

The Crystal Structure of Hydrazinium(+2) Hexafluorozirconate, $N_2H_6ZrF_6$

BY B. KOJIC-PRODIĆ, S. ŠČAVNIČAR AND B. MATKOVIĆ

Institute 'Ruđer Bošković', Zagreb, Yugoslavia

(Received 8 June 1970)

The structure of $N_2H_6ZrF_6$ has been determined by single-crystal X-ray diffraction methods. The monoclinic unit cell with $a=8.13$, $b=12.16$, $c=5.42$ Å, $\beta=101.5^\circ$, contains four formula weights of $N_2H_6ZrF_6$. In space group $C2/m$ (C_{2h}^3), No. 12, one symmetrically independent F atom and one N atom occupy general positions, two F atoms and the Zr atom occupy special positions on the mirror plane and two F atoms lie on the twofold axes. Zr is eightfold coordinated by fluorine atoms at an average distance of 2.12 Å in the shape of a bicapped trigonal prism. Each prism shares edges with two neighbouring polyhedra forming, along the [001] direction, infinite zigzag chains which are held together by N-H...F hydrogen bonds. The N-N distance in the $N_2H_6^{2+}$ ion is 1.41 Å.

Introduction

The preparation and investigation of hydrazinium fluoro complexes of transition metals using hydrazinium difluoride as a fluorinating agent were started some years ago at the Nuclear Institute 'Jožef Stefan' in Ljubljana, Yugoslavia. Numerous novel hydrazinium fluoro complexes were prepared (Slivnik & Volavšek, 1968; Slivnik, Šmalc, Sedej & Vilhar, 1964) and the crystal structure determinations of some of them [$N_2H_6ZrF_6$, $N_2H_6TiF_6$, $(N_2H_5)_2TiF_6 \cdot 2HF$ and $(N_2H_5)_3CrF_6$] were undertaken. The structure of $N_2H_6ZrF_6$ was solved to establish whether isolated $[ZrF_6]^{2-}$ ions with six-coordinated zirconium, or ZrF_8 units (formed by sharing of fluorine atoms) with eight-coordinated zirconium are present.

In this paper the crystal structure of $N_2H_6ZrF_6$ is presented and isomorphism between this compound and its Hf analogue is established (Table 1) from the close similarity of their powder photographs.

Table 1. X-ray powder data for $N_2H_6ZrF_6$ and $N_2H_6HfF_6$

<i>h k l</i>	$N_2H_6ZrF_6$			$N_2H_6HfF_6$		
	d_o	d_c	<i>I</i>	d_o	<i>I</i>	
1 1 0	6.70 Å	6.66 Å	40	6.70 Å	70	
0 2 0	6.08	6.08	100	6.07	100	
0 0 1	5.21	5.31	1	5.33	—	
1 1 $\bar{1}$	4.53	4.54	25	4.51	25	
0 2 1	4.03	4.00	1	4.01	2	
2 0 0		3.98				
1 1 1	3.89	3.85	80	3.90	50	
1 3 0	3.62	3.61	10	3.62	10	
2 0 $\bar{1}$	3.54	3.54	30	3.52	25	
2 2 0	3.35	3.33	5	3.34	2	
1 3 $\bar{1}$	3.12	3.12	1	3.12	3	
0 4 0	3.05	3.04	15	3.04	25	
2 2 $\bar{1}$		3.06				
1 3 1	2.90	2.88	1	2.88	3	
2 0 1		2.92				
0 0 2	2.67	2.66	20	2.66	25	
3 1 0	2.62	2.59	2	2.61	10	
1 1 $\bar{2}$		2.62				
2 2 1		2.63				
0 4 1		2.64				

Table 1 (cont.)

<i>h k l</i>	d_o	d_c	<i>I</i>	d_o	<i>I</i>
2 4 0	2.43	2.42	5	2.43	3
0 2 2		2.43			
2 0 $\bar{2}$		2.45			
1 5 0	2.31	2.33	3	2.30	5
2 4 $\bar{1}$		2.31			
3 3 0		2.22			
1 3 $\bar{2}$	2.25	2.24	2	2.23	4
2 2 $\bar{2}$		2.27			
3 1 1		2.17			
3 3 $\bar{1}$	2.18	2.18	15	2.18	7
1 5 $\bar{1}$		2.18			
2 4 1		2.12			
1 5 1	2.10	2.09	2	2.12	2
1 3 2	2.06	2.05	3	2.09	3
3 1 $\bar{2}$		2.07			
2 0 2		2.03			
0 6 0	2.03	2.03	20	2.03	7
4 0 $\bar{1}$		2.00			
0 4 2		2.00			
4 0 0	1.95	1.99	2	2.00	2
3 3 1		1.94			
2 2 2		1.93			
2 4 $\bar{2}$	1.91	1.91	3	1.95	3
4 2 $\bar{1}$		1.90			
4 2 0		1.89			
0 6 1	1.86	1.89	15	1.90	7
3 3 $\bar{2}$		1.86			
2 6 0		1.81			
1 5 $\bar{2}$	1.81	1.80	1	1.85	1
3 5 0		1.79			
1 1 $\bar{3}$		1.79			

Experimental

$(NH_4)_2ZrF_6$ (Wolter, 1908) has been known for some years, but $N_2H_6ZrF_6$ (Slivnik *et al.*, 1964) was prepared recently by mixing equimolar solutions of ZrO_2 and $N_2H_6F_2$ in HF. The colourless crystals of $N_2H_6ZrF_6$ belong to the monoclinic holohedral class (Fig. 1) with $a=8.13 \pm 0.01$, $b=12.16 \pm 0.03$, $c=5.42 \pm 0.01$ Å, $\beta=101.5 \pm 0.3^\circ$, $V=525.1$ Å³, $D_m=3.00$, $D_c=3.02$ g.cm⁻³, $Z=4$.
Cu K α radiation, $\mu=191.6$ cm⁻¹.

