

type *D* (Chidambaram, Sequeira & Sikka, 1964) with the bisector of the lone pairs directed toward the divalent copper ion. There are two equivalent bent O—H---Cl(2) hydrogen bonds from the water molecule. The H—O—H angle of $109.7(7)^\circ$ is significantly larger than the value of 104.5° in water vapour. It has been noted earlier also (Chidambaram, Sequeira & Sikka, 1964; Sikka & Chidambaram, 1969; Brown & Chidambaram, 1969) that trigonally coordinated water molecules with lone pair coordination of type *D* show an increased H—O—H angle compared with tetrahedrally coordinated water molecules. The uncorrected H—H distance of $1.562(11)$ Å is less than the distance of $1.61(2)$ Å found in the proton magnetic resonance study by McGrath & Silvidi (1961); this follows the tendency found in other hydrates by El Saffar (1966) and also in $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ (Sikka, Momin, Rajagopal & Chidambaram, 1968) and $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (Sequeira, Srikanta & Chidambaram, 1970).

It may be noted that the coordinates of the hydrogen atom in the asymmetric unit derived by El Saffar (1968) from the proton resonance determination of the length and orientation of the interproton vector are 0.076, 0.076, 0.178. The disagreement of the *z* coordinate from the parameter list of Table 1 is due to a different choice of origin (El Saffar, private communication) placing the Cu at $(0, 0, \frac{1}{2})$ rather than at the origin we have chosen following Wyckoff (1965).

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The Crystal Structure of $\text{Zr}_7\text{O}_9\text{F}_{10}$

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$\text{Zr}_7\text{O}_9\text{F}_{10}$, a new compound prepared from ZrF_4 and ZrO_2 , crystallizes in the orthorhombic space group *Pbam* with the unit-cell dimensions $a = 6.443$, $b = 26.851$, $c = 4.071$ Å. The structure has been refined by the method of least-squares from three-dimensional Weissenberg data. The zirconium atoms are six and seven coordinated and the coordination polyhedra (octahedra and pentagonal bipyramids) are joined by corners and edges in the (001) plane and by corners along the *c* axis. The structure is related to $\alpha\text{-UO}_3$ in much the same way as the orthorhombic U_3O_8 structure. From these similarities a building principle for a series of compounds $(MA)_{2(3n+1)}A_{4(3n+1)-2n}$ in which the composition asymptotically approaches the composition M_3A_8 is discussed.

Introduction

Several zirconium oxide fluorides have been observed by Kolditz & Feltz (1961) in their studies of thermal

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decomposition of zirconium tetrafluoride hydrates and zirconium oxide fluoride hydrates. To characterize existing compounds and to determine their structures a reinvestigation of the zirconium oxide fluoride system

has been started and this work reports the structure of the zirconium oxide fluoride, $Zr_7O_9F_{10}$, a new compound in the system.

Experimental

Crystals of the compound can be obtained from zirconium tetrafluoride and zirconium dioxide by heating the appropriate mixture in a sealed platinum tube at 800°C for several days. These are colourless with a rectangular prismatic shape. The lattice constants (Table 1) were determined from indexed powder photographs (Table 2) taken in a Guinier-Hägg camera with $Cu K\alpha_1$ radiation ($\lambda = 1.54050 \text{ \AA}$) and calibrated with KCl ($a = 6.2919 \text{ \AA}$). From a crystal with the dimensions $0.034 \times 0.032 \times 0.049 \text{ mm}$ equi-inclination Weissenberg diagrams about the c axis were taken with Ni-filtered $Cu K\alpha$ radiation. The multiple-film technique was used. The intensities of the $hk0$ and $hk1$ reflexions were estimated visually with a standard scale. Of the 390 accessible reflexions 281 were observed, but 22 of these were too intense with the exposure times employed to allow a correct estimation of their intensities. The data were corrected for absorption (Werner, 1966) and then reduced in the usual way.

