The Mo—O(3)—Mo chain is not symmetry restricted to equivalent Mo—O(3) distances, and in fact the distances are drastically different, with Mo—O(3) and Mo—O(3′) bond distances of 1·684 (7) and 2·432 (7) Å. Distorted octahedral molybdenum coordination is completed by equatorial Mo—O distances of 1·868 (2)–1·999 (6) Å. This type of coordination has been observed before for molybdenum in binary oxide compounds (Magnéli, 1953; Wyckoff, 1964).

The absence of discrete molybdate tetrahedra and the existence of oxide anions not bonded to molybdenum indicate the compound discussed herein should be formulated as a double molybdenum oxide and not as the dimolybdate $U(MoO_4)_2$. This phase appears to be unique to uranium.

The UMo_2O_8 structure presented here has structural similarities to other uranium binary oxide structures. For example, the interlayer spacing of 4·1 Å set up by short U—O—U bridges and in-plane zig-zag chains of edge-shared pentagonal bipyramids are structural features found in UVO_5 and in all phases of U_3O_8 (Ackerman, Chang & Sorrell 1977; Shih-Hua, Kovba & Spitsyn, 1963; Chevalier & Gasperin, 1970; Andresen, 1958; Loopstra, 1964, 1970*a*, *b*, 1977). The UVO_5 structure (Fig. 1) especially resembles the orthorhombic uranium molybdate structure, since in UVO_5 zig-zag chains of uranium polyhedra are connected by a single row of vanadate octahedra. The vanadium atoms are coordinated as distorted octahedra very much like the molybdenum atoms in the orthorhombic UMo_2O_8 structure.

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Orthorhombic Thorium(IV) Molybdate, $Th(MoO_4)_2$*

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Abstract. $M_r = 551{\cdot}9$, orthorhombic, *Pbca*, $a = 10{\cdot}318\,(5)$, $b = 9{\cdot}737\,(4)$, $c = 14{\cdot}475\,(6)$ Å, $V = 1454$ Å^3, $Z = 8$, $D_x = 5{\cdot}04$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}70930$ Å, $\mu = 244$ cm^{-1}, $F(000) = 1904$, $T = 298$ K, $R = 0{\cdot}038$ for 3167 unique reflections. The structure is that of a true molybdate, with nearly regular molybdate tetrahedra bridging to thorium coordinated in a nearly regular square antiprismatic environment. The structure determination generally confirms but markedly improves a rough structure previously reported.

Introduction. Actinide molybdate formation has been suggested as a possible explanation for the troublesome formation of insoluble plutonium-containing residues in nuclear-waste processing (Penneman, Haire & Lloyd, 1980). Although crystal-structure determinations have been reported for several tetravalent actinide molybdates, in most cases the reports have been inaccurate or even incorrect (Cremers, Eller, Penneman & Herrick, 1983).

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A plutonium molybdate phase with cell parameters $a = 9{\cdot}42$, $b = 10{\cdot}05$, and $c = 13{\cdot}98$ Å has been reported (Prokoshin, Ustinov, Andrianov, Chebotarev & Matyshin, 1976; Tabuteau, Pagès & Freundlich, 1972). This $Pu(MoO_4)_2$ phase does not appear to be isostructural with any reported uranium molybdate phase but seems to be more closely related to the low-temperature orthorhombic $Th(MoO_4)_2$ phase first reported by Freundlich & Pagès (1969) (cell constants: $a = 9{\cdot}74$, $b = 10{\cdot}32$, $c = 14{\cdot}46$ Å). Although Thoret (1974) reported a single-crystal study of this phase, there appear to be serious difficulties with the light-atom positions in this structure, and we have been unable to reproduce the reported bond distances using Thoret's atomic coordinates. The relatively high R factor for this determination and serious discrepancies in other structures reported in the same paper provide ample justification for a re-examination of the structure reported for orthorhombic thorium(IV) molybdate.

