Kahn, d'Yvoire & Bretey, 1985), on account of our unit occupancy factor.

The Na^+ ions lie in cavities with coordination numbers that depend on the interatomic distances considered [*i.e.* CN = 8 for Na(1)—O distances less than 3 Å]. O(7) and O(13) play a particular role in the structure since they coordinate only Na atoms, and thus participate in the shorter Na—O distances.

Close examination of the structure shows the most apparent diffusion path of Na^+ to be along the [001] direction. Average Na(1)—O (2·628 Å) and Na(2)—O (2·564 Å) distances are comparable to the values encountered in other ionic sodium conductors.

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Structure of Trigonal Thorium Molybdate

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Abstract. $Th(MoO_4)_2$, $M_r = 551·92$, trigonal, $P\bar{3}$, $a = 17·593\ (7)$, $c = 6·238\ (7)$ Å, $V = 1672·2$ Å^3, $Z = 9$, $D_x = 4·933$ g cm^{-3}, $\lambda(\text{Mo } K\alpha_1) = 0·70930$ Å, $\mu(\text{Mo } K\alpha) = 239·2$ cm^{-1}, $F(000) = 2142$, $T = 298$ K. $R = 0·024$ and $wR = 0·030$ for 990 reflections with $I \geq 3\sigma(I)$. The structure contains MoO_4 tetrahedra which bridge three-dimensionally to both six- and nine-coordinate thorium atoms. The Mo—O distances range from 1·733–1·800 Å. The octahedral Th—O distances are 2·292–2·305 Å, while the nine-coordinate Th—O bond lengths range from 2·416 to 2·488 Å.

Introduction. Recovery of plutonium from spent nuclear fuel solutions may be complicated by the undesired formation of insoluble actinide molybdate residues (Penneman, Haire & Lloyd, 1980; Cremers, Eller, Penneman & Herrick, 1983). In a previous publication we described the structure determination of the orthorhombic (low-temperature) form of thorium(IV) molybdate which contains thorium in square antiprismatic coordination and tetrahedral molybdate ligands (Cremers, Eller & Penneman, 1983). In the present paper we describe the structure of the trigonal high-temperature form of $Th(MoO_4)_2$, which has totally different thorium coordination.

Trigonal $Th(MoO_4)_2$ has been investigated previously by others but there seemed ample reason for a reinvestigation of its structure. On the basis of X-ray diffraction data from layer photographs, Thoret (1974) proposed the space group $P\bar{6}$, and that one of the thorium atoms, located at the origin, was situated in the center of a planar ring of six oxygen atoms. In our view this is an unlikely coordination for thorium. Above and below and parallel to this six-membered ring were equilateral triangles of three O atoms making the total coordination of thorium

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twelve. An alternative structure for this phase of $Th(MoO_4)_2$ was described as isostructural to the high-temperature trigonal phase of $U(MoO_4)_2$ (Serezkin, Kovba & Trunov, 1974) in which six of the U atoms are nine-coordinate tricapped trigonal prisms and three are surrounded by octahedral arrays of O atoms. However, these workers claimed to obtain only twinned crystals of $Th(MoO_4)_2$ and they had difficulties with their refinement.

In order to resolve some of the confusion in the literature regarding the technologically important actinide molybdate structures, we have carried out a single-crystal structure determination of the trigonal high-temperature $Th(MoO_4)_2$ phase. Our results are reported herein.

Experimental. Trigonal $Th(MoO_4)_2$ was prepared by fusing a mixture of ThO_2 and MoO_3 powders in a skull melter (direct high-frequency absorption) at ~1473 K. A detailed description of the apparatus can be found in previous publications (Herrick & Behrens, 1981). Unlike the case for its uranium analog, the stoichiometric ThO_2/MoO_3 melt exhibited a continuous loss of molybdenum oxide vapor and thus an MoO_3-enriched (5 mol %) mixture of the powders (MoO_3/ThO_2) was melted. The skull was slowly withdrawn from the electromagnetic field while simultaneously reducing the power input. Under these circumstances the highest-melting component, $Th(MoO_4)_2$, preferentially solidified at the solid–liquid interface. As the temperature was lowered, the vaporization of MoO_3 was reduced while further precipitation of the higher-melting phase continued. At some temperature and melt composition, the liquid phase could not be sustained and uncontrollable cooling occurred. By minimizing the excess MoO_3, solidification took place before a eutectic composition was obtained. A heterogenous pale-grey product of $Th(MoO_4)_2$ was produced containing pale-yellow nearly colorless crystals.

