The closest approach between carbon atoms in different molecules is 3·5 Å.

The hydrogen-bond formation is indicated more clearly in Fig. 8. There are two types of hydrogen bond, each of which links a pair of non-equivalent molecules; the O–O distances are 2·72 Å and 2·79 Å respectively. Every molecule is linked, by hydrogen bonds between the oxygen atoms, to two neighbours, thus forming chains of molecules; adjacent molecules in any chain are crystallographically non-equivalent. Each chain runs throughout the crystal with its length parallel to the *a* axis. Although the chains run parallel to the planes of the sheets there are no hydrogen-bond linkages between neighbouring chains; the closest distance of approach between oxygen atoms in neighbouring chains is 4·30 Å (Fig. 8).

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 500 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible; and proofs will not generally be submitted to authors. Publication will be quicker if the contributions are without illustrations.*

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Structural relations of UO_2, isometric $PbUO_4$ and orthorhombic $PbUO_4$.

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We have synthesized* isometric and orthorhombic polymorphs of $PbUO_4$ that hitherto have not been described crystallographically. The orthorhombic phase may be identical with material synthesized by Zehenter (1904). Both substances contain hexavalent uranium and the formula is more properly written $Pb(UO_2)O_2$.

Table 1

Isometric UO_2		Isometric $PbUO_4$		Orthorhombic $PbUO_4$		Orthorhombic $BaUO_4$	
hkl	2θ	*hkl*	2θ	*hkl*	2θ	*hkl*	2θ
111	28·27°	111	27·59°	102	27·14°	102	26·80°
				120	27·62	120	26·95
200	32·76	200	31·96	022	31·40	022	31·05
				200	32·40	200	31·22
220	47·00	220	45·82	004	44·30	004	33·10
				040	45·63	040	44·62
311	55·76	311	54·34	124	52·96	124	52·42
				142	53·81	142	52·85
222	58·47	222	56·96	302	54·65	302	55·03
				204	55·88	204	55·43

$d_{100} = 5·468$ Å $d_{100} = 5·600$ Å $d_{100} = 5·528$ Å
$2d_{110} = 7·733$ $2d_{110} = 7·920$ $d_{010} = 7·952$
$2d_{1\bar{1}0} = 7·733$ $2d_{1\bar{1}0} = 7·920$ $d_{001} = 8·180$

The isometric polymorph is isostructural with UO_2, with $a_0 = 5·600 \pm 0·002$ Å, in so far as can be determined by X-ray powder diffraction methods. Neutron diffraction study may reveal a multiple and perhaps a non-isometric cell. The phase was obtained by heating U_3O_8 with PbO and excess sheet lead in water at 230°–290° C. It forms orange–brown isotropic cubes with an index of refraction over 2·0. If U_3O_8 is used in molar excess over PbO, mixtures are obtained of $PbUO_4$ with stoichiometric UO_2 ($a_0 = 5·468$ Å). It may be noted that the calculated Eh–pH boundary (at 25 °C.) of the PbO/Pb couple is below that of the U_3O_8/UO_2 couple (Latimer, 1952). The isometric phase apparently is stabilized by the presence of small amounts of U^4 in solid solution. Increase in the amount of UO_2 formed concurrently is accompanied by an increase of U^4 in solid solution, to an apparent maximum of $x \sim 0·2$ in the formula $Pb(U^6_{1-x}U^4_x)O_{4-x}$. On heating in air, the U^4 is oxidized and the substance then converts to an orthorhombic polymorph. The conversion is rapid over about 450°. We also have synthesized

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the orthorhombic polymorph directly by heating U_3O_8 with sheet lead and Pb_3O_4 or PbO_2 in water at 280°.

Orthorhombic $PbUO_4$ was found by the X-ray powder method to have the unit-cell dimensions

$$a_0 = 5{\cdot}528, \quad b_0 = 7{\cdot}952, \quad c_0 = 8{\cdot}180 \text{ Å} .$$

It is isostructural with $BaUO_4$, described by Samson & Sillén (1947). The strong pairs of lines that dominate the patterns of orthorhombic $PbUO_4$ and $BaUO_4$ correspond closely in angle to the five strong inner lines in the patterns of UO_2 and isometric $PbUO_4$. These lines are listed in Table 1, together with the dimensional relations obtaining when the isometric and orthorhombic cells are mutually oriented with (100) [001] of the former parallel to (100) [110] of the latter. The indexed X-ray powder spacing data for isometric and orthorhombic $PbUO_4$ are listed in Table 2. The measurements were made in copper radiation filtered through nickel foil.

