Table 5. *Principal axes of thermal ellipsoids*

α, β, γ are the direction cosines relative to the crystallographic axes **a**, **b**, **c**. D is the mean square displacement of the atom in the given direction.

	α	β	γ	D
S	0·3166	0·1076	0·9426	0·0529
	0·6991	0·6451	−0·3081	0·0411
	0·6412	−0·7564	−0·1286	0·0325
C(1)	0·8405	0·4295	−0·3300	0·0726
	0·1195	−0·7413	−0·6603	0·0315
	0·5283	−0·5156	0·6744	0·0189
C(2)	0·1277	−0·6699	0·7313	0·0207
	0·9534	0·2860	0·0955	0·0676
	0·2732	−0·6850	−0·6752	0·0505
N(1)	0·4605	0·2077	−0·8629	0·1130
	0·7643	−0·5870	0·2666	0·0583
	0·4511	0·7824	0·4292	0·0404
N(2)	0·4984	−0·8053	0·3207	0·0378
	0·3990	0·5416	0·7398	0·1007
	0·7695	0·2407	−0·5914	0·0818

The direction cosines of the principal axes of the thermal ellipsoids and the mean square amplitudes of vibration are given in Table 5. The anisotropies are not large, and there does not appear to be anything unusual about the vibrations of the molecule.

Work on this project was begun at the California Institute of Technology in 1961, and the author wishes to thank the Chemistry Department of that Institute for the award of an A. A. Noyes postdoctoral fellowship at that time. The computer center at Montana State University has made its facilities freely available for the computations required in this determination.

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The Crystal Structure of $ThTi_2O_6$ (Brannerite)

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(*Received* 31 *March* 1966)

$ThTi_2O_6$, synthesized at 1610°C by solid-state reaction, crystallizes in the monoclinic system, space group $C2/m$, with the unit-cell dimensions $a = 9{\cdot}822$, $b = 3{\cdot}824$, $c = 7{\cdot}036$ Å, $\beta = 118{\cdot}84°$. It contains layers formed by Ti–O octahedra sharing edges and corners in a manner reminiscent of the anatase structure, and these are joined through thorium ions in interlayer octahedral positions. There are two Th–O distances of 2·36 Å and four of 2·35 Å, but the octahedron is flattened; two more oxygen atoms further away at 2·96 Å are probably unbonded. Ti–O distances ranging from 1·83 to 2·20 Å are normal. The structure was determined by Fourier methods and refined by several three-dimensional least-squares cycles.

Introduction

One of the gaps of appreciable magnitude in the structural inorganic chemistry of solids is listed in *Dana's System of Mineralogy* (1944, p. 745 *et seq.*) under the general title 'multiple oxides containing columbium (sic), tantalum and titanium'. These minerals contain a wide variety of substituent elements which may include the actinide elements thorium and uranium, and many of them are found in the *metamict* state. Although seeming to form crystals with extensive facial development, metamict minerals are imperfectly crystallized or even glassy substances, and it is widely believed that

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they have undergone extensive radiation damage during the course of time. This could have resulted either from the disintegration of radio-elements originally present in the structure, or from a nuclear bombardment originating at some nearby external natural source. Metamict crystals can be recrystallized by heating but become polycrystalline, and doubts are raised whether or not a reconstituted specimen is identical in structure with the primordial mineral. It is therefore difficult to select naturally occurring specimens belonging to this general class, and new synthetic materials must be provided for detailed study.

Patchett & Nuffield (1960) prepared UTi_2O_6 and showed that its symmetry and unit-cell size were compatible with the morphological form development of metamict brannerite recorded by Pabst (1954), and also with powder diffraction patterns of the recrystallised mineral. The compound is not isomorphous with any other AB_2O_6 compound, despite an earlier report that UTi_2O_6 made at 1000°C had the columbite structure (Schröke, 1958).