Experimental. Tabular crystals from heating the hexagonal form at 973 K for one week, followed by cooling to room temperature over a period of 1·5 d. Precession photographs exhibited Laue symmetry and systematic absences uniquely consistent with *Pbca* [a and b are interchanged in the previous study by Thoret (1974)], crystal *ca* 200 × 80 × 40 μm, automated Picker diffractometer, cell refinement with nine reflections, $2\theta > 57°$, octant of data for $3 < \theta < 35°$ collected, θ–2θ technique, two standard reflections monitored every fifty reflections, absorption corrections by Gaussian integration (transmission coefficients = 0·14–0·38), heavy-atom method, anisotropic least-squares refinement on F (including isotropic secondary extinction) to $R = 0{\cdot}038$, $R_w = 0{\cdot}025$ for 3167 unique data, 2620 with $I \geq 2\sigma(I)$, neutral-atom scattering factors, corrected for anomalous dispersion (*International Tables for X-ray Crystallography,* 1962). Other details of the refinement procedure are as previously described, including computer programs and weighting scheme (Ryan & Swanson, 1974; Ryan, Eller & Kubas, 1976). Largest feature in final difference synthesis was a peak near the thorium position about half that of a typical oxygen atom, maximum shift/error ratio = 0·03.*

Discussion. Positional parameters are listed in Table 1.

In marked contrast to the structure of hexagonal thorium(IV) molybdate, which contains both six- and nine-coordinate thorium, the orthorhombic form contains thorium in only one coordination environment (Fig. 1). Thorium is coordinated to eight oxygen atoms from molybdate tetrahedra, in the form of a slightly distorted square antiprism. The Th—O distances range from 2·360 (4) to 2·459 (4) Å [mean 2·403 (4) Å]. The O—O—O angles and the O—O separations defining the two square faces range from 84·1 (2) to 98·1 (2)° and 2·780 (6) to 2·944 (6) Å, respectively, while the separations within the triangular faces range from 2·915 (6) to 3·084 (6) Å. The molybdate coordination is nearly regular tetrahedral, with Mo—O = 1·743 (4)–1·778 (4) Å [mean 1·752 (4) Å] and O—Mo—O = 106·4 (2)–111·8 (2)°. Each oxygen is shared by one thorium and one molybdenum. Our determination generally is consistent with the far less accurate determination reported by Thoret (1974), with marked improvement in the metal–oxygen distances. The largest difference in atomic positions between Thoret's determination and ours is for O(6), 0·42 Å. There is no apparent simple relationship to the structures of orthorhombic UMo_2O_8 (Cremers *et al.*, 1983) or hexagonal $Th(MoO_4)_2$.

Table 1. *Fractional coordinates and equivalent thermal parameters for orthorhombic* $Th(MoO_4)_2$

	x	y	z	B_{eq} (Å^2)*
Th(1)	0·46581 (2)	0·27575 (2)	0·10894 (1)	0·55
Mo(1)	0·10492 (4)	0·18167 (4)	0·15184 (3)	0·76
Mo(2)	0·72440 (4)	0·00106 (4)	0·06033 (3)	0·67
O(1)	0·4975 (4)	0·2639 (4)	0·2721 (3)	1·3
O(2)	0·1119 (4)	0·0898 (4)	0·3683 (3)	1·3
O(3)	0·3603 (4)	0·0903 (4)	0·0254 (3)	1·6
O(4)	0·0728 (4)	0·2369 (5)	0·0389 (3)	1·6
O(5)	0·3289 (4)	0·1166 (4)	0·4946 (3)	1·7
O(6)	0·4173 (4)	0·5043 (4)	0·1567 (3)	1·8
O(7)	0·1773 (4)	0·3897 (4)	0·3755 (3)	1·6
O(8)	0·2645 (4)	0·2285 (4)	0·1796 (2)	1·3

* $B_{eq} = 8\pi^2(U_{11}U_{22}U_{33})^{1/3}$.