The systematic absences

$$\begin{aligned} hkl & \text{ for } h+k=2n+1 \\ h0l & \text{ for } (h=2n+1) \\ 0k0 & \text{ for } (k=2n+1) \end{aligned}$$

indicate $C2$, Cm and $C2/m$ as possible space groups, but only $C2/m$ is in agreement with the negative piezoelectric test and this space group was confirmed by solution of the structure.

The density was measured at 25°C pycnometrically with decalin as the liquid. Equi-inclination Weissenberg photographs were taken using filtered $\text{Cu } K\alpha$ radiation and the multiple-film technique (four films), and 693 independent reflexions were recorded. Intensities were estimated with a microdensitometer. To facilitate the calculation of absorption corrections, the crystals were ground to a sphere ($r=0.024$ cm) for collecting the data along the [100] and [010] directions, and to a cylinder

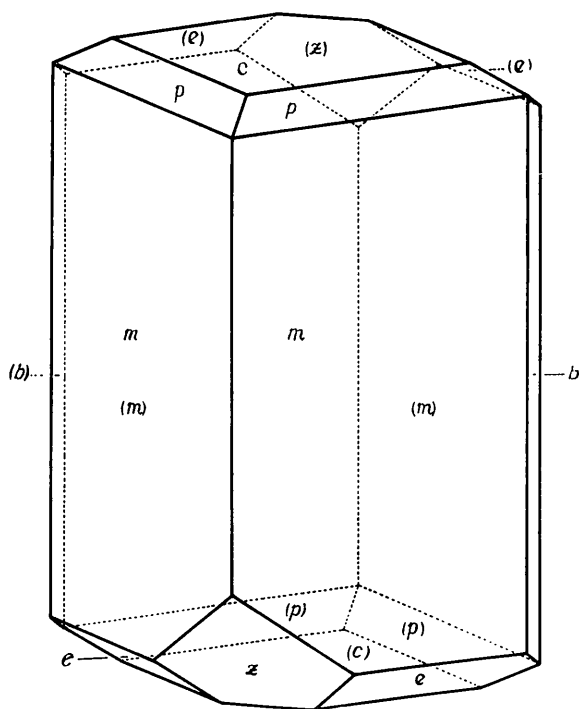


Fig. 1. The crystal of $\text{N}_2\text{H}_6\text{ZrF}_6$ with the following forms: $c\{001\}$, $b\{010\}$, $m\{110\}$, $z\{201\}$, $p\{111\}$, $e\{\bar{1}11\}$.

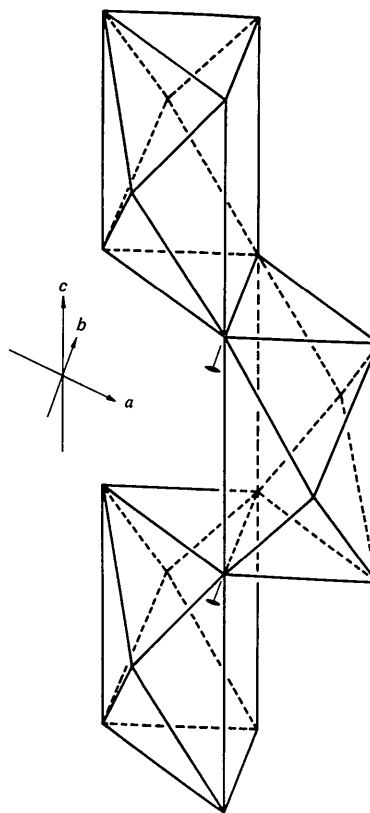


Fig. 2. The chain of bicapped trigonal prisms in the [001] direction.

($r=0.014$ cm) for the [001] direction. Absorption, Lorentz and polarization corrections were applied.

The $\text{N}_2\text{H}_6\text{ZrF}_6$ crystals used were of poor quality. At first sight they looked perfect, but they actually consisted of a number of smaller crystals with almost the same orientation.

Structure determination

Since there are four formula units in the unit cell of $C2/m$ symmetry, the zirconium atom at least must be placed in a special position. From a three-dimensional Patterson synthesis the position of the Zr atom on the mirror plane $4(i)$ was deduced, but the x and z coordi-

Table 2. Final coordinates and anisotropic thermal parameters ($\times 10^4$) with *e.s.d.*'s (in parentheses)

The thermal parameters refer to the expression: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B
N(1)	4714 (18)	1790 (10)	3682 (18)							3.5 (0.2) Å ²
F(2)	7551 (12)	1658 (8)	1974 (13)	54 (15)	40 (7)	235 (23)	26 (10)	-16 (13)	2 (10)	
F(3)	0	988 (20)	0	526 (84)	50 (18)	1737 (157)	0	758 (115)	0	
F(4)	0	1011 (17)	5000	150 (40)	29 (15)	794 (79)	0	-170 (36)	0	
F(5)	3243 (29)	0	919 (22)	344 (54)	30 (10)	183 (45)	0	134 (37)	0	
F(6)	6849 (20)	0	4284 (19)	113 (28)	19 (9)	204 (32)	0	18 (21)	0	
Zr(7)	1538 (2)	0	-2074 (2)	49 (3)	22 (1)	68 (4)	0	6 (2)	0	

$$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} = 0.087 \text{ (including unobserved reflexions)}$$

$$= 0.086 \text{ (omitting unobserved reflexions)}$$

nates could not be uniquely determined. The ambiguity was removed by means of a $P(xOz)$ Harker section. With the signs of structure factors based on the position of the Zr atom along the first three-dimensional electron density map was prepared. In this synthesis only

the reflexions with a high contribution from Zr were included. From this map the preliminary positions of five symmetrically independent F atoms and one N atom were determined: one F atom and the N atom in general positions 8(j), two F atoms on the mirror plane