Although thorium is recorded in most chemical analyses of brannerite as a minor replacement element, there is no known mineral analogue where it is an essential constituent (Frondel, 1956). Nevertheless $ThTi_2O_6$ was shown to exist in high- and low-temperature varieties (Perez y Jorba, Mondange & Collongues, 1961), but neither set of lattice parameters determined from Guinier powder patterns bore any obvious resemblance to those of UTi_2O_6 or columbite. We decided to examine $ThTi_2O_6$, and it has proved to be isostructural with UTi_2O_6 with a new type of crystal structure, which can be regarded as a derivative of the anatase form of TiO_2.

Experimental

$ThTi_2O_6$ was prepared by dry mixing weighed amounts of high purity ThO_2 and TiO_2, pressing into wafers, and then firing to 1610°C for one hour in vacuum. One specimen, heated at 1000°C in air for a further period of twelve hours, turned from black to light buff without any obvious change of powder pattern. This provided the crystal for the present study. The symmetry and approximate unit-cell size were determined by single-crystal methods, and accurate values of $\sin^2\theta$ for the low-angle reflexions were obtained on a Guinier-type focusing camera internally calibrated with potassium chloride (Table 1). The more precise lattice parameters listed in Table 2 were evaluated from these measurements by a least-squares fit. Table 2 also includes the data reported for UTi_2O_6 by Patchett & Nuffield (1960). The two compounds are clearly isostructural, with Th and U playing the same role in both structures.

This unit-cell assignment does not agree with that reported by Perez y Jorba *et al.* (1961) for either form of $ThTi_2O_6$. Their low temperature variety was stated to be orthorhombic with the unit-cell dimensions $a=16·7$, $b=14·95$, $c=4·1$ Å, while the high-temperature form was considered tetragonal with $a=7·58$, $c=10·45$ Å. Indeed the powder data in Table 1 can be indexed very roughly on this latter basis which, in view of the present new evidence, must be considered incorrect.

Table 1. *Powder pattern of* $ThTi_2O_6$, Cu $K\alpha_1$

I (obs.)	$\sin^2\theta$ (obs.)	$\sin^2\theta$ (calc.)	hkl
mw	0·01561	0·01563	001
ms	0·02607	0·02611	$20\bar{1}$
mw	0·03206	0·03209	200
ms	0·04862	0·04861	110
m	0·05141	0·05141	$20\bar{2}$
w	0·05339	0·05345	$11\bar{1}$
w	0·06251	0·06253	002
mw	0·06934	0·06933	201
w	0·07507	0·07505	111
mw	0·08958	0·08955	$11\bar{2}$
mw	0·09604	0·09604	$31\bar{1}$
vw	0·10078	0·10077	$40\bar{1}$
vw	0·11055	0·11054	$31\bar{2}$
w	0·11280	0·11281	310

Table 2. *Lattice parameters of* $ThTi_2O_6$ *with those of* UTi_2O_6 (*Patchett & Nuffield*, 1960) *included for comparison*

	$ThTi_2O_6$	UTi_2O_6
a	9·822 ± 0·005 Å	9·87 Å
b	3·824 ± 0·002	3·76
c	7·036 ± 0·005	6·95
β	118·84 ± 0·05°	119·5°
Unit-cell volume	231·4 Å^3	224·5 Å^3
D_m	6·0 ± 0·5 $g.cm^{-3}$	6·36 $g.cm^{-3}$
D_x	6·08 $g.cm^{-3}$	6·35 $g.cm^{-3}$
Z	2	2
Systematic absent reflexions	hkl with $h+k \neq 2n$	
Space group alternatives	$C2$, Cm, $C2/m$	

Intensity data were collected from a colourless crystal 0·15 × 0·05 × 0·05 mm oriented for rotation about the b axis. The levels hkl, with $k=0, 1 \cdots 5$ were recorded by the integrating Weissenberg method, using filtered molybdenum radiation to reduce absorption. Three films interleaved with tinfoil were used for each level. Intensities were measured by visual comparison with a calibrated film strip, and specimen absorption was neglected for such a small crystal. Scattering curves for Th^{4+} and Ti^{4+} were from the compilation of Cromer & Waber (1965) based upon relativistic Dirac–Slater wave functions, and corrected for both real and imaginary components of the anomalous scattering for Mo $K\alpha$, while Suzuki's data for O^{2-} were used for oxygen.