Table 1. *Crystallographic data for $Zr_7O_9F_{10}$*

Symmetry	Orthorhombic
Unit-cell dimensions	$a = 6.443 \pm 0.001 \text{ \AA}$ $b = 26.851 \pm 0.001$ $c = 4.071 \pm 0.001$
Systematically absent reflexions	$h0l$ with $h \neq 2n$ $0kl$ with $k \neq 2n$
Possible space groups	$Pba2$ (No. 32) $Pbam$ (No. 55)
Z	2
Density $g.cm^{-3}$	$D_m = 4.55$ $D_x = 4.59$

Table 2. $Zr_7O_9F_{10}$ *Guinier powder pattern, $Cu K\alpha_1$ radiation*

$I(\text{obs})$	$\sin^2 \theta(\text{obs})$	hkl	$\sin^2 \theta(\text{calc})$
w	0.01312	040	0.01317
m	0.01752	120	0.01758
w	0.02163	130	0.02170
vst	0.03584	001	0.03581
w	0.04397	160	0.04392
vst	0.05463	170	0.05461
st	0.05722	200	0.05716
m	0.05798	210	0.05799
m	0.07777	250	0.07774
w	0.07972	161	0.07972
w	0.08225	0,10,0	0.08229
vst	0.09051	171	0.09042
st	0.09304	201	0.09297
w	0.09381	211	0.09379
w	0.11387	1,11,0	0.11386
m	0.13194	320	0.13191
m	0.13279	1,12,0	0.13279
m	0.13940	2,10,0	0.13945
vst	0.14315	002	0.14322
w	0.14975	1,11,1	0.14967
w	0.15824	360	0.15824
st	0.16127	0,14,0	0.16129
st	0.16884	370	0.16894

Determination of the structure

The $hk0$, $hk1$ and $hk2$ reflexions of similar index had similar intensities, with due regard for observational errors. Since the c axis is only 4.071 \AA in length, it appeared likely that the atoms, with the possible exception of a few anions, were lying within, or were very close to, every second mirror plane characteristic of the space group $Pbam$, one of the alternatives given by the systematically absent reflexions (Table 1). The remaining anions, placed on the other set of mirror planes, could lie between two zirconium atoms but not between two anions.

A pseudo-hexagonal sub-cell, resembling the unit cell of $\alpha\text{-UO}_3$ (Zachariasen, 1948), could be distinguished on the films and was taken as evidence that the atom arrangement in the structure was approximately the same as that in $\alpha\text{-UO}_3$. From the index relationships the vector relations between the sub-cell and the true cell were found to be:

$$\begin{aligned} \mathbf{a} &= 2\mathbf{a}_{\text{hex}} + \mathbf{b}_{\text{hex}} = 3.720 \cdot \sqrt{3} \text{ \AA} \\ \mathbf{b} &= 7\mathbf{b}_{\text{hex}} = 3.836 \cdot 7 \\ \mathbf{c} &= \mathbf{c}_{\text{hex}} = 4.071 \\ V &= 14V_{\text{hex}} \end{aligned}$$

From these relations an idealized structure can be obtained for $Zr_7O_9F_{10}$. In the hexagonal $\alpha\text{-UO}_3$ structure each uranium atom is surrounded by eight oxygen atoms. The coordination group is a cube, \mathbf{c}_{hex} being one of the body diagonals. There are 14 sub-units in the true cell, each containing one cation. They give the parameters of the 14 zirconium atoms and of the 14 anions situated above the zirconium along the \mathbf{c}_{hex} axis. Furthermore, the sub-units give locations for 28 anions. As there are only 24 anions to place, four of those sites must be excluded. This was done in such a way that each of 12 zirconium atoms is surrounded by only five more anions, instead of six as in the $\alpha\text{-UO}_3$ structure. From this idealized model a trial structure was worked out by adjusting to the chosen space group ($Pbam$) and by introducing distortions of the atoms in the neighbourhood of the four empty sites. The trial structure was tested by a few cycles of least-squares refinement and was found to converge.