Table 2

Isometric $PbUO_4$ (Indexing for a_0=5·600 Å)				Orthorhombic $PbUO_4$ (Indexing for a_0=5·528, b_0=7·952, c_0=8·180 Å)			
I	d_o	d_c	*hkl*	*I*	d_o	d_c	*hkl*
100	3·230 Å	3·233	111	3	4·080 Å	4·090	002
51	2·799	2·800	002	2	3·972	3·976	020
42	1·979	1·980	220	11	3·570	3·576	021
42	1·688	1·688	113	100	3·284	3·288	102
13	1·616	1·616	222	93	3·228	3·228	120
6	1·400	1·400	004	12	3·000	3·003	121
14	1·284	1·285	133	58	2·848	2·851	022
12	1·252	1·252	024	36	2·764	2·764	200
8	1·144	1·143	224	5	2·249	2·269	220
8	1·078	1·078	333, 115	8	2·187	2·187	221
3	0·9907	0·9900	440	6	2·084	2·083	123
8	0·9472	0·9466	135	17	2·045	2·045	004
9	0·9343	0·9333	006, 442	53	1·988	1·988	040
Broad	—	0·8854	026			1·984	222
Broad	—	0·8540	335	8	1·931	1·918	104
Broad	—	0·8442	226	6	1·873	1·870	140
						1·863	231
				11	1·823	1·819	024
						1·824	141
				4	1·790	1·795	310
						1·780	042
				30	1·729	1·727	124
				20	1·703	1·701	142
				24	1·679	1·680	302
				18	1·645	1·644	204
				8	1·615	1·614	240
				5	1·585	1·583	241
				6	1·544	1·547	322
				3	1·504	1·501	242
				9	1·427	1·425	044

The relations described stem from the very similar arrangement and spacing of the heavy atoms in the isometric and orthorhombic structures. In the isometric phases, the (U, Pb) are on a face-centred-cubic lattice. In the orthorhombic polymorph, the heavy atoms are in a slightly distorted face-centred-cubic array, oriented to the isometric cell as described, but with alternate planes parallel (100) containing wholly U or (Pb, Ba) atoms. The arrangement of the relatively weakly diffracting oxygen ions, however, differs in each of the three structures. In isometric UO_2 the U^4 ions are in symmetrical eight-coordination with oxygen, with every oxygen coordinated to four U ions. In isometric $PbUO_4$ the U^6 ions are in distorted eight-coordination with oxygen, two opposing oxygen ions of the coordination group presumably becoming more closely associated with the U^6 ion to form the uranyl configuration. In this substance the linear axes of the uranyl groups, whether in ordered or disordered array, must be in non-parallel sets to conform to isometric or pseudo-isometric symmetry. In the conversion to the orthorhombic phase the uranyl ions become collinear along the new *a*-axis. The two oxygen ions of the uranyl configuration are not shared with other U ions, and the coordination number drops from eight to six. The net effect is to produce indefinitely extending orthogonal layers parallel (100) with the composition $[(UO_2)O_2]^{-2}$. The (Pb, Ba) ions are held in distorted eight-coordination between these layers.

The rhombohedral compounds $Ca(UO_2)O_2$ and $Sr(UO_2)_2$, in which the divalent metal ions are smaller, also are structurally related to UO_2 but in a different way. As shown by Zachariasen (1948), they contain hexagonal layers $[(UO_2)O_2]^{-2}$ with the U^6 ion in eight-coordination, with the structural analogy between (111) and (0001) planes of the isometric and rhombohedral phases respectively.

The transition from the three-dimensional U–O linkage in UO_2 to the two-dimensional layered phases is caused primarily by the formation and the manner of arrangement of the uranyl ions. An intermediate stage is found in the tetragonal, deformed UO_2-type structure (Alberman & Anderson, 1949) of $UO_{2\cdot2-2\cdot3}$. A rather similar relation is found between certain ammonium or nitrosyl compounds and nitronium compounds. The layered structures of nitronium nitrate (Grison *et al.*, 1950), $(NO_2)(NO_3)$, and of uranyl carbonate (Christ *et al.*, 1955), $(UO_2)(CO_3)$, are similar in principle if not in detail.

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