methods to a final discrepancy index (R) of 0·0508 for 1376 observed Cu $K\alpha_1$ reflections. The F^- coordination polyhedra are different for each of the four crystallographically independent Zr ions. Seven F^- ions are nearest neighbors to Zr(1) at the corners of a pentagonal bipyramid, and the interatomic distances are 1·99 (2) to 2·20 (2) Å. The second Zr ion has eight nearest neighbor F^- ions [1·98 (2) to 2·24 (2) Å] at the corners of an irregular antiprism. Zr(3) is octahedrally coordinated by $6F^-$ at distances of 1·90 (2) to 2·10 (2) Å. The fourth Zr ion has seven nearest neighbor F^- ions at the corners of an irregular antiprism with one corner missing. Interatomic distances Zr(4)–F are 1·95 (2) to 2·19 (2) Å. The Rb–F distances range from 2·68 (2) to 3·21 (3) Å. The structure is composed of cross-linked chains of Zr–F polyhedra. Chains are connected by Zr(2)–Zr(4) edge-sharing polyhedra and the space between the polyhedra is filled with Rb ions. Integrated intensities were measured by the θ–2θ scan technique using unfiltered Cu $K\alpha$ radiation.

Experimental

The compound $Rb_5Zr_4F_{21}$ melts congruently at 445 °C (Thoma, 1959). Crystals picked from an ingot of the stoichiometric composition were ground to approximately spherical shape in an air-driven race. An ellipsoidal crystal of dimensions $0{\cdot}26\times0{\cdot}364\times0{\cdot}2912$ mm was mounted on a computer-controlled Picker four-circle goniostat equipped with a scintillation counter detector. Independent reflections hkl, h and $k\geq0$ and all l were measured by the θ–2θ scan technique using unfiltered Cu $K\alpha$ radiation. Each reflection was step-scanned in steps of 0·01° 2θ starting 0·75° before the calculated Cu $K\alpha_1$ position and ending 0·75° beyond the the calculated Cu $K\alpha_2$ position. Each step was counted for 1 second and the background on each side of the peak was counted for 60 seconds. One reflection, $13\bar{1}$, chosen as a standard reflection, was remeasured at intervals of 20 reflections. The net-count range of $13\bar{1}$ was 124700 to 121700. The 1403 independent reflections were corrected for Lorentz and polarization effects and absorption ($\mu=358{\cdot}7$ cm^{-1}). The maximum and minimum range of absorption correction was, respectively, 0·05626 and 0·00541. Conditions, for reflection $0k0=2n$ and the diffraction symmetry $2/m$, are consistent with space groups $P2_1$ and $P2_1/m$. A statistical analysis of the normalized structure factors established that the correct space group is $P2_1$, and this is confirmed by the structure. No piezoelectric tests were made on the crystals.

Unit-cell parameters were determined by a least-squares adjustment of 12 (80–100° 2θ) Cu $K\beta$ reflections (Cu $K\beta=1{\cdot}39217$ Å, $T=24$°C). Cell parameters are; $a_0=11{\cdot}520$ (5), $b_0=11{\cdot}222$ (5), and $c_0=7{\cdot}868$ (2) Å; cos $\beta=-0{\cdot}1445$ (3), ($\beta=98{\cdot}3°$). There are two formula weights per unit cell, and the calculated density is 3·930 gm.cm^{-3}.

Initial positions of the heavy atoms were determined from a Fourier map plotted from normalized structure factors whose phases were determined by the tangent-formula method using program *PHASEM* (Drew,

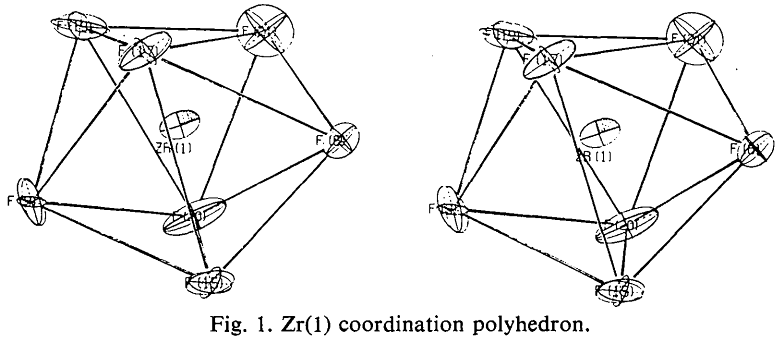

Fig. 1. Zr(1) coordination polyhedron.

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Table 1. *Atomic parameters and temperature factors*, $Rb_5Zr_4F_{21}$

Standard errors in parentheses, corresponding to the last significant digit, are given by the variance–covariance matrix. Coefficients in the temperature factor of the form:

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

Arbitrary value of *y* for Zr(1) to establish origin on 2_1 axis.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
ZR(1)	0.5932(2)	0.3000(0)	0.7830(3)	0.0043(2)	0.0026(2)	0.0044(4)	-0.0000(2)	0.0016(2)	0.0000(2)
ZR(2)	0.7721(2)	0.1589(3)	0.4964(3)	0.0036(2)	0.0028(2)	0.0046(4)	-0.0001(2)	0.0018(2)	-0.0001(2)
ZR(3)	0.0928(2)	0.1925(3)	0.8252(3)	0.0040(2)	0.0031(2)	0.0044(4)	0.0000(2)	0.0015(2)	0.0003(2)
ZR(4)	0.2758(2)	0.3401(3)	0.4648(3)	0.0039(2)	0.0029(2)	0.0046(4)	0.0002(2)	0.0018(2)	0.0004(2)
RB(1)	0.6091(3)	0.4758(4)	0.2818(4)	0.0051(2)	0.0070(4)	0.0076(5)	-0.0002(2)	0.0016(3)	0.0013(3)
RB(2)	0.4555(2)	0.1388(4)	0.1914(4)	0.0053(2)	0.0048(3)	0.0087(5)	0.0001(2)	0.0032(3)	-0.0002(3)
RB(3)	0.9057(3)	0.3282(4)	0.1650(4)	0.0059(2)	0.0067(3)	0.0093(6)	0.0006(2)	0.0034(3)	0.0012(3)
RB(4)	0.7455(3)	-0.0097(4)	0.0234(4)	0.0073(2)	0.0056(3)	0.0078(5)	0.0019(2)	0.0009(3)	-0.0005(3)
RB(5)	0.1152(3)	0.0194(4)	0.3139(4)	0.0061(2)	0.0044(3)	0.0098(6)	-0.0000(2)	0.0001(3)	0.0007(3)
F(1)	0.675(1)	-0.002(2)	0.390(2)	0.005(1)	0.004(2)	0.005(3)	-0.001(1)	0.000(1)	0.001(2)
F(2)	0.012(2)	0.109(2)	-0.017(2)	0.009(2)	0.006(2)	0.008(3)	-0.002(1)	0.005(2)	0.002(2)
F(3)	0.234(2)	0.206(2)	-0.007(3)	0.009(2)	0.009(2)	0.018(5)	0.001(2)	-0.001(2)	-0.002(3)
F(4)	0.801(1)	0.005(2)	0.649(2)	0.007(1)	0.005(2)	0.006(3)	-0.002(1)	-0.000(2)	0.003(2)
F(5)	0.034(1)	0.348(2)	0.897(2)	0.007(1)	0.004(2)	0.011(3)	-0.000(1)	0.005(2)	-0.001(2)
F(6)	0.758(1)	0.221(2)	0.763(2)	0.003(1)	0.008(2)	0.007(3)	0.001(1)	0.002(1)	-0.002(2)
F(7)	0.154(2)	0.057(2)	0.715(2)	0.010(2)	0.004(2)	0.015(4)	0.002(1)	0.005(2)	-0.001(2)
F(8)	0.179(2)	0.306(2)	0.672(2)	0.009(2)	0.004(1)	0.010(3)	-0.000(1)	0.007(2)	-0.003(2)
F(9)	0.420(1)	0.294(2)	0.656(2)	0.002(1)	0.005(2)	0.011(3)	0.002(1)	-0.002(1)	0.002(2)
F(10)	0.690(1)	0.206(2)	0.260(2)	0.006(1)	0.005(2)	0.008(3)	0.000(1)	0.002(2)	0.004(2)
F(11)	0.953(1)	0.183(2)	0.635(2)	0.004(1)	0.007(2)	0.009(3)	-0.001(1)	0.002(2)	0.000(2)
F(12)	0.125(2)	0.293(2)	0.325(3)	0.005(1)	0.005(2)	0.024(5)	-0.002(1)	-0.006(2)	-0.001(3)
F(13)	0.382(1)	0.370(2)	0.298(2)	0.007(1)	0.003(1)	0.009(3)	-0.000(1)	0.005(2)	-0.002(2)
F(14)	0.883(1)	0.097(2)	0.347(2)	0.004(1)	0.007(2)	0.011(3)	-0.000(1)	0.003(2)	0.000(2)
F(15)	0.599(1)	0.199(2)	0.545(2)	0.005(1)	0.005(1)	0.006(3)	-0.000(1)	0.001(1)	-0.003(2)
F(16)	0.302(1)	0.168(2)	0.434(2)	0.007(1)	0.003(2)	0.010(3)	0.000(1)	0.002(2)	-0.001(2)
F(17)	0.560(1)	0.145(2)	0.888(2)	0.007(1)	0.003(1)	0.008(3)	0.001(1)	0.004(2)	0.002(2)
F(18)	0.810(1)	0.331(2)	0.481(2)	0.008(1)	0.003(2)	0.012(3)	-0.001(1)	0.003(2)	-0.001(2)
F(19)	0.497(2)	0.377(2)	0.944(2)	0.009(2)	0.010(2)	0.004(3)	0.000(2)	-0.001(2)	-0.001(2)
F(20)	0.604(2)	0.438(2)	0.625(2)	0.013(2)	0.002(1)	0.009(3)	0.000(1)	0.007(2)	0.001(2)
F(21)	0.712(2)	0.398(2)	0.944(3)	0.009(2)	0.005(2)	0.017(4)	-0.001(1)	0.001(2)	-0.004(2)

