

The Crystal Structure of Sodium Tridecafluorodizirconate

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The crystal structure of sodium tridecafluorodizirconate, $\text{Na}_5\text{Zr}_2\text{F}_{13}$, has been determined from two-dimensional X-ray data. The crystal lattice is built of endless slabs of $[\text{Zr}_2\text{F}_{13}]^{5-}$ ions, running parallel to the b axis; the ions of sodium are arranged at the interstitial sites of this lattice. The coordination polyhedron around each zirconium atom is a trigonal prism, with an additional tetragonal pyramid. Two such ZrF_7 polyhedra, connected by a common fluorine atom placed at the apex of the tetragonal pyramid, form the $[\text{Zr}_2\text{F}_{13}]^{5-}$ complex ion.

Introduction

Fluorozirconates are very interesting from the crystallochemical point of view. The variety of stoichiometric compositions suggests the possibility of the existence of different structural types; on the other hand, in the complexes examined so far, some uncommon coordination relations have been found. Thus, Bode & Teufer (1956) have found a bis-disphenoid as the coordination polyhedron in potassium hexafluorozirconate, K_2ZrF_6 .

Since, to the best of our knowledge, no crystallochemical study of any of the $\text{M}_5\text{Zr}_2\text{F}_{13}$ zirconium complexes has been carried out, we thought it of interest to undertake a crystal structure analysis of sodium tridecafluorodizirconate, $\text{Na}_5\text{Zr}_2\text{F}_{13}$.

As was reported in an earlier paper (Herak, Manojlović & Malčić, 1963), sodium tridecafluorodizirconate crystallizes in the form of monoclinic zirconate, with space group $C2/m$. There are two formula units in a unit cell of the following dimensions:

$$a = 11.62 \pm 0.02, \quad b = 5.49 \pm 0.01, \quad c = 8.44 \pm 0.01 \text{ \AA};$$

$$\beta = 97.7 \pm 0.20^\circ.$$

Experimental

Crystals suitable for X-ray examination were obtained from equimolecular solutions of sodium hydrogen fluoride and $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$.

Reflexions $h0l$, recorded in zero-layer-line Weissenberg photographs taken with $\text{Mo } K\alpha$ radiation, provided the data from which the atomic positions were deduced. The intensities of the reflexions were measured by multiple-film techniques and visual comparison with a standard scale of spots of known relative exposures. The Lorentz and polarization factors were applied, but the crystal was sufficiently small for the absorption correction to be neglected ($\mu_{\text{Mo } K\alpha} = 25 \text{ cm}^{-1}$).

Determination of the structure

The shortness of the b axis and the mirror planes arranged at $y=0$ and $y=\frac{1}{2}$, made it possible to solve the structure from the data in the $[010]$ projection only. A consideration of the dimensions of atoms showed that they must lie in the mirror planes or in the planes at $y=\frac{1}{4}, \frac{3}{4}$.

The approximate x and z atomic coordinates were obtained on the basis of the Patterson function in the $[010]$ projection and space packing considerations.

The refinement of the structural parameters was carried out entirely by means of Fourier and difference Fourier syntheses. An overall temperature factor $B=0.3 \text{ \AA}^2$ was used for the structure-factor calculations. Since for the strongest reflexions F_c were always much greater than F_o , a correction for secondary extinction was applied, using the relation $F_c^2 = F_o^2 / (1 - GF_o^2)$ (Zachariasen, 1948).

In Table 1 the measured structure factors are compared with those calculated from the final atomic coordinates. The agreement residual R , derived from structure factors in Table 1, has a value of 12.6%. In this residual, an unobserved reflexion is included

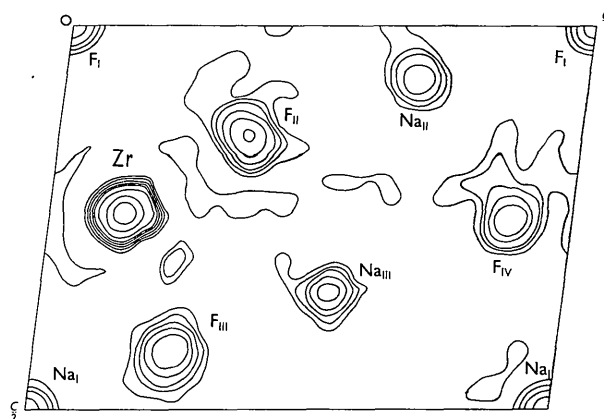


Fig. 1. Projection of the electron density along $[010]$. Contours are drawn at arbitrary equal intervals.