Refinement

The refinement proceeded *via* full-matrix least-squares with isotropic temperature factors utilizing the *Crystal Structure Calculations Systems, X-ray 63* (1964) sub-program *ORFLS*. A Hughes (1941) weighting scheme (w) was used. The unobserved data were included in the refinement and given $w=0$ for $F_o > F_c$ and $w=1$ for $F_o \leq F_c$, the F_o 's being calculated from the minimum observable intensity. The F_c 's were calculated with the ionized scattering factors for fluorine, oxygen and zirconium (*International Tables for X-ray Crystallography*, 1962).

Some efforts were made to distinguish the fluorine from the oxygen atoms by studying the isotropic temperature factors of the anions for different arrangements (Holmberg, 1966) but no significant changes were observed. However, in the final calculations oxygen atoms were assumed to be in the positions with the higher temperature factors. The final R index was 0.082 (259 reflexions). The atomic parameters with their estimated standard deviations are given in Table 3, where OF represents a fluorine or oxygen atom. Observed and calculated structure factors are listed in Table 4. The F_o 's for 7 of the 109 unobserved reflexions, marked with an asterisk, are greater than their respective F_c 's.

Description of the structure

The $Zr_7O_9F_{10}$ structure is shown in projection along the c axis in Figs. 1 and 2(a). From the list of interatomic distances in Table 5 it is seen that Zr(1) is surrounded by six anions, either oxygen or fluorine (O,F) and the other zirconium atoms by seven. Within the coordination polyhedra (the octahedron and the pentagonal bipyramids) the greatest variation in distances is observed for the Zr(4) group, 1.98 to 2.46 Å. However, the mean distances are about the same in all three pentagonal bipyramids (2.11, 2.11, 2.13 Å) and they are reasonably longer than the mean distance within the octahedron (2.05 Å). The structure is built up by

Table 3. Final atomic parameters for $Zr_7O_9F_{10}$, space group $Pbam$ (No. 55)

E.s.d.'s are given in brackets.

Point position	x	y	z	B	
Zr(1)	2(a)	0.0	0.0	0	1.12 (10) Å ²
Zr(2)	4(g)	0.4484 (4)	0.0634 (1)	0	1.01 (8)
Zr(3)	4(g)	0.0028 (5)	0.1442 (1)	0	1.16 (8)
Zr(4)	4(g)	0.4401 (5)	0.2229 (2)	0	1.90 (9)
OF(1)	4(g)	0.6879 (29)	0.0095 (8)	0	2.43 (43)
OF(2)	4(g)	0.1230 (34)	0.0722 (9)	0	2.85 (48)
OF(3)	4(g)	0.7308 (29)	0.1040 (7)	0	1.92 (40)
OF(4)	4(g)	0.3573 (29)	0.1429 (8)	0	1.89 (39)
OF(5)	4(g)	0.7560 (26)	0.1969 (7)	0	1.67 (38)
OF(6)	4(g)	0.1332 (30)	0.2167 (8)	0	0.87 (39)
OF(7)	2(b)	0	0	$\frac{1}{2}$	3.24 (160)
OF(8)	4(h)	0.4569 (44)	0.0681 (13)	$\frac{1}{2}$	2.50 (104)
OF(9)	4(h)	0.9933 (46)	0.1437 (10)	$\frac{1}{2}$	2.94 (125)
OF(10)	4(h)	0.4439 (41)	0.2188 (11)	$\frac{1}{2}$	2.36 (95)

Table 4. Final structure factor table for $Zr_7O_9F_{10}$

The data are listed in groups of constant h and l . The three columns within each group are k , $10F_o$ and $10F_c$. Those data not included in the refinement are marked with an E and the unobserved data are indicated with an asterisk.