1967). Normalized structure factors were calculated by a least-squares method of Levy, Thiessen & Brown (1970). Positions of the fluorine atoms were determined from Fourier and difference Fourier maps. The structure was refined by iterative least-squares adjustment using a modification of computer program *ORFLS* (Busing, Martin & Levy, 1962). The quantity minimized by the least-squares program was $\sum w||F_o^2|-|F_c^2||$ with weights, w, equal to the reciprocals of the variances estimated from the empirical equation:

$$\sigma^2(F_o^2)=\{T+B+[0\cdot03(T-B)]^2\}/[A(\mathrm{Lp})^2]\,,$$

where T = total counts, B = background counts, A = absorption correction, and Lp = Lorentz and polarization corrections (Brown & Levy, 1964). Scattering factors for the ions were taken from Cromer & Waber (1965), and the anomalous dispersion terms for Rb and Zr for Cu $K\alpha$ radiation were taken from Cromer (1965). Discrepancy indices were:

$$R^1=\sum||F_o^2|-|F_c^2||/\sum|F_o^2|=0\cdot1014 \text{ for 1376 reflections} > \sigma$$
$$=0\cdot1017 \text{ for all reflections.}$$
$$R^2=\sum||F_o|-|F_c||/\sum|F_o|\;=0\cdot0508 \text{ for 1376 reflections} > \sigma$$
$$=0\cdot0521 \text{ for all reflections.}$$

The standard deviation of an observation of unit weight $[\sum w(F_o-F_c)^2/(n_o-n_v)]^{1/2}$ is 2·637, where n_o is the number of reflections (1376) and n_v is the number of variables (271). Atomic parameters and temperature factors are listed in Table 1; interatomic distances are given in Table 2, and the observed and calculated structure factors are shown in Table 3. An extinction

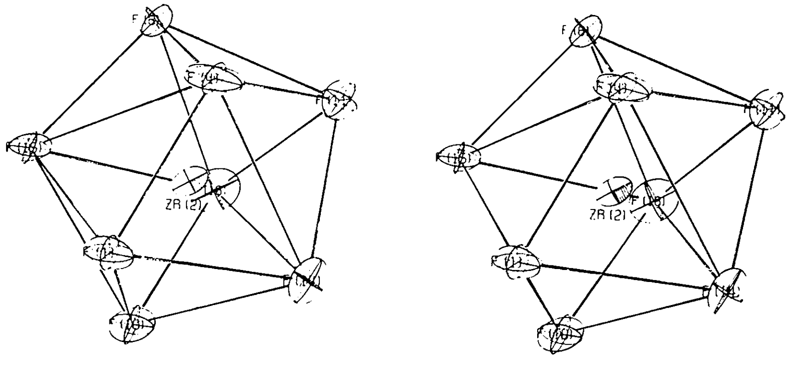

Fig. 2. Zr(2) coordination polyhedron.