A total of 296 non-symmetry-related reflexions were recorded, and these data, scaled by comparison with structure factors calculated for the final model, are given in Table 3. All calculations were made on the Division's Elliott 803 Computer with the programming system of Daly, Stephens & Wheatley (1963) kindly made available by Dr P. J. Wheatley.

Structure determination

A satisfactory solution of the structure was found by assuming the space group $C2/m$, and no attempt was made to lower the symmetry group to either of the two possible alternatives, $C2$ or Cm. As there are two formula units in the unit cell, the Th atom can be placed at the origin in the point position $2(a)$. A projection of the Patterson function $P(u,w)$ immediately gave an approximate position for Ti in a general position $4(i)$. Fourier projections on to (010) were made, one a normal F_o synthesis and the other with the Th atom excluded in a partial difference map. Two of the three oxygen atoms were clearly visible in this latter case (Fig. 1), while the contours of the Ti atom were rather elongated, suggesting that the third oxygen atom was overlying it in the projection.

From this it was possible to derive a complete structure satisfying the space group and formula criteria. Refinement continued with a number of three-dimensional least-squares cycles, using individual isotropic temperature factors for each atom. The weighting scheme of Cruickshank (1961):

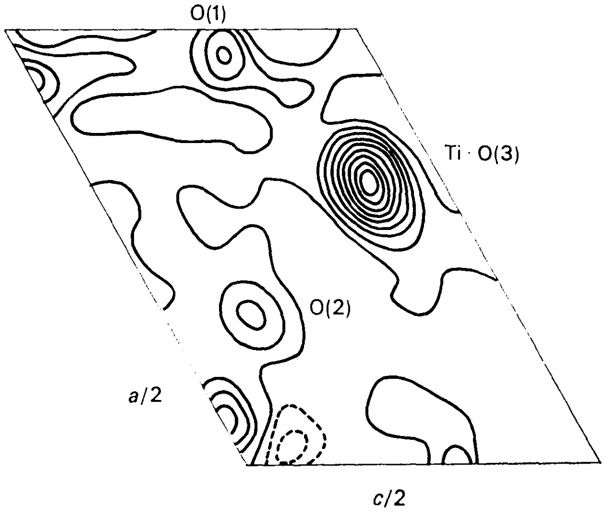

Fig. 1. $F_o - F_{Th}$ projection on to (010), contoured at arbitrary intervals. Ti (plus an overlying oxygen atom), and two additional oxygen atoms are visible. There is evidence at (0,0) for anisotropic thermal motion of the Th, removed from this position.

Table 3. *Observed and calculated structure factors* (× 10)