4 249 503	31 933 1023	11 303 265	25 394 359	14 667 46P	5 113* 23	18 582 622	4 441 1	17 302* 214
6 139 117	2 400	12 1262E 1462	26 183* 234	15 292 15C	6 463* 419	19 548 535	0 1149 127L	18 957 515
8 434 417	0 1141E 3052	13 440 617	27 355 433	16 215* 124	7 1816E 2433	20 315* 166	1 092 914	19 271* 183
10 767 605	1 1050E 1122	15 572 617	28 015 013	17 220* 95	8 224 155	21 302* 29	2 494 204	20 619 501
12 151* 24	2 223 205	16 243* 35	5 44* C	18 624 525	9 171 147	22 527 568	3 202* 106	21 853 699
14 1654C 4557	3 118* 107	17 893 866	1 461 756	19 451 012	10 222* 79	23 451 423	4 253 206	22 240* 135
16 321 307	4 265 207	18 516 485	2 067 260	20 780 215	11 749 760	24 778 865	5 1449 1312	23 221* 72
18 914 1166	5 080E 740	19 254* 228	3 54 543	21 152* 73	12 1360 1368	25 362 354	6 783 744	24 274 220
20 423 377	6 197 124	20 856 849	4 546 455	7 44* C	13 210 131	26 284* 71	7 271* 23	
22 111 621	7 125* 19	21 1521 1644	5 466 434	1 1091 1105	14 214* 49	27 284* 248	8 561 583	
24 1360 1577	8 358 424	22 250* 184	6 404 1092	2 520 501	15 488 517	28 833 757	9 445 306	0 315* 305
26 135* 92	9 137* 23	23 246* 212	7 1073 1038	3 236 251	16 252* 18	29 350 317	10 054* 137	1 602 538
28 1134 124C	10 1403E 1538	24 289 275	8 623 512	4 200* 226	17 1207 1170	30 221* 176	11 278 315	2 422 338
30 343 34C	11 577 537	25 302 283	9 246* 210	5 359 337	18 246 218	31 196* 171	12 491* 215	3 302* 71
	12 191* 106	26 875 820	10 246* 19	6 480 434	19 284* 55	13 711 746	13 711 746	4 461 392
	13 908 1065	27 552 562	11 657 549	7 206* 1	20 291* 163	14 739 709	14 739 709	5 1080 934
1 142 157	14 1874E 2830	28 187* 54	12 1690 1263	8 347 736	21 1216 1253	1 700 678	15 366* 210	6 1020 1053
2 246 565	15 265 214	29 498 489	13 1024 519	9 322 272	22 396* 246	2 1361 1364	16 326* 305	7 296* 85
3 401 472	16 288 261	30 360 452	14 250* 9	10 201* 120	23 340 316	3 340 316	17 020* 295	8 841 852
4 132 148	17 292 278	15 582 605	11 638 585	25 421 747	24 302* 181	4 247 186	18 222* 58	9 461 394
5 97* 37	18 746 743	4 44* C	16 246* 178	12 627 560	26 444 474	5 222 212	19 1141 1175	10 291* 220
6 644 724	19 717 707	0 1403E 1810	17 246 277	13 1032 1034	27 498 474	6 1198 1188	20 617 639	11 381 382
7 1180E 4241	20 317 156	1 1113E 1317	18 589 617	14 283 191	28 271* 6	7 1895E 2498	21 202* 144	12 304 340
8 472 379	21 243* 58	1 1113E 1317	19 239 229	15 541 575	29 527 544	8 950 892	22 412 373	13 769 670
9 212 153	22 681 643	3 172* 125	20 676 712	16 239 229	30 218 155	9 162 234	23 514 456	14 535 530
10 133* 64	23 668 445	4 397 352	21 888 822	17 239 229	31 788 859	10 224 218	24 364 349	15 258* 50
11 117 474	24 899 1006	5 1254E 1641	22 201 56	18 878 902	12 1100 1161	11 253 233	25 327 333	16 252* 72
12 1478E 1690	25 431 410	6 923 937	23 143* 110	19 437 476	13 1100 1161	12 224 206	26 224 206	17 240* 91
13 196* 97	26 227* 88	7 180* 42	24 265 248	20 457 476	14 1100 1161	13 555 529	27 465 333	18 413 449
14 164* 93	27 352 331	8 857 724	25 243 224	21 176* 24	15 1100 1161	14 278* 37	19 689 785	19 689 785
15 265 618	28 901 985	9 537 459		22 176* 24	16 1100 1161	15 846 518	20 597 707	20 597 707
16 168* 46	29 375 288	10 196* 227		23 176* 24	17 1100 1161	16 992 723		
17 1113E 1399	30 180* 192	11 451 393		24 176* 24	18 1100 1161	17 694 723		
18 126 261	31 164* 199	12 120 286		25 176* 24	19 1100 1161	18 468 468		
19 223* 67		13 966 1018		26 176* 24	20 1100 1161	19 302* 186		
20 276 267		14 1232 1074		27 176* 24	21 1100 1161	20 637 659		
21 1378E 1766		15 481 602		28 176* 24	22 1100 1161	21 468 468		
22 374 320		16 341 308		29 176* 24	23 1100 1161	22 288 288		
23 432 376		17 375 298		30 176* 24	24 1100 1161	23 132E 132E		
24 508 207		18 248 72		31 176* 24	25 1100 1161	24 802 802		
25 794 886		19 1324 1400		32 176* 24	26 1100 1161	25 420 405		
26 225 594		20 938 939		33 176* 24	27 1100 1161	26 761 749		
27 476 465		21 250* 130		34 176* 24	28 1100 1161	27 534 528		
28 219* 4		22 406 429		35 176* 24	29 1100 1161	28 227* 73		
29 249 603		23 511 477		36 176* 24	30 1100 1161	29 414 444		
30 244 210		24 449 471		37 176* 24	31 1100 1161	14 302* 7		
						15 459 518		
						16 294* 200		