Table 2. *Interatomic distances for* $Rb_5Zr_4F_{21}$ *in* Å

Zr(1)-F(17)	1.99(2)	Zr(1)-F(19)	1.99(2)	Zr(1)-F(20)	2.00(2)
Zr(1)-F(21)	2.04(2)	Zr(1)-F(9)	2.10(2)	Zr(1)-F(6)	2.12(2)
Zr(1)-F(15)	2.20(2)	Zr(2)-F(14)	1.98(2)	Zr(2)-F(18)	1.99(2)
Zr(2)-F(10)	2.03(2)	Zr(2)-F(4)	2.10(2)	Zr(2)-F(15)	2.13(2)
Zr(2)-F(1)	2.22(2)	Zr(2)-F(11)	2.22(2)	Zr(2)-F(6)	2.24(2)
Zr(3)-F(2)	1.90(2)	Zr(3)-F(7)	1.93(2)	Zr(3)-F(3)	1.95(2)
Zr(3)-F(5)	1.99(2)	Zr(3)-F(11)	2.04(2)	Zr(3)-F(8)	2.10(2)
Zr(4)-F(13)	1.95(2)	Zr(4)-F(16)	1.98(2)	Zr(4)-F(12)	1.99(2)
Zr(4)-F(8)	2.14(2)	Zr(4)-F(9)	2.14(2)	Zr(4)-F(1)	2.14(2)
Zr(4)-F(4)	2.19(2)	Rb(1)-F(20)	2.74(2)	Rb(1)-F(7)	2.88(2)
Rb(1)-F(13)	2.90(2)	Rb(1)-F(17)	2.90(2)	Rb(1)-F(19)	3.00(2)
Rb(1)-F(18)	3.07(2)	Rb(1)-F(16)	3.17(2)	Rb(1)-F(10)	3.18(2)
Rb(1)-F(21)	3.19(2)	Rb(2)-F(10)	2.73(2)	Rb(2)-F(16)	2.80(2)
Rb(2)-F(20)	2.81(2)	Rb(2)-F(17)	2.82(2)	Rb(2)-F(3)	2.89(2)
Rb(2)-F(13)	2.90(2)	Rb(2)-F(15)	3.10(2)	Rb(2)-F(1)	3.19(2)
Rb(2)-F(19)	3.19(2)	Rb(3)-F(12)	2.68(2)	Rb(3)-F(21)	2.74(3)
Rb(3)-F(5)	2.75(2)	Rb(3)-F(7)	2.86(3)	Rb(3)-F(18	2.86(2)
Rb(3)-F(14)	2.99(2)	Rb(3)-F(10)	3.02(2)	Rb(3)-F(2)	3.17(3)
Rb(4)-F(17)	2.84(2)	Rb(4)-F(5)	2.99(2)	Rb(4)-F(14)	3.04(2)
Rb(4)-F(13)	3.05(2)	Rb(4)-F(1)	3.11(2)	Rb(4)-F(4)	3.11(2)
Rb(4)-F(19)	3.12(3)	Rb(4)-F(10)	3.17(2)	Rb(4)-F(8)	3.19(2)
Rb(4)-F(3)	3.21(3)	Rb(5)-F(18)	2.72(2)	Rb(5)-F(16)	2.77(2)
Rb(5)-F(14)	2.86(2)	Rb(5)-F(2)	2.89(2)	Rb(5)-F(5)	2.93(2)
Rb(5)-F(12)	3.09(3)	Rb(5)-F(7)	3.15(2)	F(1)-F(10)	2.56(3)
F(1)-F(4)	2.32(2)	F(1)-F(9)	2.55(3)	F(1)-F(8)	2.82(3)
F(1)-F(14)	2.70(3)	F(1)-F(15)	2.76(3)	F(2)-F(5)	2.78(3)
F(1)-F(13)	3.00(3)	F(2)-F(3)	2.77(3)	F(3)-F(8)	2.75(3)
F(2)-F(11)	2.84(3)	F(2)-F(7)	2.91(3)	F(4)-F(12)	2.52(3)
F(3)-F(7)	2.80(3)	F(3)-F(5)	2.82(3)	F(4)-F(13)	2.67(3)
F(4)-F(6)	2.66(3)	F(4)-F(11)	2.67(3)	F(6)-F(21)	2.54(3)
F(4)-F(14)	2.87(3)	F(5)-F(9)	2.65(2)	F(6)-F(17)	2.75(2)
F(5)-F(11)	2.83(3)	F(6)-F(15)	2.34(2)	F(8)-F(12)	2.72(3)
F(6)-F(11)	2.62(2)	F(6)-F(19)	2.68(3)	F(8)-F(16)	2.95(3)
F(7)-F(11)	2.71(3)	F(7)-F(8)	2.83(3)	F(9)-F(15)	2.58(3)
F(8)-F(9)	2.80(3)	F(8)-F(11)	2.93(3)	F(9)-F(17)	2.80(3)
F(9)-F(19)	2.49(3)	F(9)-F(16)	2.50(3)	F(10)-F(14)	2.54(3)
F(9)-F(20)	2.71(3)	F(10)-F(18)	2.49(3)	F(11)-F(18)	2.52(3)
F(9)-F(13)	2.92(3)	F(11)-F(14)	2.49(3)	F(14)-F(18)	3.00(3)
F(10)-F(15)	2.61(2)	F(13)-F(16)	2.73(3)	F(15)-F(18)	2.95(3)
F(12)-F(16)	2.53(3)	F(15)-F(17)	2.97(3)	F(19)-F(21)	2.48(3)
F(15)-F(20)	2.76(3)	F(17)-F(19)	2.75(3)		
F(16)-F(20)	2.85(3)				
F(20)-F(21)	2.67(3)				

correction was applied to F_c by Zachariasen's (1967, 1968) method. The range of extinction corrections was 0·7797–1·000 and Zachariasen's $r^*=0{\cdot}0169$ (2) Å. The absolute configuration of the crystal could not be determined by Hamilton's (1965) significance test on the discrepancy indices. Ratio $R_2(+\Delta f'')/R_2(-\Delta f'')$ for 1376 reflections $>\sigma$ is 1·002, which is not significant at the 0·005 significance level for a one-dimensional hypothesis and 1105 degrees of freedom [$R_2(-\Delta f'')=0{\cdot}0507$]. The same argument holds for any of the other discrepancy indices. Dr C. K. Johnson suggested that a similar test of absolute configuration could be made using a modification of *ORFLS* (Busing, Martin & Levy, 1962) which allows one to make $\Delta f''$ a variable parameter in the least-squares refinement. All variable parameters of each of the two models, $+\Delta f''$ and $-\Delta f''$, were refined first and subsequently $\Delta f''$ was varied. In both cases, the least-squares refinement diverges, and $\Delta f''$ expands rapidly to a large positive number. The standard error for $\Delta f''$ is 0·7 in both cases: *cf.* $\Delta f''(\mathrm{Rb})=1{\cdot}81$e and $\Delta f''(\mathrm{Zr})=2{\cdot}42$e for Cu $K\alpha$ (Cromer, 1965).

Table 3. *The observed and calculated structure factors, and phase angles for* $Rb_5Zr_4F_{21}$