Table 3. Observed and calculated structure factors

M K L 10FO 10FC				M K L 10FO 10FC				M K L 10FO 10FC				M K L 10FO 10FC				M K L 10FO 10FC				M K L 10FO 10FC										
2	0	0	497	-518	7	7	1	286	308	7	7	2	586	-358	0	0	6	32	-22	7	3	-5	427	417	0	0	4	234	205	
4	0	0	110	25	0	8	1	322	241	2	8	2	673	616	2	0	3	32	-32	9	3	-3	409	430	0	10	4	202	214	
6	0	0	918	761	2	8	1	730	721	4	8	2	287	247	2	0	4	732	-718	1	3	4	3	536	-561	0	12	4	150	182
8	0	0	193	220	4	8	1	694	-802	6	8	2	470	-469	2	0	5	284	-242	1	3	4	4	474	-393	0	8	5	441	447
8	0	0	418	-462	4	8	1	211	-223	1	9	2	261	-279	6	0	6	603	-594	1	3	4	6	594	-516	1	1	3	335	407
1	1	0	849	899	8	8	1	393	453	3	9	2	783	854	4	0	3	674	682	1	3	6	6	409	429	1	7	3	671	-758
3	1	0	531	-567	1	9	1	440	438	5	9	2	407	-378	4	0	5	430	-384	3	3	3	3	389	371	1	9	3	677	-522
3	1	0	11	56	7	9	1	114	56	7	9	2	232	-211	4	0	3	332	-308	3	3	3	3	491	510	1	5	1	564	-619
7	1	0	664	659	5	9	1	690	-702	2	10	2	536	565	6	0	4	381	432	3	3	5	6	546	-525	1	13	3	327	-420
9	1	0	319	-309	7	9	1	404	409	4	10	2	183	184	8	0	2	67	3	0	6	7	6	78	145	1	7	4	535	-461
9	1	0	1667	1730	10	9	1	1172	-118	6	10	2	462	-405	8	0	3	332	-308	3	3	4	4	493	510	0	10	5	264	-239
2	2	0	704	-650	2	10	1	551	557	11	2	94	-80	9	1	2	465	531	5	3	4	4	708	670	1	11	4	239	-256	
4	2	0	1085	-1058	4	10	1	572	-593	3	11	2	699	675	1	3	-1	1027	-1025	5	3	5	7	2	-91	1	7	5	436	449
6	2	0	999	945	6	10	1	150	-143	5	11	2	198	-220	3	1	-1	312	-219	7	3	3	3	557	-559	1	9	5	311	402
8	2	0	72	-56	1	11	1	708	694	2	12	2	598	536	5	1	-1	821	904	7	3	4	4	2	-124	1	6	448	472	
10	2	0	396	-337	3	11	1	172	-132	1	13	2	52	-139	7	1	-1	143	-80	8	4	2	2	252	200	1	1	-1	1052	-1025
1	3	0	640	722	5	11	1	397	-422	3	13	2	428	430	9	1	-1	535	-481	4	4	-1	3	339	387	1	3	-1	574	-591
3	3	0	516	-553	0	12	1	247	158	2	14	2	325	303	3	1	-2	1196	-1236	10	4	-1	1	102	-4	1	1	-1	735	-727
5	3	0	167	-79	2	12	1	386	425	1	1	-1	720	-726	5	1	-2	162	146	10	4	-2	3	375	366	1	7	-1	795	-778
7	3	0	678	650	4	12	1	426	-399	2	2	-2	745	-744	7	1	-2	519	-498	2	4	-3	3	702	722	1	9	-1	489	-395
9	3	0	318	-385	6	12	1	75	-180	4	2	-2	1305	1292	9	1	-2	141	94	2	4	-4	4	427	438	1	11	-1	457	-416
0	4	0	1097	1045	1	13	1	572	554	6	2	-2	454	-485	1	1	-3	265	217	2	4	-5	3	316	-283	1	13	-1	477	-394
2	4	0	786	-876	3	13	1	93	-69	8	2	-2	517	-402	1	1	-4	1299	1322	4	4	-3	3	151	115	1	15	-1	229	-200
4	4	0	1204	-1169	0	14	1	211	148	10	2	-2	390	402	1	1	-5	231	221	4	4	-4	4	549	-566	1	1	-2	781	-726
6	4	0	896	796	2	14	1	794	2	14	3	5	463	-493	3	1	-5	494	-468	4	4	-3	3	449	-437	3	3	-2	647	-593
8	4	0	119	-106	4	14	1	336	-290	3	3	-2	650	610	3	1	-3	663	737	4	4	-6	3	661	732	1	5	-2	1054	-1111
1	5	0	94	-204	1	15	1	343	350	5	3	-2	402	391	3	1	-4	336	-362	6	4	-3	3	666	-732	1	7	-2	792	-784
3	5	0	11	58	1	15	1	758	597	3	3	2	74	-643	3	1	-3	752	-727	6	4	-2	4	135	-482	2	2	3	357	-313
5	5	0	302	-208	4	0	1	847	-905	9	3	-2	301	258	3	1	-6	267	-213	6	4	-6	5	518	539	1	11	-2	430	-440
7	5	0	434	440	6	0	1	265	-311	2	4	-2	997	-954	5	3	-3	521	-519	6	4	-6	2	220	181	1	13	-2	452	-438
9	5	0	275	-25	8	0	1	628	-593	4	4	-2	1002	1026	5	1	-4	470	-468	6	4	-3	3	305	361	3	3	2	279	-217
0	6	0	1855	1814	2	0	-1	1854	-1902	6	4	-2	343	554	5	1	-5	270	230	8	4	-4	4	454	422	1	3	-3	244	169
2	6	0	990	-1039	6	0	-1	336	267	8	4	-2	449	-375	5	1	-6	455	572	0	4	3	3	591	-595	1	5	-3	221	179
4	6	0	468	-454	8	0	-1	577	-566	1	5	-2	1080	-1111	7	3	-3	200	-221	0	4	4	4	234	251	1	7	-2	255	208
6	6	0	572	-475	1	0	-1	642	-562	10	4	-2	652	-605	7	1	-4	592	546	0	5	5	5	606	564	1	9	-3	168	71
8	6	0	94	108	9	3	-1	411	-346	5	5	-2	162	-145	7	1	-5	430	360	0	4	6	6	130	-91	1	11	-3	179	75
1	7	0	296	303	2	4	-1	948	-1018	7	5	-2	558	-567	9	1	-3	545	536	2	4	3	3	432	-395	1	13	-3	163	122
3	7	0	629	-623	3	4	-1	732	574	6	5	-2	76	282	9	1	-2	115	115	2	4	-4	4	640	-658	1	11	-1	457	-416
5	7	0	148	-80	8	4	-1	536	-483	2	6	-2	331	-390	1	1	3	1155	-1171	2	4	5	5	116	-31	1	3	-4	813	729
7	7	0	503	505	1	5	-1	694	-727	4	6	-2	710	733	1	1	4	539	-507	2	4	6	6	444	520	1	5	-4	1102	1073
9	7	0	207	-206	3	5	-1	246	-213	6	6	-2	209	-247	5	1	-4	690	590	1	4	3	3	949	893	1	7	-4	977	-922
0	8	0	946	1029	5	5	-1	866	872	8	6	-2	376	-404	1	1	6	526	540	4	4	0	2	2	9	1	5	-4	635	600
2	8	0	475	-399	7	5	-1	75	-42	3	7	-2	768	-784	3	1	3	403	347	4	4	5	4	514	-467	1	11	-4	627	700
4	8	0	802	-695	9	5	-1	358	-383	3	7	-2	678	669	3	1	4	436	-365	6	4	3	3	236	-247	1	1	-5	244	221
6	8	0	615	613	2	0	-1	613	-615	2	8	-2	401	-402	1	1	-4	450	450	1	2	-1	2	411	420	1	5	-5	243	272
8	8	0	0	-24	4	6	-1	333	347	7	7	-2	412	-459	3	1	6	69	21	8	4	3	3	194	-267	1	5	-5	229	202
1	9	0	616	621	6	6	-1	345	297	9	7	-2	52	88	5	1	3	320	278	1	5	-3	2	223	179	1	7	-5	223	204
3	9	0	362	-306	8	6	-1	561	-400	2	8	-2	380	-417	2	1	-4	690	590	1	4	-4	4	1088	1073	1	9	-5	154	178
5	9	0	79	45	1	7	-1	787	-778	4	8	-2	874	844	5	1	5	137	-92	1	5	-5	2	230	202	1	1	-6	491	-468
7	9	0	475	516	3	7	-1	315	-311	6	8	-2	344	-343	7	1	3	518	-493	1	5	-6	3	361	-431	1	3	-6	353	-345
0	10	0	896	1082	5	7	-1	647	639	1	9	-2	991	-313	8	2	2	328	289	3	5	-3	3	652	601	1	5	-6	364	431
2	10	0	116	-107	3	8	-1	316	309	5	8	-2	609	581	2	2	-1	612	-612	4	4	-4	4	451	-456	1	7	-6	311	-390
4	10	0	152	-455	9	7	-1	379	-408	5	9	-2	297	330	4	2	-1	443	486	3	5	-5	6	682	-702	2	8	3	362	-397
6	10	0	613	641	2	8	-1	705	-665	7	9	-2	371	-440	6	2	-1	625	677	3	5	-6	6	160	-200	2	10	3	286	-310
8	10	0	347	311	4	8	-1	252	242	4	10	-2	239	8	4	0	292	-238	5	4	-5	5	588	566	2	3	2	306	-104	
3	11	0	522	-445	6	8	-1																							