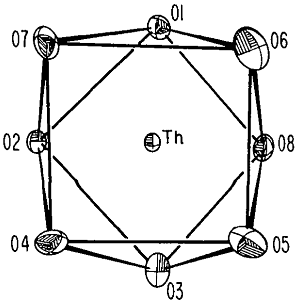

Fig. 1. Thorium coordination in orthorhombic $Th(MoO_4)_2$. Th—O(1) 2·386 (4), Th—O(2) 2·378 (3), Th—O(3) 2·431 (4), Th—O(4) 2·410 (4), Th—O(5) 2·415 (4), Th—O(6) 2·384 (4), Th—O(7) 2·459 (4), Th—O(8) 2·360 (4); mean Th—O 2·403 (4) Å.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38556 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Ammonium Trifluoroberyllate(II), $(NH_4)[BeF_3]$, at Room Temperature

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Abstract. $M_r = 84$, monoclinic, Pn, $a = 5{\cdot}770\,(2)$, $b = 4{\cdot}619\,(3)$, $c = 12{\cdot}819\,(1)$ Å, $\beta = 90{\cdot}12\,(2)^\circ$, $V = 341{\cdot}6\,(4)$ Å^3, $Z = 4$, $D_m = 1{\cdot}63\,(2)$, $D_x = 1{\cdot}632\,(3)$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54051$ Å, $\mu = 2{\cdot}04$ mm^{-1}, $F(000) = 168$. Final $R = 0{\cdot}049$ for 536 observed reflections. At room temperature the crystal is ferroelastic. Hydrogen-bonded chains of BeF_4 tetrahedra run along the b axis and undergo a pronounced thermal motion around this axis. Diffuse streaks observed at room temperature on Weissenberg photographs are probably connected with the phase transition to the orthorhombic phase at 334·3 K.

Introduction. NH_4BeF_3 crystals undergo successive phase transitions at 252·2, 334·3 and 347·3 K. Below 334·3 K the crystal is ferroelastic and at room temperature exhibits spontaneous polarization along the a axis and spontaneous strain (Makita & Suzuki, 1980; Czapla, Czupiński & Waśkowska, 1982). Weissenberg photographs taken at temperatures corresponding to the particular phases revealed the symmetry of each phase (Łukaszewicz, Waśkowska & Tomaszewski, 1983). On heating, the sequence of the phases is as follows:

$$\mathrm{IV}\ (P1) \xrightarrow{252\cdot2\ \mathrm{K}} \mathrm{III}\ (Pn) \xrightarrow{334\cdot3\ \mathrm{K}} \mathrm{II}\ (P2_12_12_1) \xrightarrow{347\cdot3\ \mathrm{K}} \mathrm{I}\ (Pmnb).$$

Observations at room temperature under a polarizing microscope indicated that the crystal was twinned with the (105) plane as a twin plane. The earlier paper of Milkova & Porai-Koshits (1962) described the twinning of NH_4BeF_3, as well as giving a preliminary model of the structure. A full crystal-structure determination of the room-temperature phase is now presented as a part of X-ray studies on the phase-transition mechanism in this crystal.

Experimental. D_m measured by flotation in gradient column. Plates elongated in **b** (from water solution) ground to sphere ($2r = 0{\cdot}35$ mm). Syntex $P2_1$ diffractometer, monochromated Cu $K\alpha$. 15 reflections in least-squares determination of lattice parameters. Three standard reflections showed only statistical fluctuations during data collection. 736 independent reflections (h 7, k 5, $l \pm 16$) with $\theta < 70^\circ$, 536 with $|F| > \sigma(|F_o|)$. $R_{\mathrm{int}} = 6{\cdot}3\%$. Lp and isotropic extinction ($g = 3{\cdot}326$) corrections applied, absorption ignored. Space-group choice Pn based on physical properties [piezoelectric signal observed at room temperature by Makita & Suzuki (1980)]. Direct methods (*MULTAN*78, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Anisotropic full-matrix least-squares refinement on F (XRAY76, Stewart, 1976). Three H atoms around each NH_4^+ ion fixed at positions found from ΔF synthesis with refined B_{iso}, fourth H calculated from geometry. $R = 0{\cdot}049$, $R_w = 0{\cdot}054$; $w = 1/\sigma^2(F_o)$. Ratio of max. LS shift to error $\frac{1}{3}\sigma$. Max. and min. height in final ΔF map 0·3 and 0·5 e Å^{-3}. Scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974).

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