ALPHA = phase angle $\alpha \times 10$

L	FOBS	FCAL	ALPHA	L	FOBS	FCAL	ALPHA	L	FOBS	FCAL	ALPHA	L	FOBS	FCAL	ALPHA	L	FOBS	FCAL	ALPHA	L	FOBS	FCAL	ALPHA	L	FOBS	FCAL	ALPHA
	0 0 L			5	64	67	1752	3	47	44	1519	-4	11	4	1152		2 11 L			-6	73	69	762	-4	105	98	1369
1	51	55	1753	6	110	120	39	4	44	43	300	-3	148	132	1424	-3	86	80	198	-5	26	25	105	-3	155	144	1622
2	74	79	1779	7	34	36	33	5	29	15	1240	-2	23	23	1188	-2	24	21	317	-4	123	114	577	-2	157	154	251
3	63	65	1708		1 1 L			6	54	57	1049	-1	69	60	51	-1	46	45	832	-3	32	31	862	-1	205	217	54
4	131	138	58	-8	65	62	582		1 8 L			0	51	46	404	0	111	109	1695	-2	93	90	913	0	58	62	1129
5	22	8	36	-7	94	86	1542	-6	72	68	1635	1	70	66	1169	1	26	26	313	-1	77	79	1085	1	49	54	420
6	156	159	42	-6	70	66	953	-5	123	110	1191	2	44	43	1350	2	78	78	198	0	22	17	1618	2	62	68	1498
7	26	26	1713	-5	37	33	880	-4	72	67	729	3	64	67	1266	3	37	38	899	1	37	37	977	3	36	38	296
	0 1 L			-4	190	164	623	-3	48	45	535	4	50	51	554		2 12 L			2	95	99	818	4	12	16	324
1	43	37	275	-3	63	60	1559	-2	56	53	469	5	91	94	475	-1	56	56	239	3	51	53	565	5	104	112	151
2	62	58	41	-2	110	97	1051	-1	6	7	1250	6	36	39	931	0	73	73	1792	4	114	121	1183	6	21	16	189
3	44	44	1112	-1	53	45	1009	0	58	56	1481		2 4 L			1	17	16	236	5	16	15	1426		4 3 L		
4	56	57	533	0	27	32	453	1	136	136	1130	-8	61	61	687		3 0 L				3 7 L			-9	35	34	1650
5	13	13	1534	1	22	18	1177	2	20	11	621	-7	18	15	162	-9	19	23	1736	-7	44	46	608	-7	45	45	1521
6	122	133	510	2	250	240	870	3	119	119	601	-6	52	45	1792	-7	8	12	45	-6	79	74	1363	-6	41	39	874
7	42	46	1602	3	74	73	1587	4	36	35	171	-5	128	114	1503	-6	19	19	174	-5	64	63	243	-5	111	102	641
	0 2 L			4	72	75	704	5	49	54	448	-4	101	91	349	-5	59	55	8	-4	47	44	716	-4	23	21	1475
0	97	89	1780	5	37	37	1739	6	38	42	1103	-3	126	114	1470	-4	96	89	30	-3	19	15	991	-3	50	47	1521
1	34	31	154	6	107	117	943		1 9 L			-2	20	20	1759	-3	0	2	574	-2	96	94	1033	-2	52	47	1599
2	20	16	190		1 2 L			-5	67	62	1418	-1	21	16	1496	-2	17	17	111	-1	29	34	76	-1	42	39	1321
3	250	260	47	-9	52	51	1042	-4	50	45	753	0	70	67	1548	-1	7	14	1740	0	99	102	624	0	27	25	439
4	12	6	1144	-7	53	51	1233	-3	61	56	579	1	289	288	1670	0	41	46	1774	1	103	104	745	1	94	99	294
5	60	64	1665	-6	44	41	1668	-2	49	47	1013	2	99	99	237	1	0	6	260	2	73	76	968	2	57	59	1150
6	61	66	1236	-5	135	124	1479	-1	104	97	1121	3	70	72	1409	2	78	82	0	3	62	61	906	3	60	64	1759
7	72	76	106	-4	90	82	630	0	38	36	1636	4	38	40	1304	3	49	50	56	4	67	69	642	4	56	55	588
	0 3 L			-3	103	95	692	1	61	56	455	5	83	86	1545	4	40	41	1771	5	57	60	680	5	119	128	736
1	131	119	1763	-2	31	29	802	2	42	40	820	6	37	38	133	5	23	21	1762	6	63	68	1196		4 4 L		
2	14	14	0	-1	78	64	1257	3	81	81	1182		2 5 L			6	139	145	1748		3 8 L			-8	38	41	199
3	142	146	530	0	57	50	1144	4	54	55	1410	-7	58	58	918		3 1 L			-6	52	51	818	-7	90	90	793
4	64	67	255	1	35	36	1244	5	75	78	759	-6	140	127	1409	-8	19	17	706	-5	71	69	1450	-6	59	59	999
5	41	42	714	2	23	22	1165		1 10 L			-5	105	97	41	-7	56	54	747	-4	86	81	993	-5	39	38	126
6	45	45	927	3	103	105	718	-5	17	12	747	-4	76	69	1051	-6	114	109	1538	-3	41	40	437	-4	44	42	1233
	0 4 L			4	33	35	315	-4	21	20	1289	-3	84	78	162	-5	72	69	180	-2	69	69	120	-3	14	12	522
0	0	6	1462	5	99	107	227	-3	56	51	1480	-2	50	47	823	-4	138	125	865	-1	136	139	785	-2	77	73	94
1	38	33	295	6	20	17	937	-2	36	31	905	-1	82	78	334	-3	63	53	733	0	75	74	902	-1	123	129	41
2	124	121	1491		1 3 L			-1	41	31	893	0	164	161	1626	-2	65	63	1004	1	91	90	1106	0	134	141	1456
3	191	193	97	-8	18	13	65	0	35	31	502	1	56	54	138	-1	41	39	1219	2	37	38	1691	1	53	55	184
4	21	20	624	-7	104	86	803	1	43	41	602	2	89	86	23	0	232	250	907	3	35	35	1120	2	45	49	1051
5	8	12	458	-6	53	47	755	2	16	7	1525	3	66	70	1288	1	47	49	672	4	16	22	378	3	75	81	173
6	25	21	1479	-5	174	160	1021	3	47	48	622	4	72	74	1218	2	52	54	267	5	33	37	520	4	36	41	1543
	0 5 L			-4	144	132	981	4	40	41	1675	5	33	35	1454	3	27	26	888		3 9 L			5	90	96	75
1	49	46	405	-3	139	125	562		1 11 L				2 6 L			4	66	72	1043	-5	29	27	728		4 5 L		
2	54	51	708	-2	66	61	731	-3	37	33	1134	-7	22	19	1707	5	19	12	587	-4	6	10	1149	-7	55	56	1591
3	38	42	393	-1	417	360	915	-2	37	36	1694	-6	88	81	1375	6	89	94	1061	-3	79	74	800	-6	80	77	763
4	136	141	1525	0	49	41	1072	-1	10	15	858	-5	63	56	334		3 2 L			-2	37	37	518	-5	123	116	1738
5	60	62	687	1	44	43	8	0	20	17	1718	-4	54	48	514	-8	51	54	0	-1	67	70	824	-4	73	68	414
6	39	39	843	2	89	86	648	1	27	25	1343	-3	9	14	1691	-7	108	107	418	0	41	42	1189	-3	69	69	1021
	0 6 L			3	115	117	1002	2	40	41	904	-2	274	261	1714	-6	95	92	749	1	60	63	614	-2	142	143	191
0	326	312	47	4	56	59	1800	3	39	37	914	-1	84	81	89	-5	52	50	1445	2	59	60	473	-1	111	113	1745
1	67	62	1660	5	203	218	807		1 12 L			0	96	91	1449	-4	61	54	972	3	84	86	936	0	17	21	618
2	56	53	551	6	42	43	681	-2	99	97	1128	1	107	109	133	-3	143	129	675	4	27	26	1203	1	20	22	1712
3	102	100	1749		1 4 L			-1	27	28	958	2	72	71	1497	-2	83	81	421	5	44	45	1306	2	56	58	274
4	82	79	190	-8	71	69	1588	0	78	75	654	3	40	42	642	-1	63	62	581		3 10 L			3	43	41	1713
5	41	44	1096	-7	98	91	1203	1	22	20	514	4	179	190	1739	0	86	89	782	-4	38	33	570	4	50	54	648
6	98	100	107	-6	31	34	186		2 0 L			5	36	37	306	1	21	14	703	-3	53	53	1079	5	20	19	1233
	0 7 L			-5	66	60	1688	-8	35	36	1770		2 7 L			2	18	25	1619	-2	34	33	1517		4 6 L		
1	12	10	1257	-4	55	49	1050	-7	61	61	1770	-7	52	50	1013	3	82	87	1784	-1	30	30	658	-7	43	43	1548
2	64	62	567	-3	67	59	1671	-6	100	95	1722	-6	23	21	319	4	17	16	123	0	32	28	682	-6	35	33	1476
3	25	23	1460	-2	45	40	1678	-5	116	108	46	-5	24	23	1540	5	52	56	44	1	38	36	759	-5	40	35	323
4	32	29	1759	-1	34	31	1075	-4	85	79	51	-4	58	55	552	6	34	33	832	2	47	46	728	-4	97	91	64
5	37	39	1341	0	66	61	606	-3	69	66	1800	-3	66	64	1541		3 3 L			3	20	20	1272	-3	3	4	1497
6	84	88	256	1	62	57	534	-2	416	362	1765	-2	127	118	35	-8	41	42	790	4	20	20	457	-2	65	64	56
7	39	40	1185	2	19	9	1792	-1	40	41	54	-1	48	43	1161	-7	67	67	844		3 11 L			-1	96	100	1729
	0 8 L			3	92	91	762	0	62	70	1761	0	83	81	1705	-6	110	104	980	-3	9	14	1580	0	28	25	185
0	44	41	1717	4	25	25	1789	1	217	226	24	1	17	21	56	-5	80	73	809	-2	29	29	319	1	29	29	905
1	45	42	370	5	114	120	521	2	46	46	1699	2	92	94	11	-4	25	22	1665	-1	17	14	702	2	197	213	73
2	50	50	296	6	21	24	365	3	4	2	73	3	45	45	1282	-3	300	282	902	0	44	42	928	3	40	42	1627
3	105	104	14		1 5 L			4	311	324	1763	4	78	80	1457	-2	58	57	1015	1	44	44	811	4	41	45	620
4	11	14	174	-7	60	56	252	5	59	56	73	5	28	25	256	-1	66	63	1275	2	15	11	1250	5	47	49	1587
5	33	31	1550	-6	70	62	1142	6	36	39	61	6	38	42	976	0	61	61	884	3	13	11	572		4 7 L		
6	22	21	1284	-5	46	41	796		2 1 L				2 8 L			1	20	19	1100		4 0 L			-6	78	77	796
	0 9 L			-4	132	122	1014	-8	65	62	339	-6	40	35	886	2	13	7	463	-8	51	52	65	-5	56	52	475
1	144	142	1643	-3	76	71	822	-7	29	23	1005	-5	58	53	1701	3	290	321	894	-7	60	61	1752	-4	112	107	1782
2	20	13	836	-2	90	80	1283	-6	104	96	453	-4	38	35	1631	4	66	68	1088	-6	100	95	1764	-3	80	81	404
3	66	67	161	-1	94	85	821	-5	97	87	1731	-3	64	61	1373	5	56	59	1126	-5	75	72	16	-2	35	36	938
4	57	56	171	0	17	14	1282	-4	28	25	762	-2	39	36	694	6	30	34	523	-4	241	224	32	-1	39	39	586
5	20	20	944	1	70	70	1320	-3	96	91	1711	-1	72	67	137		3 4 L			-3	11	5	11	0	81	84	1632
	0 10 L			2	178	174	902	-2	148	130	206	0	33	31	1266	-8	10	11	1340	-2	153	148	39	1	44	44	314
0	40	37	243	3	40	40	944	-1	83	76	1680	1	122	123	1786	-7	55	52	559	-1	91	94	1737	2	42	41	1317
1	75	73	14	4	63	66	845	0	47	46	1672	2	19	17	1602	-6	51	50	906	0	46	51	1800	3	16	16	16
2	75	73	1581	5	56	60	496	1	41	40	1468	3	25	27	899	-5	70	64	257	1	137	147	8	4	28	29	564
3	64	65	162	6	82	86	1396	2	43	42	45	4	41	42	82	-4	47	41	469	2	383	396	33	5	19	19	1635
4	30	30	1097		1 6 L			3	59	59	713	5	73	78	1073	-3	201	190	831	3	88	88	1743	6	42	41	1341
5	64	66	124	-7	18	12	140	4	87	90	1177	6	15	18	1719	-2	92	87	1166	4	16	13	1738		4 8 L		
	0 11 L			-6	30	24	826	5	25	28	542		2 9 L			-1	88	82	932	5	45	46	1737	-6	43	41	369
1	32	32	341	-5	67	62	866	6	19	21	1201	-5	77	71	242	0	36	36	668	6	84	85	79	-5	95	89	267
2	56	56	330	-4	103	95	1367		2 2 L			-4	0	2	1574	1	41	42	475		4 1 L			-4	36	34	1374
3	25	23	44	-3	28	25	1153	-8	74	76	623	-3	139	132	1569	2	13	16	956	-8	94	96	1292	-3	75	73	1517
	0 12 L			-2	203	188	1073	-7	61	59	198	-2	10	14	525	3	99	104	1668	-7	68	67	0	-2	32	32	161
0	31	29	346	-1	22	19	873	-6	45	42	1658	-1	78	76	151	4	14	17	1188	-6	28	26	567	-1	86	91	61
1	51	50	1502	0	142	133	845	-5	124	115	1512	0	48	50	217	5	14	19	1205	-5	89	85	421	0	70	73	28
2	88	88	88	1	27	27	657	-4	20	15	849	1	31	31	1484		3 5 L			-4	199	180	1621	1	41	42	8
	1 0 L			2	90	89	407	-3	114	100	1695	2	38	41	1470	-7	44	41	1726	-3	100	91	162	2	48	47	1678
-8	112	111	1744	3	72	71	1030	-2	54	51	57	3	46	46	1800	-6	40	39	332	-2	99	98	1389	3	55	57	969
-7	36	36	66	4	57	58	1097	-1	96	89	214	4	36	38	41	-5	33	30	1198	-1	81	83	76	4	39	39	381
-6	76	76	18	5	32	33	1406	0	57	57	1443	5	83	89	278	-4	114	109	750	0	61	68	1491	5	63	65	143
-5	17	13	59		1 7 L			1	279	274	1779		2 10 L			-3	68	65	1313	1	53	57	479		4 9 L		
-4	147	138	1757	-7	37	35	1187	2	7	12	1607	-5	37	36	1774	-2	128	123	670	2	121	129	1255	-5	84	81	301
-3	36	35	32	-6	21	19	551	3	24	23	166	-4	84	78	275	-1	51	50	463	3	89	91	38	-4	19	23	1528
-2	45	46	1800	-5	30	28	1365	4	76	81	131	-3	39	39	1605	0	218	221	875	4	48	47	212	-3	20	20	1631
0	0	21	1696	-4	91	84	779	5	79	82	1635	-2	21	18	1435	1	75	73	1020	5	14	15	1442	-2	51	55	1523
1	18	18	73	-3	97	90	1339	6	9	11	970	-1	90	90	1800	2	61	61	1221	6	40	39	1046	-1	35	38	1676
	1 0 L			-2	96	89	971		2 3 L			0	39	36	448	3	39	42	438		4 2 L			0	17	15	260
1	17	18	73	-1	59	56	893	-8	23	20	1255	1	66	67	1574	4	59	62	252	-8	46	46	817	1	99	102	146
2	106	112	41	0	99	95	935	-7	43	41	1127	2	72	72	251	5	20	22	686	-7	71	74	816	2	47	46	1732
3	5	3	1284	1	79	76	1157	-6	45	40	34	3	81	84	1719		3 6 L			-6	52	51	557	3	95	98	1541
4	40	41	1784	2	118	119	1007	-5	123	112	706	4	8	12	1122	-7	46	43	806	-5	140	129	69	4	21	21	141