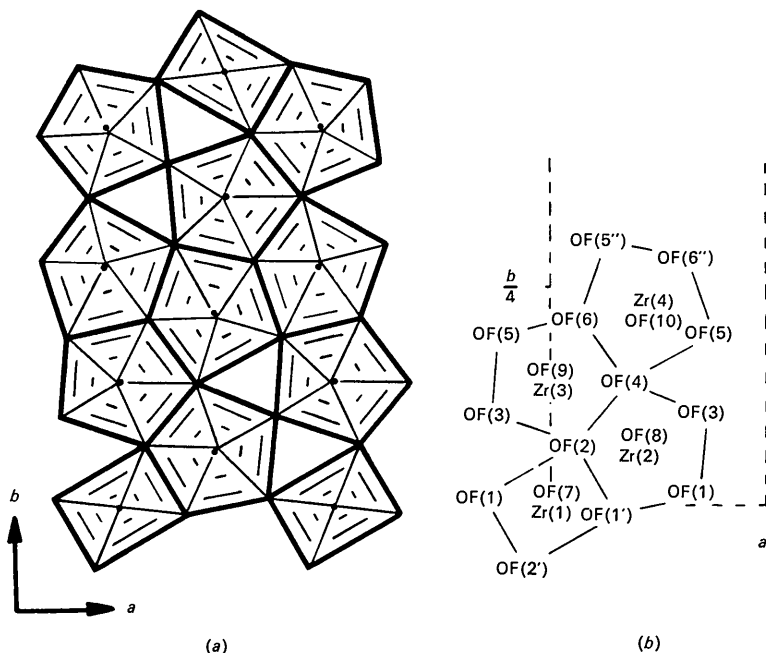


Fig. 1. Part of the $Zr_7O_9F_{10}$ structure viewed along the c axis. The zirconium atoms are represented by filled circles.

corner and edge sharing between these coordination polyhedra. In the (001) plane they are joined in both ways, but along the c axis only by corner sharing. In Table 6, giving the (O, F)–(O, F) distances, the distances between atoms common to two coordination groups

are marked with (s.e.). As expected the shared edges are shorter than the unshared edges of the coordination polyhedron.