h	k	l	F_o	F_c
0	0	1	371	407
0	0	2	1446	1502
0	0	3	1617	1531
0	0	4	353	476
0	0	5	1224	1143
0	0	6	451	556
0	0	7	501	721
0	0	8	651	622
2	0	0	1022	957
2	0	1	1857	1960
2	0	2	217	197
2	0	3	1355	1380
2	0	4	1093	1041
2	0	5	443	530
2	0	6	1113	1010
2	0	−1	1023	1491
2	0	−2	1597	1450
2	0	−3	977	1028
2	0	−4	1739	1691
2	0	−5	599	640
2	0	−6	561	921
2	0	−7	593	906
2	0	−9	705	632
4	0	0	1234	1156
4	0	1	901	923
4	0	2	1739	1404
4	0	3	579	602
4	0	4	1153	1054
4	0	5	499	569
4	0	7	419	601
4	0	−1	1103	1292
4	0	−2	277	359
4	0	−3	1436	1307
4	0	−4	710	916
4	0	−5	931	976
4	0	−6	1255	1190
4	0	−7	327	477
4	0	−8	720	673
6	0	0	1527	1421
6	0	1	796	936
6	0	2	609	577
6	0	3	881	857
6	0	4	363	324
6	0	−1	348	421
6	0	−2	1033	1312
6	0	−3	695	954
6	0	−4	445	521
6	0	−5	951	1004
6	0	−6	609	556
6	0	−7	311	737
6	0	−8	621	576
6	0	−9	549	439
6	0	−10	730	450
8	0	0	443	395
8	0	1	943	798
8	0	−1	730	795
8	0	−2	767	934
8	0	−3	579	652
8	0	−4	531	562
8	0	−5	429	456
8	0	−6	786	651
8	0	−7	489	409
8	0	−8	369	343
8	0	−9	559	529
10	0	−1	499	405
10	0	−2	337	360
10	0	−3	521	660
10	0	−5	599	555
10	0	−6	781	561
10	0	−7	363	294
10	0	−8	665	433
10	0	−9	408	289
1	1	0	1472	1767
1	1	1	1619	1410
1	1	2	563	544
1	1	3	1697	1716
1	1	4	327	307
1	1	6	901	793
1	1	8	551	556
1	1	−1	732	612
1	1	−2	1661	1351
1	1	−3	1095	1113
1	1	−4	1009	1023
1	1	−5	1203	1106
1	1	−6	732	659
1	1	−7	947	963
3	1	0	1137	1256
3	1	1	1619	1594
3	1	2	913	899
3	1	3	907	773
3	1	4	1007	771
3	1	6	417	660
3	1	7	545	556
3	1	−1	1513	1550
3	1	−2	901	1347
3	1	−3	827	1034
3	1	−4	1137	1151
3	1	−5	371	430
3	1	−6	1033	1032
3	1	−7	637	660
3	1	−8	497	503
3	1	−9	773	652
5	1	0	1149	1229
5	1	1	505	555
5	1	2	955	355
5	1	3	[illegible]	520
5	1	4	652	519
5	1	5	505	659
5	1	−1	995	953
5	1	−2	796	934
5	1	−3	1162	1605
5	1	−4	491	597
5	1	−5	314	939
5	1	−6	514	775
5	1	−8	693	656
7	1	0	693	753
7	1	1	840	806
7	1	3	693	746
7	1	−2	974	1033
7	1	−3	524	606
7	1	−4	759	799
7	1	−5	995	839
7	1	−6	517	566
7	1	−7	914	706
7	1	−9	531	454
9	1	1	693	627
9	1	−1	773	698
9	1	−3	517	557
9	1	−4	605	544
9	1	−6	796	674
9	1	−9	539	445
11	1	−3	559	518
11	1	−5	691	436
11	1	−7	511	260
0	2	1	999	659
0	2	2	1265	1158
0	2	3	1297	1197
0	2	−4	375	458
0	2	−5	1075	954
0	2	−6	439	513
0	2	−7	693	622
0	2	−8	521	544
2	2	0	1024	795
2	2	1	1609	1477
2	2	2	337	310
2	2	3	1100	1103
2	2	4	391	369
2	2	6	951	964