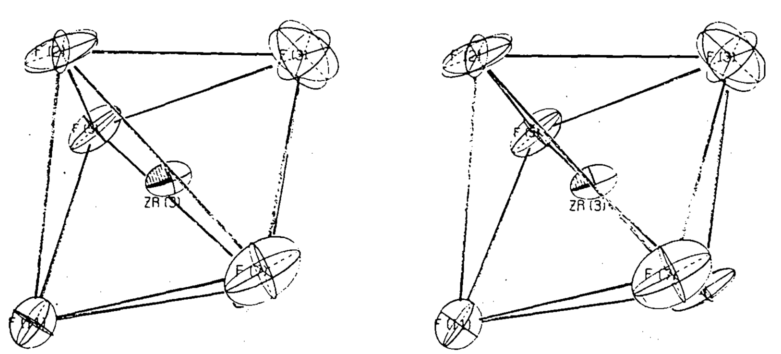

Fig. 3. Zr(3) coordination polyhedron.

Results

The four Zr ions in the asymmetrical unit have seven, eight, six, and seven nearest neighbors, respectively, at the corners of irregular polyhedra illustrated in Figs. 1–4. The seven nearest neighbors to Zr(1) appear to be at the corners of a pentagonal bipyramid at distances 1·99(2) to 2·20 (2) Å. Zr(2)'s nearest neighbors are at the corners of an irregular antiprism with interatomic distances of 1·98 (2) to 2·24 (2) Å. Octahedral coordination of Zr(3) is the easiest to see, and the distances are 1·90 (2) to 2·10 (2) Å. The seven nearest neighbors of Zr(4) are at the corners of a polyhedron that looks like an irregular antiprism with one corner missing. The Zr(4)–F distances are 1·95 (2) to 2·19 (2) Å. Interatomic distances are comparable to those of Burbank & Bensey (1956) (2·05 to 2·18 Å), Sears & Burns (1964) (2·05 to 2·16 Å) for an eight Zr–F coordination, and Brunton (1969) (2·012 to 2·167 Å) for a seven coordination. Interatomic distances for six-, seven- and eight-coordinated Zr^{4+} $-$F$^-$, calculated from the empirical radii of Shannon & Prewitt (1969), are respectively 2·05, 2·11, and 2·13 Å for comparison.