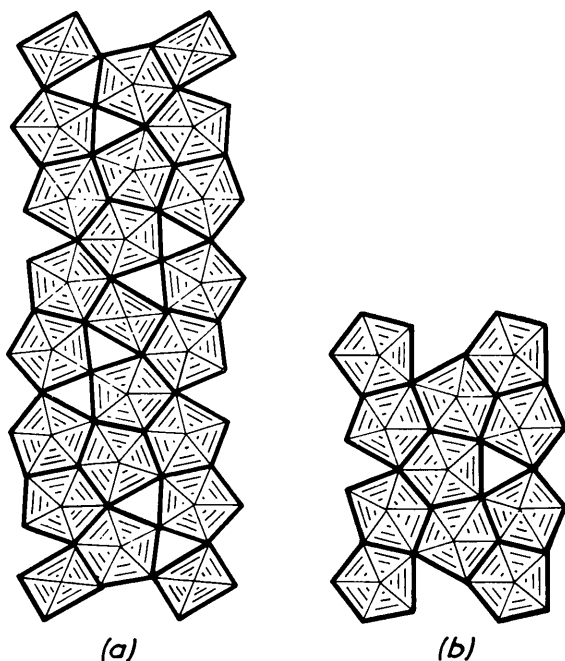


Fig. 2. Projections along the c_0 direction of the $Zr_7O_9F_{10}$ structure (a) and the U_3O_8 structure (b).

Table 5. Coordination around the zirconium atoms, distances with e.s.d.'s (Å)

Zr(1)–OF(1)	2.03 ± 0.02 (2)
–OF(2)	2.09 ± 0.03 (2)
–OF(7)	2.04 ± 0.01 (2)
Zr(2)–OF(1)	2.12 ± 0.02 (1)
–OF(1 ¹)	2.15 ± 0.02 (1)
–OF(2)	2.11 ± 0.03 (1)
–OF(3)	2.12 ± 0.02 (1)
–OF(4)	2.21 ± 0.02 (1)
–OF(8)	2.04 ± 0.01 (2)
Zr(3)–OF(2)	2.08 ± 0.03 (1)
–OF(3)	2.06 ± 0.02 (1)
–OF(4)	2.28 ± 0.02 (1)
–OF(5)	2.13 ± 0.02 (1)
–OF(6)	2.12 ± 0.02 (1)
–OF(9)	2.04 ± 0.01 (2)
Zr(4)–OF(4)	2.21 ± 0.02 (1)
–OF(5)	2.15 ± 0.02 (1)
–OF(6)	1.98 ± 0.02 (1)
–OF(5 ¹¹)	2.46 ± 0.02 (1)
–OF(6 ¹¹)	2.04 ± 0.03 (1)
–OF(10)	2.04 ± 0.01 (2)

Table 6. Interatomic distances (Å)

E.s.d.'s are less than 0.03 Å.

OF(7)–OF(1)	2.87	OF(1)–OF(2)	3.27
–OF(2)	2.92	OF(2)–OF(11)	2.51 (s.e.)
OF(8)–OF(1)	2.97	OF(11)–OF(1)	2.48 (s.e.)

Table 6 (cont.)

-OF(2)	2.96	OF(1) -OF(3)	2.55
-OF(3)	2.86	OF(3) -OF(4)	2.62
-OF(4)	2.93	OF(4) -OF(2)	2.43 (s.e.)
-OF(1')	3.06		
OF(9)-OF(2)	2.92	OF(2) -OF(3)	2.67
-OF(3)	2.85	OF(3) -OF(5)	2.50
-OF(4)	3.11	OF(5) -OF(6)	2.49 (s.e.)
-OF(5)	2.92	OF(6) -OF(4)	2.45 (s.e.)
-OF(6)	2.97		
OF(10)-OF(4)	2.94	OF(4) -OF(5)	2.95
-OF(5)	2.92	OF(5) -OF(6 ¹¹)	2.45 (s.e.)
-OF(6)	2.86		
-OF(5 ¹¹)	3.28		
-OF(6 ¹¹)	2.94		

Discussion

The relationship of $Zr_7O_9F_{10}$ to the hexagonal $\alpha-UO_3$ structure is similar to its relationship to the orthorhombic U_3O_8 (Zachariasen, 1945; Andresen, 1958; Loopstra, 1964), Fig. 2(b). Neglecting small shifts from the ideal positions, the cations form a pseudo-hexagonal arrangement with the following relation to the $\alpha-UO_3$ unit cell:

$$\begin{aligned} \mathbf{a}_o &= 2\mathbf{a}_{\text{hex}} + \mathbf{b}_{\text{hex}} \\ \mathbf{b}_o &= \mathbf{b}_{\text{hex}} & a_o &\neq b_o \cdot \sqrt{3} \\ \mathbf{c}_o &= \mathbf{c}_{\text{hex}} \\ V_o &= 2V_{\text{hex}}. \end{aligned}$$