2	2	−1	1100	1111
2	2	−2	1659	1443
2	2	−3	795	794
2	2	−4	1317	1307
4	2	0	935	904
4	2	1	792	705
4	2	2	1125	1124
4	2	3	407	524
4	2	4	977	999
4	2	−1	966	1062
4	2	−2	324	393
4	2	−3	1215	1359
4	2	−4	617	707
4	2	−5	769	724
4	2	−6	1011	[illegible]
6	2	0	1075	1131
6	2	1	693	599
6	2	2	427	504
6	2	3	642	727
6	2	−1	363	402
6	2	−2	977	1030
6	2	−3	629	725
6	2	−4	375	465
6	2	−5	935	940
6	2	−6	421	491
6	2	−7	642	621
8	2	1	642	680
8	2	−1	595	656
8	2	−2	573	639
8	2	−4	579	723
8	2	−6	629	555
1	3	0	1129	1079
1	3	1	1603	920
1	3	2	594	619
1	3	3	1257	1127
1	3	4	545	568
1	3	5	585	595
1	3	6	448	599
1	3	−1	602	481
1	3	−2	1223	995
1	3	−3	775	704
1	3	−4	739	730
1	3	−5	739	736
1	3	−6	425	437
1	3	−7	456	650
3	3	0	791	711
3	3	1	1215	1023
3	3	2	577	652
3	3	3	342	557
3	3	4	658	732
3	3	−1	1102	1042
3	3	−2	531	700
3	3	−3	650	719
3	3	−4	771	917
3	3	−5	271	377
3	3	−6	715	753
3	3	−7	384	420
5	3	0	721	[illegible]
5	3	1	327	[illegible]
5	3	2	635	632
5	3	3	367	465
5	3	4	319	461
5	3	5	339	504
5	3	−1	619	643
5	3	−3	945	1020
5	3	−5	619	631
5	3	−6	505	563
7	3	0	573	538
7	3	−2	675	725
7	3	−4	491	577
7	3	−5	577	575
7	3	−7	449	525
9	3	1	472	466
9	3	−1	441	507
9	3	−6	545	499
0	4	1	646	469
0	4	2	1007	676
0	4	3	799	710
0	4	4	291	323
0	4	5	615	601
0	4	6	325	343
0	4	7	340	414
0	4	8	361	371
2	4	0	701	510
2	4	1	1079	925
2	4	2	279	290
2	4	3	646	669
2	4	4	423	552
2	4	6	495	569
2	4	−1	538	642
2	4	−2	325	303
2	4	−3	476	490
2	4	−4	905	767
2	4	−5	299	356
2	4	−6	313	451
2	4	−7	333	461
4	4	0	623	544
4	4	1	406	462
4	4	2	723	676
4	4	4	561	573
4	4	−1	774	651
4	4	−2	271	315
4	4	−3	755	771
4	4	−4	406	462
4	4	−5	423	456
4	4	−6	538	627
4	4	−8	344	358
6	4	0	661	684
6	4	1	437	436
6	4	3	406	471
6	4	−2	646	612
6	4	−3	414	468
6	4	−4	295	309
6	4	−5	429	533
6	4	−6	313	319
6	4	−7	406	411
8	4	−3	307	345
8	4	−4	445	462
8	4	−5	313	266
8	4	−6	325	362
1	5	0	891	574
1	5	1	627	502
1	5	2	371	342
1	5	3	659	627
1	5	5	259	350
1	5	−1	255	294
1	5	−2	730	554
1	5	−3	377	356
1	5	−4	333	418
1	5	−5	402	449
1	5	−7	303	392
3	5	0	371	391
3	5	1	697	559
3	5	2	383	372
3	5	3	276	317
3	5	4	408	433
3	5	−1	575	569
3	5	−2	319	391
3	5	−3	377	409
3	5	−4	543	459
3	5	−6	357	441
5	5	0	466	495
5	5	2	350	367
5	5	−1	377	353
5	5	−2	267	363
5	5	−3	537	557
5	5	−5	344	354
5	5	−6	296	326
7	5	0	293	306
7	5	−2	395	412
7	5	−4	290	314
7	5	−5	296	340
7	5	−7	299	310