Table 3 (*cont.*)

L	FOBS	FCAL	ALPHA
4 10 L			
4	26	24	432
3	88	89	60
2	41	42	575
-1	41	40	364
0	77	78	1691
1	73	75	164
2	24	18	298
3	68	70	129
4 11 L			
-3	47	46	1095
-2	119	121	143
-1	59	61	1651
0	33	32	1100
1	34	34	1658
2	11	14	124
5 0 L			
-8	28	28	47
-7	62	65	1761
-6	79	75	1743
-5	31	27	1800
-4	16	14	11
-3	27	28	20
-2	16	15	1723
-1	6	10	102
0	37	32	1782
1	100	106	1782
2	7	6	229
3	68	66	18
4	146	149	45
5	49	47	1766
5 1 L			
-9	92	94	82
-7	35	37	1320
-6	54	51	894
-5	118	110	1358
-4	88	83	500
-3	80	76	647
-2	157	155	780
-1	142	151	1506
0	75	84	922
1	62	67	360
2	34	31	1733
3	19	20	622
4	152	154	959
5	33	36	1099
5 2 L			
8	45	44	1018
7	38	37	112
-6	76	74	1029
-5	100	92	1001
4	52	51	1446
-3	92	89	1237
-2	192	191	1048
1	49	52	772
0	12	12	155
1	73	79	538
2	94	97	1081
3	31	35	1514
4	18	24	1362
5	30	36	23
5 3 L			
8	51	52	960
[illegible]	34	36	1104
-6	40	41	852
-5	130	120	791
4	58	55	817
3	137	132	952
2	123	126	834
1	53	56	717
0	49	51	1195
1	255	285	927
2	76	81	853
3	42	42	286
4	31	36	1334
5	68	69	1309
5 4 L			
-7	57	58	1682
6	62	64	1383
-5	129	119	870
4	40	38	408
3	43	44	1770
2	86	88	1172
1	63	67	1261
0	32	33	196
1	98	102	685
2	53	55	884
3	31	34	854
4	18	19	841
5	53	55	700
5 5 L			
[illegible]	46	49	637
6	97	92	1077
5	74	72	379
-4	81	78	1413
-3	27	25	1150
-2	137	142	943
-1	62	66	621
0	71	71	671
1	56	59	1124
2	81	85	1378
3	42	45	1234
4	112	120	711
5 6 L			
[illegible]	41	42	1746
[illegible]	55	50	1458
-5	44	42	1598
-4	17	18	1158
-3	54	56	565
-2	35	36	1001
-1	42	43	1040
0	120	127	1039
1	45	49	1201
2	89	94	772
3	21	22	121
4	86	88	312
5	39	41	1467
5 7 L			
-6	25	25	340
-5	26	22	1396
-4	38	37	679
-3	56	57	1055
-2	78	82	915
-1	107	112	1215
0	60	61	791
1	69	72	796
2	72	73	1067
3	29	29	779
4	51	53	1021
5	55	57	980
5 8 L			
-6	89	87	701
-5	23	24	1789
-4	72	70	1730
-3	101	97	1091
-2	88	89	855
-1	30	35	170
0	38	40	895
1	25	25	466
2	31	33	1491
3	74	76	1026
4	23	23	857
5	41	43	609
5 9 L			
-5	43	42	800
-4	13	13	885
-3	33	32	1170
-2	26	25	977
-1	27	25	806
0	38	40	1292
1	95	98	1065
2	36	37	624
3	63	65	518
4	27	27	1481
5 10 L			
-4	57	57	438
-3	16	14	1190
-2	39	41	1200
-1	44	44	1311
0	45	46	838
1	22	23	643
2	13	8	693
3	16	11	436
5 11 L			
-2	43	43	905
-1	40	42	996
0	15	18	976
1	21	21	1191
6 0 L			
-8	36	37	48
-7	32	33	1757
-6	23	20	1789
-5	96	93	1769
-4	90	95	1738
-3	108	106	41
-2	55	53	56
-1	64	65	1754
0	241	255	1759
1	31	32	108
2	7	5	440
3	87	86	37
4	47	47	1716
5	11	9	33
6 1 L			
-8	30	33	1495
-7	73	76	1588
-6	104	102	51
-5	24	23	337
-4	76	74	717
-3	151	147	1752
-2	51	47	254
-1	44	46	1466
0	119	126	119
1	131	139	1761
2	32	29	1021
3	36	34	1588
4	80	78	35
5	10	9	734
6 2 L			
-8	46	49	1463
-7	51	53	1657
-6	83	86	556
-5	88	89	555
-4	61	58	1437
-3	87	87	1460
-2	99	100	1156
-1	87	93	1653
0	66	72	147
1	55	59	386
2	33	37	1700
3	168	171	1691
4	18	12	452
5	30	31	11
6 3 L			
-7	76	80	991
-6	9	13	960
-5	29	29	1650
-4	47	45	259
-3	38	37	51
-2	36	36	1370
-1	110	118	1413
0	54	56	703
1	54	58	99
2	54	57	895
3	103	106	1025
4	24	23	950
6 4 L			
-7	15	11	1059
-6	67	67	564
-5	36	34	970
-4	127	123	1776
-3	43	42	1324
-2	103	109	499
-1	71	73	1789
0	37	38	1604
1	61	63	1702
2	34	33	1786
3	105	107	1653
4	47	50	208
6 5 L			
-7	79	83	91
-6	36	33	1752
-5	63	62	1065
-4	121	120	1354
-3	138	140	20
-2	61	63	1560
-1	64	68	71
0	33	35	1596
1	67	70	439
2	74	78	1800
3	66	66	92
4	9	9	1586
5	29	31	1238
6 6 L			
-6	37	39	1092
-5	36	32	1692
-4	59	58	1712
-3	57	58	202
-2	19	20	145
-1	65	67	1442
0	127	135	1731
1	33	34	463
2	59	61	1406
3	56	56	410
4	59	60	1437
5	23	26	184
6 7 L			
-6	78	80	92
-5	42	44	1329
-4	26	27	292
-3	12	13	845
-2	65	68	597
-1	52	55	1568
0	107	116	203
1	58	61	1687
2	22	25	1407
3	14	15	307
4	58	58	133
5	36	34	1749
6 8 L			
-5	81	81	465
-4	18	19	694
-3	52	52	1740
-2	67	67	1639
-1	54	57	1712
0	50	51	162
1	64	67	396
2	18	15	1427
3	82	87	1739
4	31	32	1724
6 9 L			
-4	72	73	83
-3	41	42	42
-2	23	24	1397
-1	88	93	1639
0	57	56	119
1	46	48	139
2	20	19	698
3	30	31	1334
6 10 L			
-3	4	4	294
-2	64	66	190
-1	21	23	1375
0	34	33	1772
1	81	81	1722
2	28	28	200
7 0 L			
-7	54	57	40
-6	15	19	1738
-5	42	41	1789
-4	19	21	1789
-3	44	45	15
-2	86	66	24
-1	23	25	57
0	36	35	33
1	43	45	1766
2	89	90	1761
3	29	30	33
4	41	41	31
7 1 L			
-7	80	80	171
-6	28	28	1498
-5	73	74	1076
-4	71	68	1449
-3	80	78	0
-2	106	104	830
-1	24	26	976
0	65	68	1485
1	63	65	1022
2	119	119	729
3	58	59	576
4	42	38	1040
7 2 L			
-7	72	72	1049
-6	45	46	140
-5	91	91	206
-4	119	120	697
-3	68	72	1283
-2	44	45	915
-1	124	128	793
0	43	53	684
1	18	20	319
2	63	66	695
3	46	44	752
4	26	26	1720
7 3 L			
-7	7	6	1330
-6	67	67	1017
-5	50	51	1021
-4	88	85	876
-3	71	72	874
-2	53	54	944
-1	177	188	931
0	34	36	1233
1	85	87	965
2	54	54	685
3	20	20	775
4	19	21	268
7 4 L			
-7	74	76	980
-6	25	28	1282
-5	48	46	571
-4	89	88	505
-3	36	36	80
-2	12	15	1704
-1	129	139	1041
0	80	86	949
1	41	41	496
2	11	9	1234
3	62	61	925
4	32	30	1329
7 5 L			
-6	76	77	407
-5	10	12	1771
-4	47	45	630