Instead of describing these structures in relation to $\alpha-UO_3$ it is more convenient to relate them to a hypothetical orthorhombic MA_3 structure with the above defined unit cell and with all the common edges of the coordination polyhedra lying within the (001) plane [Fig. 3(a)]. If the formula is written $(MA)_2A_4$, the two groups of A atoms with different functions in the structure are better recognized. In Figs. 3(b) and (c) the structures of U_3O_8 and $Zr_7O_9F_{10}$ are shown in an idealized way. The U_3O_8 structure can be derived from three parent units by removing one A atom from every third plane perpendicular to \mathbf{b}_o . This changes the coordination of the M atoms from eight to seven and the composition to $(MA)_6A_{12-2}$. The sequence of A atoms which have been removed is $\overline{133}$. The $Zr_7O_9F_{10}$ structure can be derived from seven parent units by

removing A atoms in the sequence $\overline{43434}$ which gives the composition $(MA)_{14}A_{28-4}$. This implies that the coordination is unchanged for two of the fourteen M atoms. However, the rearrangement of the atoms around the empty sites (Fig. 4) increases the distances between these two cations and two of the anions [thus $Zr(1)-OF(3) = 3.29 \text{ \AA}$]. This leaves six anions as close neighbours, mean distance 2.05 \AA in $Zr_7O_9F_{10}$.

Starting from the hypothetical $(MA)_2A_4$ structure, a series of structures can be postulated in which the ratio between seven and eight coordinated M atoms may increase. Their compositions will be $(MA)_{2(3n+1)} \times A_{4(3n+1)-2n}$ where $(3n+1)$ is the number of parent units in which $2n$ A atoms have been removed. The

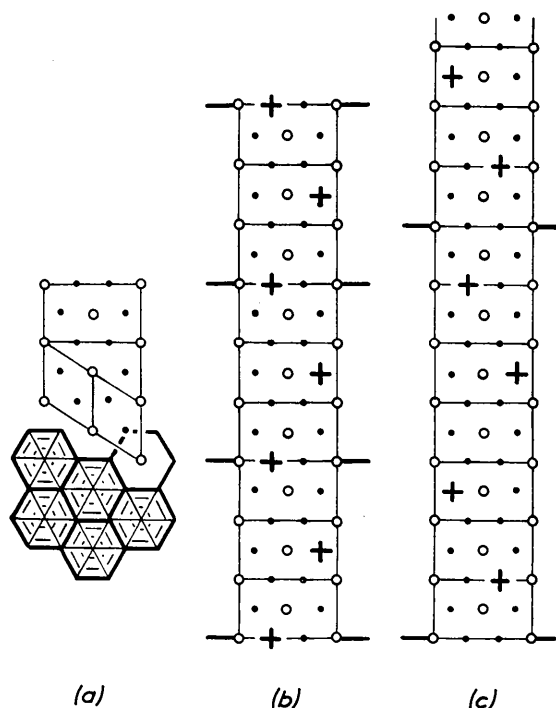


Fig. 3. The hypothetical orthorhombic MA_3 structure and its relation to $\alpha-UO_3$. Open circles represent M atoms at $z_0=0$ and A atoms at $z_0=\frac{1}{2}$ and small filled circles A atoms at $z_0=0$ (a). Idealized representation of the U_3O_8 (b) and the $Zr_7O_9F_{10}$ (c) structures. The crosses indicate A atoms subtracted from the MA_3 matrix.