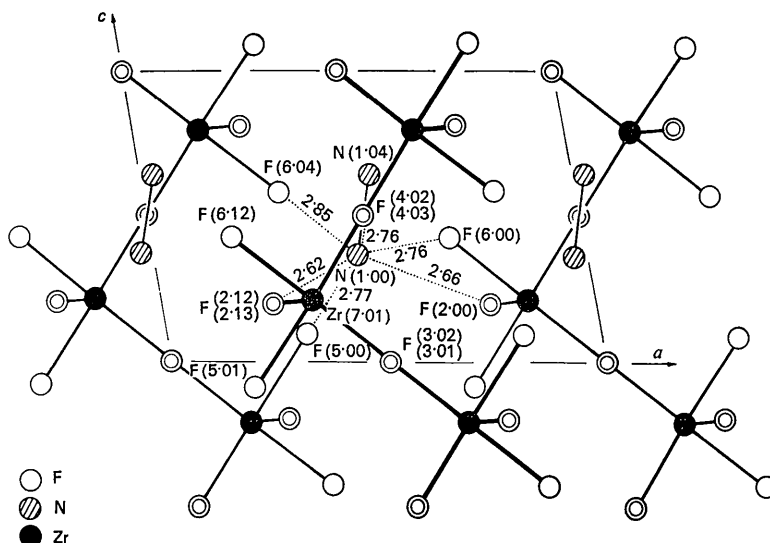


Fig. 3. The zigzag chains of polyhedra projected on (010); the first and third chains are at height $y=0$, the middle chain at $y=\frac{1}{2}$. Double open circles represent two F atoms with the same x, z values. The nearest $N \cdots F$ contacts are designated by dotted lines.

4(*i*), and two F atoms on the twofold axes 4(*h*) and 4(*g*). This Fourier synthesis showed marked elongation of the nitrogen atom peak perpendicular to the twofold axis and in the direction of the N–N bond. A second Fourier synthesis, calculated on the basis of Zr and all the F atoms, gave better shaped and resolved maxima of the light atoms.