-3	74	74	1432
-2	107	110	847
-1	64	70	713
0	104	109	667
1	53	54	667
2	138	140	973
3	15	11	1767
4	24	26	1769
5	46	45	324
7 6 L			
-6	37	37	1154
-5	70	69	937
-4	36	34	1099
-2	74	77	512
-1	71	72	661
0	37	40	1007
1	36	37	1532
2	44	46	1705
3	21	19	82
4	44	45	698
5	31	30	552
7 7 L			
-5	79	81	822
-4	30	27	1467
-3	67	67	462
-2	21	24	864
-1	35	35	883
0	62	61	1000
1	15	14	563
2	31	31	281
3	63	63	794
4	65	64	1027
7 8 L			
-5	75	75	513
-4	73	75	319
-3	66	69	1264
-2	71	73	873
-1	30	30	295
0	17	17	284
1	84	86	878
2	74	72	806
3	14	8	1309
7 9 L			
-4	24	22	1025
-3	32	31	312
-2	11	11	798
-1	44	45	847
0	12	13	1000
1	61	62	1109
2	29	29	435
7 10 L			
-2	41	42	976
-1	48	50	1120
0	29	26	930
1	18	14	11
8 0 L			
-7	79	82	47
-6	37	38	49
-5	46	48	1766
-4	62	63	1755
-3	102	103	31
-2	72	71	48
-1	23	39	8
0	76	76	53
1	44	42	1729
2	21	19	1800
3	24	23	60
4	162	156	47
8 1 L			
-7	32	33	1075
-6	73	75	1289
-5	83	84	41
-4	20	18	294
-3	25	24	191
-2	135	137	1764
-1	83	82	50
0	15	16	823
1	68	68	175
2	70	66	1665
3	50	47	995
4	64	61	1234
8 2 L			
-7	52	54	1117
-6	29	30	203
-5	52	50	1099
-4	92	93	498
-3	101	102	196
-2	50	52	1749
-1	100	104	1365
0	69	69	124
1	114	115	152
2	38	38	964
3	20	23	44
4	33	33	1067
8 3 L			
-7	14	14	905
-6	39	38	1588
-5	24	25	1121
-4	56	56	880
-3	56	52	697
-2	40	40	1236
-1	26	25	638
0	81	80	1107
1	52	52	1105
2	38	38	767
3	54	53	379
4	40	39	1263
8 4 L			
-6	60	62	47
-5	57	57	1066
-4	65	68	1002
-3	27	27	621
-2	17	16	61
-1	38	39	517
0	52	52	75
1	55	54	221
2	72	73	1527
3	49	48	410
4	44	43	99
5	38	37	491
8 5 L			
-6	75	78	619
-5	77	79	1735
-4	53	53	533
-3	67	69	1738
-2	62	65	322
-1	42	43	1587
0	69	69	175
1	92	94	1598
2	53	52	63
3	23	21	1418
4	54	52	669
8 6 L			
-5	22	23	1541
-4	42	42	1328
-3	38	38	136
-2	42	43	11
-1	24	25	332
0	35	35	263
1	26	25	1420
2	21	21	631
3	22	21	907
4	95	94	54
8 7 L			
-5	49	48	496
-4	47	48	811
-3	18	19	202
-2	88	92	1658
-1	54	56	115
0	27	27	880
1	12	7	1278
2	57	56	1646
3	38	38	267
8 8 L			
-4	86	88	272
-3	65	66	180
-2	36	37	1722
-1	71	73	1494
0	24	26	303
1	79	80	21
2	39	39	37
8 9 L			
-3	47	46	323
-2	40	39	1570
-1	15	17	588
0	47	46	1564
1	15	14	1222
9 0 L			
-6	61	63	47
-5	47	50	1739
-4	82	83	1753
-3	73	72	1777
-2	4	5	94
-1	68	65	16
0	47	27	23
1	32	32	1776
2	30	29	1776
3	16	14	1638
4	5	2	1777
9 1 L			
-6	69	73	338
-5	58	57	1404
-4	43	45	1138
-3	45	41	1010
-2	54	56	441
-1	80	81	805
0	58	54	1222
1	59	57	1530
2	77	71	807
3	35	23	178
4	23	21	1544
9 2 L			
-6	83	89	1105
-5	37	38	290
-4	45	44	1139
-3	84	88	791
-2	59	53	1061
-1	55	57	1590
0	128	125	1022
1	63	63	842
2	26	24	97
3	41	41	306
4	71	67	1061
9 3 L			
-6	17	18	856
-5	44	46	1265
-4	58	61	776
-3	29	29	755
-2	58	58	760
-1	80	81	904
0	63	62	1087
1	40	36	1173
2	25	24	993
3	105	100	936
4	28	26	610
9 4 L			
-6	68	73	1212
-5	21	20	1585
-4	19	20	1004
-3	129	131	791
-2	64	66	894
-1	30	31	1569
0	41	41	1114
1	61	59	1039
2	35	33	11
3	44	43	615
4	72	68	1124
9 5 L			
-5	85	90	613
-4	74	76	884
-3	39	42	947
-2	88	90	1313
-1	29	32	812
0	72	74	783
1	55	56	559
2	33	30	655
3	74	68	1330
4	24	21	1356
9 6 L			
-5	36	39	1641
-4	43	44	1588
-3	38	39	1688
-2	24	23	770
-1	50	50	530
0	21	22	355
1	25	21	1334
2	62	60	1055
3	47	42	1098
9 7 L			
-4	18	18	858
-3	18	17	1128
-2	48	50	687
-1	50	52	902
0	19	18	1475
1	58	56	1051
2	59	57	769
9 8 L			
-3	15	17	1427
-2	35	34	1453
-1	69	71	962
0	72	71	963
1	38	37	991
10 0 L			
-6	33	34	43
-5	30	32	1735
-3	76	77	1752
-2	50	50	1730
-1	0	23	74
1	56	50	1749
2	86	81	1743
3	19	18	71
4	33	27	[illegible]
10 1 L			
-6	18	17	1734
-5	22	22	[illegible]
-4	95	98	6
-3	43	43	1607
-2	39	40	[illegible]
-1	81	80	1662
0	75	66	[illegible]
1	28	23	1110
2	54	50	104
3	87	79	1633
4	15	12	699
10 2 L			
-6	72	79	1391
-5	35	38	[illegible]
-4	28	33	303
-3	77	81	546
-2	40	41	1602
-1	38	39	1575
0	66	60	1175
1	47	45	1210
2	43	40	633
3	45	40	43
4	33	33	1633
10 3 L			
-5	50	51	371
-4	49	50	965
-3	35	34	1144
-2	44	43	533
-1	18	14	[illegible]
0	32	31	1007
1	43	39	1513
2	38	34	527
3	14	14	54
10 4 L			
-5	14	12	225
-4	23	21	964
-3	48	48	1259
-2	72	72	1710
-1	21	21	[illegible]
0	41	40	466
1	60	55	1722
2	42	38	1565
3	15	14	1265
10 5 L			
-4	40	41	1784
-3	45	47	857
-2	34	33	1426
-1	83	85	[illegible]
0	69	[illegible]	[illegible]
1	35	33	35
2	33	30	[illegible]
10 6 L			
-4	30	31	[illegible]
-3	51	52	[illegible]
-2	36	37	1599
-1	14	13	570
0	29	26	[illegible]
1	32	30	1667
2	53	50	[illegible]
10 7 L			
3	35	36	[illegible]
2	32	31	[illegible]
-1	28	28	1086
0	25	23	83
1	44	43	[illegible]
11 0 L			
-5	48	50	57
-4	34	33	1730
-3	34	33	1784
-2	30	29	1792
-1	42	42	37
0	18	15	57
1	35	33	[illegible]
2	18	15	24
3	60	53	1767
11 1 L			
-5	29	31	6
-4	47	46	[illegible]
-3	48	48	939
-2	16	14	854
-1	48	48	353
0	57	52	982
1	32	29	1730
2	17	14	[illegible]
3	20	19	745
11 2 L			
-5	66	69	[illegible]
-4	51	51	[illegible]
-3	35	[illegible]	[illegible]
-2	81	81	[illegible]
-1	[illegible]	65	[illegible]
0	21	[illegible]	[illegible]
1	66	61	1053
2	74	66	506