Table 4. *Fractional atomic coordinates and standard deviations*

Space group $C2/m$, $(0,0,0)\ (\frac{1}{2},\frac{1}{2},0)+$

	Point position	x	y	z	$\sigma(x)$	$\sigma(z)$	B (Å^2)	$\sigma(B)$
Th(1)	2 (a)	0	0	0	0	0	1·26	0·05
Ti(1)	4 (i)	0·8220	0	0·3945	0·0015	0·0021	1·42	0·17
O(1)	4 (i)	0·974	0	0·314	0·005	0·007	1·1	0·6
O(2)	4 (i)	0·660	0	0·117	0·006	0·008	1·3	0·7
O(3)	4 (i)	0·298	0	0·411	0·009	0·012	3·3	1·4

$$w = \frac{1}{a + |F_o| + c|F_o|^2}, \quad a = 2|F_{\min}|, \quad c = \frac{2}{|F_{\max}|}$$

was adopted, and the matrix inversion involved the block diagonal approximation.

After each cycle the scaling factors for the various levels were adjusted by comparison with the calculated structure amplitudes. It soon became obvious that the *h*3*l* data were not as accurate as those from other levels owing to some malfunction of the camera during the lengthy exposure. Consequently the reflexions from this level were excluded, and the refinement continued until shifts of thermal and positional parameters were less than one-fourth the estimated standard deviations. These parameters are listed in Table 4. Finally three further cycles were made assuming the Th and Ti atoms were vibrating anisotropically. There is some evidence for this in the partial difference map (Fig. 1). This reduced the *R* value for the five levels of data from 14·3 to 11·6%. The corrections to the metal atoms expressed as the six mean-square-amplitude tensors U_{ij} (Cruickshank, 1965) are given in Table 5, and were used in the final calculations of structure factors (Table 3). The *h*3*l* terms are also included in this table; their inclusion raised the overall *R* value from 11·6 to 12·2%.

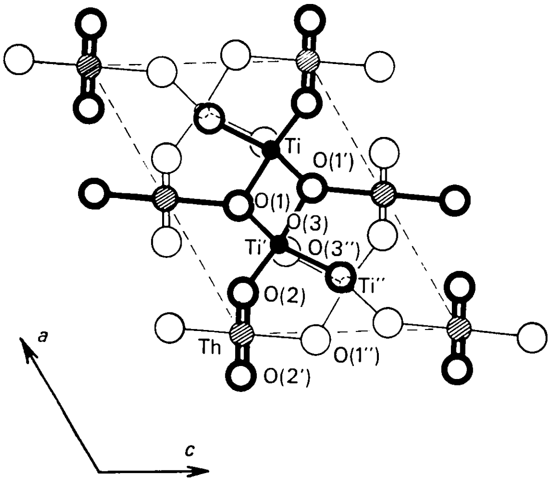

Fig. 2. Structure of $ThTi_2O_6$. Smallest circles Ti, largest O. The Th atoms are hatched.

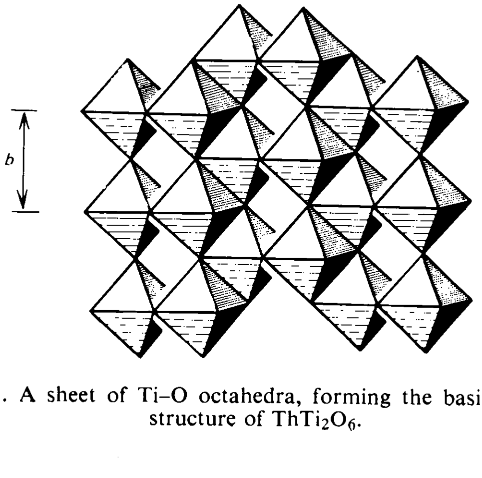

Fig. 3. A sheet of Ti–O octahedra, forming the basis of the structure of $ThTi_2O_6$.

Table 5. *Anisotropic thermal corrections to metal atoms*

Mean-square-amplitude tensors U_{ij}

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Th(1)	0·0271	0·0152	0·0115	0·0000	0·0000	0·0100
Ti(1)	0·0318	0·0180	0·0180	0·0000	0·0000	0·0066

Description

The structure is illustrated as a ball-and-spoke drawing in Fig. 2 and as an assemblage of octahedra in Fig. 4(*a*). All the atoms are located in mirror planes normal to the *b* axis and at the two levels, $y=0$ and $\frac{1}{2}$. There are two Ti atoms at $y=\frac{1}{2}$ octahedrally coordinated to oxygen and joined by a common edge [the atoms O(1)], while identical pairs centred at $y=0$ are united to it at opposite ends by additional edge-sharing. These build up into infinite zigzag sheets centred about the (100) planes (Fig. 3) and there are no atoms common to adjacent sheets. These Ti–O octahedra, all of which are crystallographically identical, are somewhat distorted (Table 6), the Ti–O distances ranging from 1·83 ± 0·04 Å to 2·20 ± 0·07 Å with an average value of 1·97 Å. The shortest oxygen–oxygen distance of 2·41 ± 0·06 Å is between the atoms O(1).