Table 1. *Observed and calculated structure factors*

h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c
2 0 0	58	70	4 0 5	99	-113	10 0 9	64	80	$\bar{2}$ 0 8	92	98
4	60	-60	6	35	29	10	47	45	9	72	59
6	46	48	7	35	31				10	43	38
8	101	-103	8	80	84				11	65	-64
10	39	-29	9	46	-33	12 0 1	51	53	12	0	11
12	64	66	10	0	-1	2	52	-51	13	45	39
14	96	90	11	66	56	3	52	-58	14	0	-18
16	60	80	12	0	.3	4	44	35	15	37	-37
18	0	8	13	53	-46	5	55	48			
20	62	-69	14	0	-24	6	31	-11	$\bar{4}$ 0 1	52	56
			15	49	44	7	55	-63	2	41	-17
						8	44	37	3	34	-25
0 0 1	0	-5							4	63	47
2	108	-139	6 0 1	54	47	14 0 1	25	-24	5	76	66
3	55	-41	2	86	87	2	67	-71	6	156	154
4	101	105	3	25	14	3	47	59	7	80	-86
5	32	22	4	114	-114	4	74	90	8	49	-52
6	116	-116	5	33	-33	5	0	8	9	38	25
7	0	-14	6	81	88	6	63	-68	10	48	39
8	92	94	7	62	48	7	0	-13	11	33	-26
9	47	30	8	77	-71						
10	101	-101	9	57	-68				$\bar{6}$ 0 1	36	31
11	49	-43	10	54	71	16 0 1	62	-65	2	265	257
12	82	106				2	34	-25	3	82	-80
13	54	47	8 0 1	40	-33	3	0	15	4	112	-119
			2	181	189	4	56	52	5	51	-34
2 0 1	105	-125	3	18	-14	5	35	-46	6	100	103
2	73	-71	4	65	-65	6	48	-57	7	24	24
3	0	15	5	77	74	7	54	71	8	76	-83
4	290	282	6	93	87	8	50	70	9	0	-18
5	30	-25	7	0	-25				10	62	65
6	55	-71	8	88	-94	18 0 1	47	-54	11	0	23
7	50	37	9	0	18	2	0	0	12	74	-75
8	62	57	10	70	80	3	43	38	13	0	-2
9	36	-30	11	0	5	4	0	15	14	91	102
10	72	-73	12	68	-61	5	36	-55			
11	31	27	13	0	-28				$\bar{8}$ 0 1	96	-93
12	73	67	14	73	74	20 0 1	0	8	2	114	119
13	33	-8				2	52	71	3	85	81
14	81	-71	10 0 1	82	86				4	90	-90
15	0	-15	2	41	52	$\bar{2}$ 0 1	82	95	5	81	-77
16	81	85	3	81	-95	2	91	-91	6	69	63
			4	22	-24	3	37	-38	7	68	68
4 0 1	39	-46	5	23	5	4	75	68	8	76	-69
2	44	38	6	64	73	5	74	67	9	27	-20
3	92	94	7	45	-34	6	114	-96	10	88	96
4	50	-31	8	29	-25	7	76	-64	11	54	45
			h k l	F _o	F _c	h k l	F _o	F _c			
			$\bar{8}$ 0 1 2	0	-17	$\bar{12}$ 0 1 0	60	-59			
			13	76	-81						
			$\bar{10}$ 0 1	89	-93	$\bar{14}$ 0 1	28	-25			
			2	0	9	2	64	-56			
			3	76	86	3	46	-40			
			4	0	-8	4	82	92			
			5	0	-8	5	35	34			
			6	51	45	6	67	-75			
			7	69	49	7	56	-54			
			8	41	31	8	57	68			
			9	95	-99	9	50	70			
			10	0	-5	$\bar{16}$ 0 1	58	53			
			11	44	43	2	54	-47			
			$\bar{12}$ 0 1	32	29	3	68	-72			
			2	40	-33	4	52	49			
			3	38	17	5	71	90			
			4	91	82	$\bar{18}$ 0 1	61	72			
			5	76	-77						
			6	56	-46	$\bar{20}$ 0 1	0	-10			
			7	0	10	2	58	53			
			8	71	71						
			9	0	-7						

only if $|F_c|$ exceeds $\frac{1}{2}|F_{o(\min)}|$, the minimum observed structure amplitude in the appropriate range of $\sin\theta$; in this case, a term $(\frac{1}{2}|F_{o(\min)}| - |F_c|)$ is added to the numerator only. The final Fourier synthesis, based on measured structure amplitudes and calculated signs, is presented in Fig. 1.