The least-squares refinement was performed with isotropic temperature factors using a local version of the *ORFLS* program (Polić, 1968). Coordinates, individual isotropic temperature factors and inter-layer

scale factors were varied and the resulting *R* index was about 0.12 (including unobserved reflexions). On introducing anisotropic temperature factors the *R* index dropped to 0.09 (including unobserved reflexions). Refinement was continued with unit weights until the parameter shifts were less than the estimated standard deviations. Atomic scattering factors for N, F and Zr were taken from *International Tables for X-ray Crystallography* (1962). The final values of atomic coordinates and anisotropic thermal parameters with their standard deviations are given in Table 2, and the observed and calculated structure factors in Table 3. Some thermal parameters (Table 2), especially for F(3), are high and physically quite unlikely, and are probably due to imperfections in the crystals or an error in the absorption correction. Attempts to locate hydrogen atoms were unsuccessful.

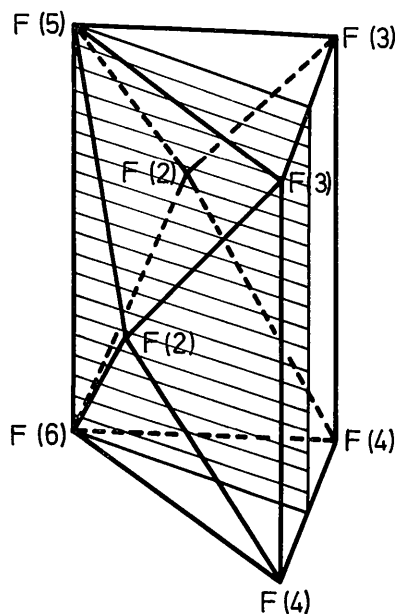


Fig. 4. The hendecahedron (or bicapped trigonal prism) around the zirconium atom; the mirror plane is shaded.

Description and discussion of the structure

The atomic numbering system is described in Table 4 and the interatomic distances and bond angles listed in Table 5. The zirconium atom exhibits eightfold coordination and the basic structural unit is a bicapped trigonal prism. The coordination polyhedron consists of one F atom in a general position – F(2) and its pair across the mirror plane, two F atoms on the twofold axes – F(3) and F(4) and with them the two F atoms related by a mirror plane, and finally two F atoms on the mirror plane – F(5) and F(6). The atoms F(3) and F(4) with their symmetry-related counterparts act as bridges between zirconium atoms, thus each prism shares two edges with two neighbouring polyhedra (Fig. 2). The polyhedra are connected in a zigzag infinite chain-like fashion with the chains running along the [001] direction at levels $y=0$ and $y=\frac{1}{2}$ (Fig. 3).

Table 4. *Numbering of the atoms*

Designation of the atoms is according to the Busing, Martin & Levy (1964) ORFFE program. Only those atoms are numbered which are mentioned in the Tables and Figures.

Atoms	Coordinates		
N(1·00)	x	y	z
F(3·01), F(5·01), Zr(7·01)	$\frac{1}{2}-x$	$\frac{1}{2}-y$	$-z$
F(3·02), F(4·02)	$\frac{1}{2}+x$	$\frac{1}{2}+y$	z
F(4·03)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	z
F(2·13)	$\frac{1}{2}+x+1$	$\frac{1}{2}-y$	z
F(2·12), F(6·12)	$\frac{1}{2}+x+1$	$\frac{1}{2}+y$	z
N(1·04)	$1-x$	y	$1-z$

Table 5. *Interatomic distances, angles and their standard deviations (in parentheses)*

Within Zr-polyhedron	Distance
Zr(7·01)–F(2·12)	2·15 (0·01) Å
Zr(7·01)–F(3·02)	2·20 (0·01)
Zr(7·01)–F(4·02)	2·19 (0·01)
Zr(7·01)–F(5·01)	1·91 (0·02)
Zr(7·01)–F(6·12)	1·95 (0·01)
F(2·12)–F(2·13)	4·03 (0·02)
F(2·12)–F(5·01)	2·56 (0·01)
F(2·12)–F(6·12)	2·50 (0·01)
F(3·01)–F(3·02)	2·40 (0·05)
F(4·02)–F(4·03)	2·46 (0·04)
F(3·01)–F(4·03)	2·71 (0·00)
F(4·02)–F(6·12)	2·80 (0·02)
F(5·01)–F(3·02)	2·85 (0·02)
F(5·01)–F(6·12)	2·81 (0·01)
F(2·13)–F(3·01)	2·57 (0·01)
F(2·13)–F(4·03)	2·44 (0·01)
Angle	
F(3·01)–Zr(7·01)–F(3·02)	66· (1)°
F(4·02)–Zr(7·01)–F(4·03)	68·4 (0·9)
F(3·02)–Zr(7·01)–F(4·02)	76·2 (0·4)
F(5·01)–Zr(7·01)–F(3·01)	87·5 (0·4)
F(6·12)–Zr(7·01)–F(5·01)	93·3 (0·6)
F(6·12)–Zr(7·01)–F(4·03)	85·0 (0·3)
F(2·12)–Zr(7·01)–F(2·13)	140·2 (0·5)
F(2·13)–Zr(7·01)–F(4·03)	68·6 (0·5)
F(2·13)–Zr(7·01)–F(3·01)	72·6 (0·5)
F(2·13)–Zr(7·01)–F(5·01)	77·9 (0·2)
F(2·13)–Zr(7·01)–F(6·12)	75·2 (0·2)
F(3·02)–F(3·01)–F(4·03)	90·6 (0·5)
F(3·02)–F(4·02)–F(4·03)	89·4 (0·5)
F(3·02)–F(5·01)–F(3·01)	49·9 (0·9)
F(4·02)–F(6·12)–F(4·03)	52·1 (0·8)
F(5·01)–F(3·12)–F(3·01)	65·1 (0·5)
F(5·01)–F(3·01)–F(4·03)	89·7 (0·3)
F(5·01)–F(6·12)–F(4·03)	88·7 (0·4)
F(6·12)–F(2·12)–F(5·01)	67·4 (0·3)
F(6·12)–F(5·01)–F(3·01)	89·3 (0·5)
F(6·12)–F(4·03)–F(3·01)	92·2 (0·3)
In $N_2H_6^{2+}$	
N(1·00)–N(1·04)	1·41 (0·03) Å
$N \cdots F$ distances shorter than 3·25 Å	
N(1·00)–F(6·04)	2·85 (0·02) Å
N(1·00)–F(5·00)	2·77 (0·02)
N(1·00)–F(6·00)	2·76 (0·02)
N(1·00)–F(4·03)	2·76 (0·03)
N(1·00)–F(2·00)	2·66 (0·02)
N(1·00)–F(2·13)	2·62 (0·02)
Shortest distances between the other atoms	
N(1·00)–N(1·03)	4·42 (0·01) Å
Zr(7·01)–Zr(7·02)	3·68 (0·00)