L	FOBS	FCAL	ALPHA
11 3 L			
4	72	72	1028
3	43	42	806
2	31	30	821
-1	49	50	822
0	40	36	915
1	44	41	950
2	26	22	1210
11 4 L			
-4	32	32	741
-3	45	47	395
-2	64	64	647
-1	35	32	847
0	40	35	1723
1	80	75	879
2	82	74	721
11 5 L			
-3	9	6	1582
-2	20	20	1169
-1	64	65	1245
0	52	50	742
1	56	52	553
11 6 L			
-2	40	38	1311
-1	23	24	38
12 0 L			
-3	8	12	1752
-2	49	48	1736
-1	33	33	67
0	6	8	36
1	52	44	47
12 1 L			
-3	72	73	165
-2	31	26	1428
-1	16	17	
0	70	65	1704
1	87	77	48
12 2 L			
-3	16	16	1530
-2	71	71	426
-1	56	55	56
1	56	48	1592
12 3 L			
-3	24	25	1283
-2	37	36	947
-1	26	26	645
0	30	26	861

The complete structure of Rb$_5$Zr$_4$F$_{21}$ is shown in Fig. 5. Zr polyhedra, labeled according to the central occupant, form chains parallel to the a_0 axis. In each chain of polyhedra, Zr(1) shares an edge with Zr(2) and a corner with Zr(4). Zr(2) also shares a corner with Zr(3). The chain is completed with Zr(3) sharing another corner with Zr(4). Chains are connected along the b axis by Zr(2) sharing an edge with Zr(4).

The Zr(1)–Zr(2) shared edge [F(6)–F(15), 2·34 (2) Å] and the Zr(2)–Zr(4) shared edge [F(1)–F(4), 2·32 (2) Å] are the shortest F–F distances in the structure (Table 2). The Zr(2)–Zr(3) corner is F(11) and the Zr(3)–Zr(4) corner is F(8). Zr–F distances are the greatest for the shared F atoms in each case for each Zr ion. The Rb ions fill the space between the Zr polyhedra.

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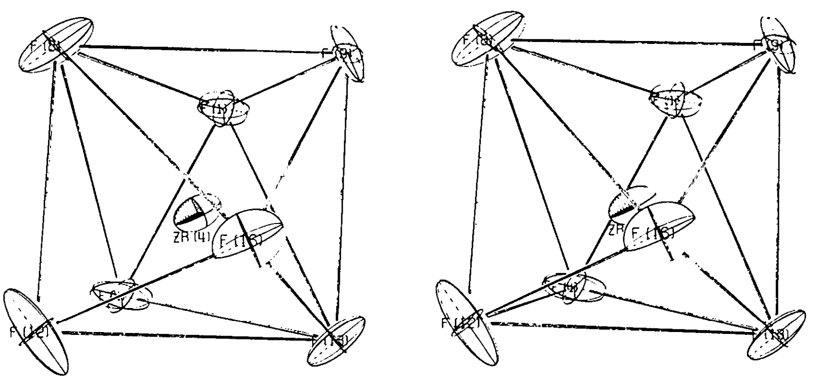

Fig. 4. Zr(4) coordination polyhedron.

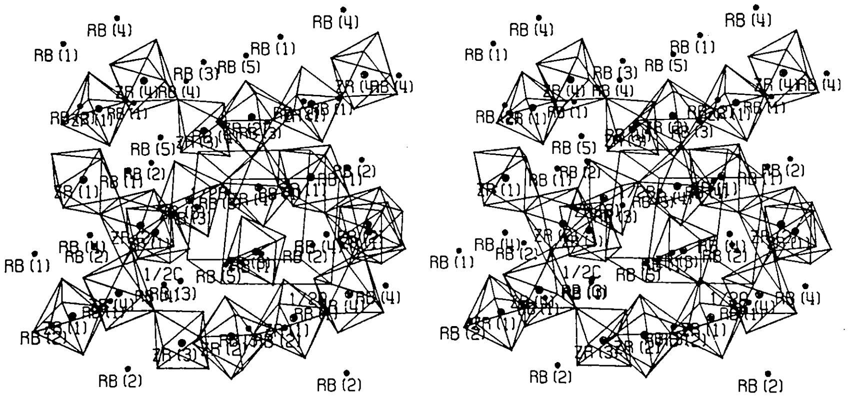

Fig. 5. Structure of $Rb_5Zr_4F_{21}$.

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The Crystal and Molecular Structures of Some Molecules Showing S···O Interaction. I. The Desaurin from Acetophenone.

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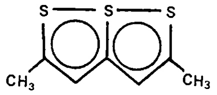
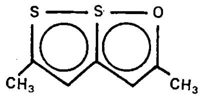
The crystal structure of the 'desaurin from acetophenone', $C_{18}H_{12}O_2S_2$, has been determined as part of a program to investigate the S···O interactions in a range of molecules. The crystals belong to the monoclinic space group $P2_1/c$ with $a=5{\cdot}740$ (8), $b=4{\cdot}848$ (12), $c=28{\cdot}299$ (8) Å, $\beta=96{\cdot}9$ (1)°. The structure was solved from the Patterson function using 1020 photographically determined intensities and refined to $R=0{\cdot}124$. The molecule shows an S···O distance of 2·640 (6) Å.

Introduction

The two-dimensional crystal structure analysis of 2,5-dimethylthiothiophthene (I) by Bezzi, Mammi & Garbuglio (1958)



(I)



(II)

indicated a symmetrical molecule with S···S distances of 2·36 Å. This early crystal structure analysis has since been subjected to three-dimensional refinement in these Laboratories (Leung & Nyburg, 1969) and S···S determined as 2·358 (1) Å. As pointed out by Bezzi *et al.* at the time, this is substantially longer than any 'formal' S–S bond known. A subsequent examination of S–S bond lengths by Hordvik (1966) suggests that the longest possible S–S bond, *i.e.* a single bond with no π character, would be 2·10 Å long. On the other hand, an examination of a number of sulphur-containing crystal structures shows that the minimum van der Waals radius of sulphur is about 1·65 Å [a value as high as 1·85 Å has been suggested by Pauling (1960)]. Accordingly, 2,5-dimethylthiothiophthene was the first