Table 7. The series $(MA)_{2(3n+1)}A_{4(3n+1)-2n}$

Member	Number of parent units $(3n+1)$	Number of removed A atoms $(2n)$	Sequence	$(MA)_{2(3n+1)}A_{4(3n+1)-2n}$	$\frac{A}{M} = 3 - \frac{2n}{2(3n+1)}$	Compound
0	1	0		$(MeA)_2A_4$	3	
1	4	2	$\overline{144}$	$(MeA)_8A_{14}$	2.750	
2	7	4	$\overline{43434}$	$(MeA)_{14}A_{24}$	2.714	$Zr_7O_9F_{10}$
3	10	6	$\overline{134333333333}$	$(MeA)_{20}A_{34}$	2.700	
7	22	14	$\overline{1333433333334333}$	$(MeA)_{44}A_{74}$	2.682	
∞	3	2	$\overline{133}$	$(MeA)_6A_{10}$	2.667	U_3O_8

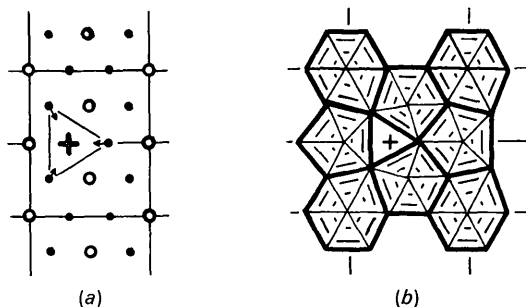


Fig. 4. The rearrangement of the nearest *A* neighbours to a subtracted *A* atom (a) connected with the coordination change from eight to seven (b).

sequences will be $\overline{44,43434}$, $\overline{343343}$ and so on. Thus, the structure of $Zr_7O_9F_{10}$ is the second member of this series and the U_3O_8 structure the end member, Table 7.

To reduce the anion to cation ratio below $\frac{8}{3}$ (M_3A_8) requires the introduction of six coordination by removing *A* atoms with the sequence 2, which very likely occurs in the oxygen deficient non-stoichiometric U_3O_8 (Sato, Doi, Ishii & Ushikoshi, 1961). This con-

cept will be further discussed in a forthcoming article on the structure of $Nb_5O_{12}F$.

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Aminoboranes. The Crystal Structure of 1, 3-Di-*p*-chlorophenyl-2-triethylcarbinyl-4-ethyl-5,5-diethyl-1,3-diaza-2,4-diborolidine, $C_{26}H_{38}N_2B_2Cl_2$ *

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The structure of 1,3-di-*p*-chlorophenyl-2-triethylcarbinyl-4-ethyl-5,5-diethyl-1,3-diaza-2,4-diborolidine, $C_{26}H_{38}N_2B_2Cl_2$, has been determined by a three-dimensional single-crystal X-ray diffraction study. The crystals are tetragonal, space group $P4_2/m$, $a = 16.943 \pm 0.008$, $c = 9.599 \pm 0.005$ Å at approximately -125°C with four molecules per unit cell. The structure was solved independently by Patterson map analysis and by the direct method. The molecule contains a heterocyclic five-membered ring which is isoelectronic with cyclopentadiene. Bond lengths in this ring are $N(1)-B(2) = 1.433$ (10), $B(2)-N(3) = 1.489$ (9), $N(3)-B(4) = 1.421$ (10), $B(4)-C(5) = 1.576$ (11) and $C(5)-N(1) = 1.492$ (10) Å. Crystal symmetry requires the molecule to have $m(C_s)$ symmetry which is, however, pseudosymmetry due to disorder of one of the ethyl groups. The residual is 0.072 for 1814 observed data.

Introduction

The heterocyclic compound, $C_{26}H_{38}N_2B_2Cl_2$, was synthesized by Casanova & co-workers (Casanova, Kiefer, Kuwada & Boulton, 1965; Casanova, 1966; Casanova & Kiefer, 1969) who suggested the problem to us as one which needed structural proof and as part of a con-

tinuing collaboration to determine fundamental chemical and structural information about aminoboranes. Our preliminary communication (Tsai & Streib, 1968) reported the correct structure to contain a diazadiborolidine ring. We present here the completed study and a more detailed interpretation of our results.

Experimental

The colorless crystals grew as needles of square cross-section when recrystallized from methanol. Preliminary

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