In $N_2H_6ZrF_6$ the zirconium polyhedron has C_s symmetry but its shape is very close to C_{2v} symmetry (Fig. 4). The maximum deviation of the lengths of pyramidal edges [with F(2·12) at the apex] from the mean value of 2·52 Å is $\pm 0·05$ Å. The quadrilateral F(3), F(4), F(5) and F(6), which serves as the base of the pyramid, approximates a square: the deviation of angles from 90° is $\pm 2^\circ$ and the deviation of the edges from the average value of 2·79 Å is $\pm 0·08$ Å. A 'free' prismatic face, formed by the atoms F(3·01), F(3·02), F(4·02) and F(4·03) has a nearly rectangular shape: the two short edges F(3·01)–F(3·02) of 2·40 Å and F(4·02)–F(4·03) of 2·46 Å are common for two neighbouring polyhedra.

The mean value of eight Zr–F bonds (Table 5) of 2·12 Å is nearly equal to the sum of the ionic radii ($r_{Zr^{4+}}=0·80$ Å, $r_{F^-}=1·36$ Å, Pauling, 1960) but with a stretching of the Zr–F bonds to bridging fluorine atoms [Zr(7·01)–F(3·02)=2·20 and Zr(7·01)–F(4·02)=2·19 Å] and a shortening of the Zr–F bonds to fluorine atoms on a mirror plane and opposite to shared edges [Zr(7·01)–F(5·01)=1·91 and Zr(7·01)–F(6·12)=1·95 Å].

The nitrogen atoms are grouped in pairs related by twofold axes, so the N–N bonds in the $N_2H_6^{2+}$ ion are perpendicular to the twofold axes, but the configuration of the $N_2H_6^{2+}$ ion could not be predicted from its symmetry. The N–N bond length of 1·41 Å is in agreement with the values reported earlier, e.g. 1·43 Å in $N_2H_6(H_2PO_4)_2$ (Liminga, 1966), 1·40 Å in $N_2H_6SO_4$ (Nitta, Sakurai & Tomii, 1951), 1·42 Å in $N_2H_6F_2$ (Kronberg & Harker, 1942) and $N_2H_6Cl_2$ (Donohue & Lipscomb, 1942).

Chains of polyhedra are joined to other chains by ionic interaction between $[N_2H_6]^{2+}$ and $[ZrF_6]^{2-}$ ions and through N–H \cdots F hydrogen bonds. There are two very short N \cdots F distances which suggest the existence

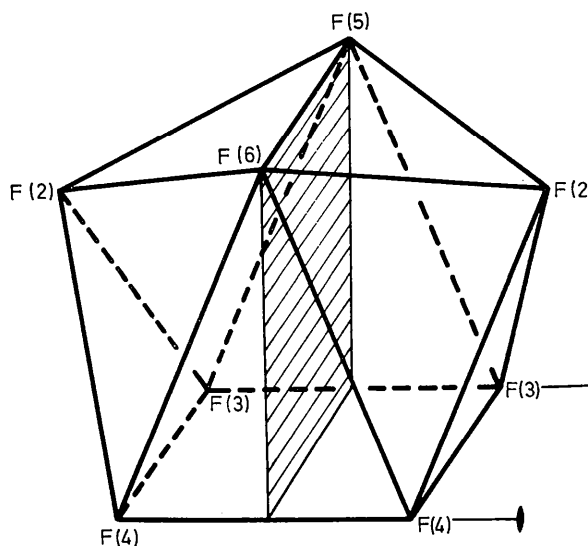


Fig. 5. The ZrF_6 polyhedron in the $N_2H_6ZrF_6$ structure as a derivative of a square antiprism; the mirror plane is shaded.

of hydrogen bonds: $N(1\cdot00)\cdots F(2\cdot00)$, 2.66 Å and $N(1\cdot00)\cdots F(2\cdot13)$, 2.62 Å. The distance of 2.62 Å is less than the $N-H\cdots F$ bond length of 2.63 Å in NH_4F (Wells, 1962) and equal to the $N-H\cdots F$ distances in $N_2H_6F_2$ (Kronberg & Harker, 1942) and $N_2H_6TiF_6$ (Prodić, 1968). Four more fluorine atoms are rather close to the nitrogen atom. One of them, $F(5\cdot00)$ with a distance $N(1\cdot00)\cdots F(5\cdot00)$ of 2.77 Å might also be involved in $N-H\cdots F$ hydrogen bonds. This distance is quite close to the $N-H\cdots F$ value of 2.775 Å in $NH_4CuTiF_7\cdot 4H_2O$ (de Cian, Fischer & Weiss, 1967) and 2.80 Å in NH_4HF_2 (Hadži & Thomson, 1959). The remaining three fluorine atoms $F(6\cdot00)$, $F(6\cdot04)$ and $F(4\cdot03)$ are disposed around the $N-N$ bond on a plane which passes along the twofold axis, bisects the $N(1\cdot00)-N(1\cdot04)$ bond and is nearly normal (83°) to this bond. The shortening of the observed distances: $N(1\cdot00)\cdots F(4\cdot03) = N(1\cdot04)\cdots F(4\cdot03) = 2.76$, $N(1\cdot00)\cdots F(6\cdot00) = N(1\cdot04)\cdots F(6\cdot04) = 2.76$ and $N(1\cdot00)-F(6\cdot04) = N(1\cdot04)-F(6\cdot00) = 2.85$ Å might be attributed to the interaction between the opposite charges on nitrogen and fluorine atoms.