The computation performed in this work was carried out by means of Beever's-Lipson strips (Lipson & Beever, 1936).

Discussion of the structure

The final fractional coordinates of the atoms are listed in Table 2. The projection of the structure along $[010]$, illustrated in Fig. 2, shows that the crystal lattice is built of $[\text{Zr}_2\text{F}_{13}]^{5-}$ complex ions, which form rows parallel to the b axis. The sodium ions occupy the interstitial sites of this lattice.

Table 2. Final fractional atomic coordinates

		x	y	z
4 Zr	(i):	0.072 ₇	0	0.242 ₆
2 F _I	(a):	0	0	0
8 F _{II}	(j):	0.180	0.250	0.148
8 F _{III}	(j):	0.131	0.250	0.424
8 F _{IV}	(j):	0.439	0.250	0.252
2 Na _I	(c):	0	0	0.500
4 Na _{II}	(i):	-0.163	0	0.075
4 Na _{III}	(i):	0.277	0	0.346

In the $[\text{Zr}_2\text{F}_{13}]^{5-}$ ion, each zirconium atom has a sevenfold coordination. The fluorine atoms are placed at the corners of the coordination polyhedron composed of a trigonal prism and a tetragonal pyramid. Two such ZrF_7 polyhedra, joined together through

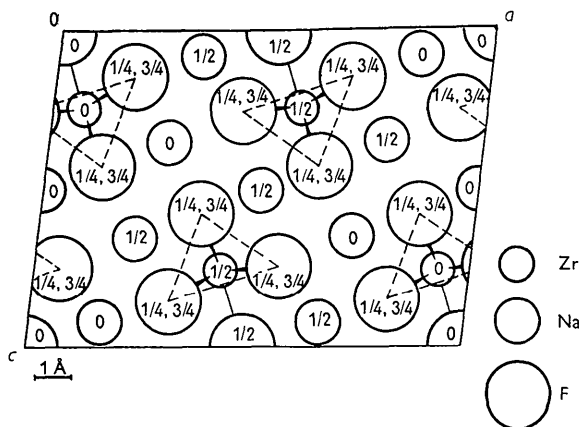


Fig. 2. Projection of the structure along $[010]$.

the common apex of the pyramids, form the $[\text{Zr}_2\text{F}_{13}]^{5-}$ complex ion (Fig. 3). The interatomic distances in

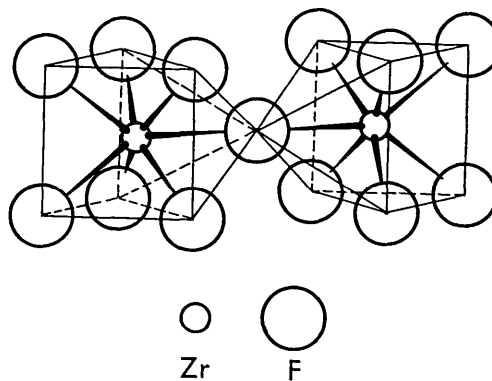


Fig. 3. Coordination polyhedron of the $[\text{Zr}_2\text{F}_{13}]^{5-}$ ion in $\text{Na}_5\text{Zr}_2\text{F}_{13}$

this ion, calculated according to data from Table 2, are found to be:

Zr-F _I (1 ×)	2.10 Å	Zr-F _{III} (2 ×)	2.10 Å
Zr-F _{II} (2 ×)	2.07 Å	Zr-F _{IV} (2 ×)	2.00 Å

The distances F-F range within the interval 2.50–3.01 Å.

In sodium tridecafluorodizirconate, $\text{Na}_5\text{Zr}_2\text{F}_{13}$, a new structural type of zirconium compound has been found.

It is known that in potassium heptafluorozirconate, K_3ZrF_7 , the zirconium atom also has a coordination number seven (Wells, 1962). However, the ion $[\text{ZrF}_7]^{3-}$ has a pentagonal bipyramidal arrangement of fluorine atoms around the central zirconium atom. Comparing this ion with the isoelectronic $[\text{TaF}_7]^{2-}$ ion in potassium heptafluorotantalate, K_2TaF_7 , Addison (1962) pointed out that, somewhat surprisingly, the latter has a different structure, in which six of the fluorine atoms are at the corners of a trigonal prism and the remaining one is at the centre of one of the faces. However, the results of our investigations have shown that the $[\text{Zr}_2\text{F}_{13}]^{5-}$ complex ion in sodium tridecafluorodizirconate has a structure similar to that of the $[\text{TaF}_7]^{2-}$ ion.

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