Table 6. *Interatomic distances and e.s.d's* (Å)

Th —O(2)	2·35 ± 0·04 (4)
Th —O(1'')	2·36 ± 0·05 (2)
O(2)—O(2')	2·76 ± 0·06 (2)
O(2)–O(1'')	3·38 ± 0·06 (8)
O(2)—O(2)	3·824 (2)
Ti—O(1)	1·83 ± 0·04 (1)
Ti—O(2)	1·83 ± 0·05 (1)
Ti—O(3)	1·94 ± 0·07 (2)
Ti—O(3'')	2·20 ± 0·07 (1)
Ti—O(1')	2·06 ± 0·04 (1)
O(1)—O(1')	2·41 ± 0·06 (1)
O(1)—O(2)	2·70 ± 0·06 (1)
O(2)—O(3'')	3·15 ± 0·08 (1)
O(3'')–O(1')	2·92 ± 0·08 (1)
O(1)—O(3)	2·87 ± 0·08 (2)
O(2)—O(3)	2·66 ± 0·08 (2)
O(3)—O(3'')	2·69 ± 0·10 (2)
O(3)—O(1')	2·87 ± 0·08 (2)
Ti—Ti'	3·07 ± 0·02
Ti—Ti''	3·15 ± 0·02

The Th atoms, binding the sheets together, are located in octahedral interlayer positions. Although the Th–O bonds are not significantly different, two of 2·36 ± 0·04 Å and four of 2·35 ± 0·05 Å, the octahedron is far from regular (Table 6). Further away at 2·96 ± 0·07Å are the two symmetry related atoms O(3), but they are unbonded according to Pauling's electrostatic bond length criterion. If they were bonded, the coordination would be eightfold, a hexagonal bipyramid. Thorium usually is in cubic coordination in oxides, and we can find no previous report of an environment similar to the present one.

Discussion

Most AB_2O_6 compounds fall into a small number of distinct groups (Wyckoff, 1965, p.361 *et seq.*) with little or no obvious resemblance to the present case. Since the lattice constants for low temperature UTi_2O_6 recorded by Schröke (1958) were considered to be characteristic of the columbite structure, the diffraction pattern for low temperature $ThTi_2O_6$ (Perez y Jorba *et al.*, 1961) should perhaps be reassessed with this in view. Although Th^{4+} and U^{4+} are much larger than is usual for the A ions in this particular class, the columbite structure, which is built up from layers of hexagonally close-packed oxygen atoms, might be sufficiently elastic to provide sites of suitable size for these large ions and for the much smaller Ti^{4+} ions as well.

Compounds of this type, however, generally contain Nb^{5+}, Ta^{5+} or Sb^{5+} in the B positions. On the other hand the presence of octahedra joined by edges in pairs, or in linear groups of three, is a much more characteristic feature of titanates (Andersson & Wadsley, 1962) and may ultimately prove to be just as important a structure-determining criterion as the more conventional considerations of ionic size, charge and lattice energy. It was not altogether surprising to find that $ThTi_2O_6$ could be related to the anatase form of TiO_2, which is shown in Fig.4(*b*). If we imagine this latter structure to be sliced along the (101) direction at intervals of one unit cell, the sheets of octahedra are identical with those in $ThTi_2O_6$ shown in Figs.3 and 4(*a*). The relative positions of adjacent sheets give rise to the large flattened octahedral holes into which the Th ions fit, and in so doing provide charge neutrality and maintain structural stability.

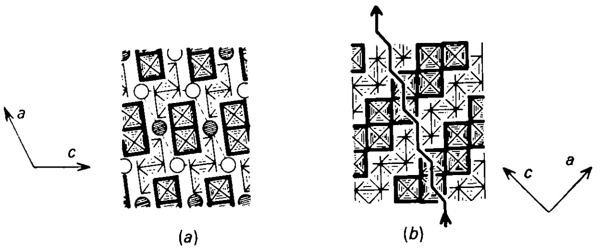

Fig.4. (*a*) Idealized octahedral drawing of $ThTi_2O_6$ projected on to (010). The Th atoms are drawn as circles. (*b*) Idealized drawing of TiO_2 (anatase). The row of octahedra highlighted with a thick arrowed line is common also to (*a*). The axial directions are shown by the smaller arrows.

One of us (R.R.) wishes to thank the Ian Potter Foundation for a grant enabling him to visit Australia for a period of study leave, and A.J. Gaskin and L.S. Williams for having arranged it. We are grateful to H.O. Bielstein for kindly preparing the specimens.

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