The coordination number eight is very common for lanthanide and actinide ions because of their high formal charges and relatively large atomic radii, and also for early transition-metal ions – especially for those with d^0 , d^1 , d^2 and in some cases d^{10} electronic configurations. Zr^{IV} with a d^0 configuration belongs to the second group. According to the accessible literature the dodecahedron and the square antiprism (with D_{2d} and D_{4d} symmetries respectively) were the only known polyhedra for eight-coordinated zirconium. An antiprismatic arrangement of ligands has been found in $Zr(AcAc)_4$ (Silverton & Hoard, 1963), $ZrOCl_2\cdot 8H_2O$ and $ZrOBr_2\cdot 8H_2O$ (McWhan & Lundgren, 1963), $\alpha-ZrF_4$ (Burbank & Bensey, 1956), $Zr(IO_3)_4$ (Larson & Cromer, 1961), $Zr(SO_4)_2\cdot 4H_2O$ (Singer & Cromer, 1959), $Cu_2ZrF_8\cdot 12H_2O$ (Fischer, Elchinger & Weiss, 1967), $Cu_3Zr_2F_{14}\cdot 16H_2O$ (Fischer & Weiss, 1967), $Zr(OH)_2SO_4$ (McWhan & Lundgren, 1966), $Na_7Zr_6F_{31}$ (Burns, Ellison & Levy, 1968); the dodecahedral arrangement has been established in $Zr_2(OH)_2(SO_4)_3\cdot 4H_2O$ (McWhan & Lundgren, 1966), $Na_4Zr(C_2O_4)_4\cdot 3H_2O$ (Glen, Silverton & Hoard, 1963), $Zr(OH)_2(NO_3)_2(H_2O)_4$ (McWhan & Lundgren, 1963), $ZrSiO_4$ (Krstanović, 1958), $Li_3BeF_4ZrF_8$ (Sears & Burns, 1964), K_2ZrF_6 (Bode & Teufer, 1956), $K_2Zr[N(OAc)_3]_2\cdot H_2O$ (Hoard, Willstadter & Silverton, 1965), $ZrF_4\cdot 3H_2O$ (Waters, 1964), $Zr_2(SO_4)_4(H_2O)_8\cdot 6H_2O$ (Bear & Mumme, 1969), and α - and β - $Zr_2(SO_4)_4(H_2O)_8\cdot 2H_2O$ (Bear & Mumme, 1969). A trigonal prism with one centred face is known for seven-coordinated zirconium, e.g. $Na_5Zr_2F_{13}$ (Herak, Malčić & Manojlović, 1965).

Among the eight-coordination polyhedra the C_{2v} hendecahedron is of lower symmetry than the other two of D_{4d} and D_{2d} symmetry. The C_{2v} hendecahedron can be derived from a trigonal prism by adding two ligands out of two square faces. This type of polyhedron

was first proposed by Zachariasen (Zachariasen, 1948) for some lanthanide and actinide halides.

Because of the similarity of the antiprism and hendecahedron (one of the square faces of an antiprism is replaced by two triangles) the coordination polyhedron can be described in two ways: as a deformed square-antiprism or as a bicapped trigonal prism (hendecahedron). Fig. 5 illustrates the ZrF_8 polyhedron in the $N_2H_6ZrF_6$ structure as a derivative of the square antiprism. There is a large deformation in one 'square' of the antiprism obvious from a dihedral angle of 151.4° between two triangles [with corners at $F(5\cdot01)$, $F(2\cdot13)$, $F(6\cdot12)$ and at $F(6\cdot12)$, $F(2\cdot12)$, $F(5\cdot01)$] and from the set of tabulated lengths of edges (Table 5). It is therefore more realistic to describe the polyhedron around the zirconium atom in $N_2H_6ZrF_6$ as a bicapped trigonal prism.

References

- BEAR, I. J. & MUMME, W. G. (1969). *Acta Cryst.* **B25**, 1558, 1566.
- BODE, H. & TEUFER, G. (1956). *Acta Cryst.* **9**, 929.
- BURBANK, R. D. & BENSEY, F. N. (1956). US Atomic Energy Commission Report K-1280.
- BURNS, J. H., ELLISON, R. D. & LEVY, H. A. (1968). *Acta Cryst.* **B24**, 230.
- BUSING, R. W., MARTIN, K. O. & LEVY, H. A. (1964). ORNL-TM-306. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- CIAN, A. DE, FISCHER, J. & WEISS, R. (1967). *Acta Cryst.* **22**, 340.
- DONOHUE, J. & LIPSCOMB, W. N. (1947). *J. Chem. Phys.* **15**, 115.
- FISCHER, J. & WEISS, R. (1967). *Chem. Comm.* p. 328.
- FISCHER, J., ELCHINGER, R. & WEISS, R. (1967). *Chem. Comm.* p. 329.
- GLEN, G. L., SILVERTON, J. V. & HOARD, J. L. (1963). *Inorg. Chem.* **2**, 250.
- HADŽI, D. & THOMPSON, H. W. (1959). *Hydrogen Bonding*, pp. 7, 23. London: Pergamon Press.
- HERAK, R. M., MALČIĆ, S. S. & MANOJLOVIĆ, L. M. (1965). *Acta Cryst.* **18**, 520.
- HOARD, J. L., WILLSTADTER, E. & SILVERTON, J. V. (1965). *J. Amer. Chem. Soc.* **87**, 1610.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- KRONBERG, M. L. & HARKER, D. (1942). *J. Chem. Phys.* **10**, 309.
- KRSTANOVIĆ, I. R. (1958). *Acta Cryst.* **11**, 896.
- LARSON, A. C. & CROMER, D. T. (1961). *Acta Cryst.* **14**, 128.
- LIMINGA, R. (1966). *Acta Chem. Scand.* **20**, 2483.
- MCWHAN, D. B. & LUNDGREN, G. (1963). *Acta Cryst.* **16**, 136.
- MCWHAN, D. B. & LUNDGREN, G. (1966). *Inorg. Chem.* **5**, 284.
- NITTA, I., SAKURAI, K. & TOMIIE, Y. (1951). *Acta Cryst.* **4**, 289.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca, New York: Cornell Univ. Press.
- POLIĆ, S. (1968). Private communication (to be published). A local version of the Busing-Martin-Levy Full Matrix Program (1962).

- PRODIĆ, B. (1968). Ph. D. Thesis, Faculty of Science, University of Zagreb.
- SEARS, D. R. & BURNS, J. A. (1964). *J. Chem. Phys.* **41**, 3478.
- SILVERTON, J. V. & HOARD, J. L. (1963). *Inorg. Chem.* **2**, 243.
- SINGER, J. & CROMER, D. T. (1959). *Acta Cryst.* **12**, 719.
- SLIVNIK, J., ŠMALC, A., SEDEJ, B. & VILHAR, M. (1964). July NIJS Report R-430, Nuclear Institute 'Jožef Stefan', Ljubljana, Yugoslavia.
- SLIVNIK, J. & VOLAVŠEK, B. (1968). October NIJS Report R-548-Nuclear Institute 'Jožef Stefan', Ljubljana, Yugoslavia.
- WATERS, T. N. (1964). *Chem. and Industr.* p. 713.
- WELLS, A. F. (1962). *Structural Inorganic Chemistry*, 3rd ed. Oxford: Clarendon Press.
- WOLTER, L. (1908). *Chem. Zig.* **32**, 606.
- ZACHARIASEN, W. H. (1948). *Acta Cryst.* **1**, 265.

Acta Cryst. (1971). **B27**, 644

The Crystal Structure of Diethyldixanthogen

BY YASUNARI WATANABE

The Institute of Physical and Chemical Research, Yamato-machi, Kita-Adachi-gun, Saitama, Japan

(Received 3 June 1970)

The crystal structure of diethyldixanthogen, $(SSCOC_2H_5)_2$, is monoclinic with $a=18.958$ (0.005), $b=4.394$ (0.002), $c=6.990$ (0.004) Å; $\beta=107.27$ (0.03)°; the space group is $P2/a$ and $Z=2$. A molecule of $(SSCOC_2H_5)_2$ consists of two almost planar $SSCOC_2H_5$ groups linked by a twofold rotation axis at a S-S distance of 2.054 (0.004) Å, which is comparable with the S-S single bond distance. The dihedral angle C-S-S-C is 107.2 (1.0)°. The molecules are held together by van der Waals sulphur-sulphur, sulphur atom-alkyl group, sulphur atom-methyl end and methyl end-methyl end contacts.

Introduction

In connexion with the study of the action of xanthate on sulphide mineral surfaces in a froth flotation process, the determination of the molecular structure of dixanthogen, an oxidation product of xanthate, is important. Dixanthogen is supposed by some authors to play an important role in making sulphide mineral surfaces hydrophobic, (1) by coating the xanthate ions already adsorbed on the mineral surfaces by van der Waals forces (Leja, 1956), or (2) by being adsorbed dissociatively on the mineral surface so that one xanthate radical is coordinated to one metal atom in the substrate (Poling & Leja, 1963). In the present paper the molecular structure of diethyldixanthogen in the crystalline state is reported.

Crystal data

The crystallographic data for diethyldixanthogen are as follows:

Cell constants and cell volume

$$a=18.958 (0.005) \text{ \AA}, b=4.394 (0.002), \\ c=6.990 (0.004), \\ \beta=107.27 (0.03)^\circ, V=556.1 (0.4) \text{ \AA}^3.$$

Space group $P2/a$

Formula units per cell: $Z=2$

Observed and calculated density

$$d_o=1.30 \text{ g.cm}^{-3} \text{ (floatation)} \\ d_c=1.28 \text{ g.cm}^{-3}$$

Linear absorption coefficient for Cu radiation

$$\mu=85.54 \text{ cm}^{-1}.$$

Experimental

Diethyldixanthogen was obtained by mixing aqueous solutions of purified potassium ethylxanthate and iodine drop by drop. The light yellowish green substance obtained in the form of an emulsion was dissolved in ethanol and crystallized by evaporation of the solvent at a temperature of about 15°C. The crystal, in the shape of a rectangular plate, was stable in air up to the melting point (28.0°C). The specimen used had a cross section of 0.35 × 0.85 mm in the b -axis setting and 0.14 × 0.08 mm in the c -axis setting of the crystal.

Equi-inclination photographs of the 0 to 4th layers around the b axis and the 0 to 5th layers around the c axis were taken with the use of an integrating cassette at a temperature of $12 \pm 2^\circ\text{C}$ with Ni-filtered $\text{Cu } K\alpha$ radiation. The intensity measurement was carried out with a microphotometer. Of the recorded 1121 independent reflexions, about 88% of the total number of those observable with $\text{Cu } K\alpha$ radiation, 353 reflexions were too weak to give any numerical values. Observed intensities were corrected for Lorentz and polarization factors. An absorption correction, in which the crystal was approximated to a cylinder, and a spot-size correction (Phillips, 1956) were applied, but no extinction correction was made. The unit-cell dimensions were determined by the use of a Straumanis-type cassette.

Determination of the crystal structure

Systematic extinction showed the crystal to be monoclinic with space group $P2/a$ or Pa . Because the unit