A needle about 0·15 mm in length by 0·10 mm thick was mounted on a standard goniometer head. Data were collected by θ–2θ scans on a CAD-4 automated diffractometer using Mo $K\alpha$ (0·70930 Å) radiation and a graphite monochromator. Cell dimensions were determined by least-squares refinement of 25 centered reflections ($18 \leq 2\theta \leq 42°$) and are $a = 17{\cdot}593\,(7)$ and $c = 6{\cdot}238\,(7)$ Å. The choice of space group ($P\bar{3}$) was based on the lack of systematically absent reflections, the observed Laue symmetry and subsequent successful refinement. Reflections in a quadrant with Miller indices $h = 0$–16, $k = 0$–± 16 and $l = 0$–6 and $2\theta_{\max} \leq 45°$ were merged and averaged to yield 1160 reflections with $I \geq \sigma(I)$. During the merge process, the Miller indices were converted to a 'standard' hexagonal data set with $h = 0$–16, $k = 0$–16 and $l = 0$–± 6. 2 standard reflections, average intensity variation 2%. Data correction including a combination of spherical and psi absorption corrections was made (transmission: max. = 0·083, min. = 0·036) and corrections for Lorentz and polarization factors were performed as previously described (Ryan & Swanson, 1974). The R value based on F_o for the merge of equivalent reflections was 0·028 for trigonal symmetry and 0·083 for hexagonal symmetry. The structure was solved by standard Patterson methods and refined by full-matrix least squares employing the Los Alamos *Generalized Crystal Structure Analysis System* (Larson & Von Dreele, 1986). The function minimized was $\sum w(|F_o| - |F_c|)^2$ and weights were determined by $w = [2F_o/\sigma(F_o)^2]^2$, where $\sigma(F_o) = \sigma(F_o)^2/2F_o$ and $\sigma(F_o)^2 = (\text{Lorentz and polarization})\sigma I$ with $\sigma I = \sqrt{(I + B)}$. The final residuals were $R = 0{\cdot}024$ and $wR = 0{\cdot}030$ for the 990 reflections having $I \geq 3\sigma(I)$. The total number of positional and thermal variables plus a scale factor and extinction parameter ($1{\cdot}03 \times 10^{-6}$) (Larson, 1976; Zachariasen, 1967) was 151 variables for the 990 observations with $I \geq 3\sigma(I)$. Concerning the weak or unobserved reflections, in all cases these were calculated weak for this model. Scattering factors, including those for anomalous dispersion, were taken from Vol. IV of *International Tables for X-ray Crystallography* (1974). In a final difference Fourier map, no significant peaks were present. The largest peak in the difference map was 2·8 e Å^{-3} and located at $00\frac{1}{2}$. An attempt was made to refine the structure in the space group $P3$, as suggested by Serezkin *et al.* (1974) with less than satisfactory results.

Discussion. Both six- and nine-coordinate thorium atoms occur in this structure. Th(1) has threefold symmetry and is bound to O(9) and O(12), with Th(1)—O distances of 2·305 (9) and 2·289 (9) Å in the form of a slightly distorted octahedron. Th(2) has $\bar{3}$ point symmetry and is bound to six O(6) atoms at 2·292 (9) Å in a regular octahedral array. Th(3) occupies a general position and is coordinated to nine different oxygen atoms in the form of a slightly distorted tricapped trigonal prism as shown in Fig. 1. A packing diagram showing the molybdenum tetrahedra for $Th(MoO_4)_2$ is illustrated in Fig. 2 and a closer view of the channel structure about Th(2) and along [001] is given in Fig. 3. Positional parameters are presented in Table 1. Selected distances appear in Table 2.*

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* The calculated and observed structure factors, anisotropic temperature factors and values for the O—Mo—O and O—Th—O angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52016 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The molybdenum atoms occupy general positions and are all tetrahedrally coordinated, with each tetrahedron having one long and one short Mo—O distance. These tetrahedra serve as interconnecting links between the thorium polyhedra. Each oxygen is connected to one thorium and one molybdenum. As shown in Table 2, the long bond connects the tetrahedron to an octahedrally coordinated thorium, while the short distance connects it to a cap of the nine-coordinate thorium. A bond-length–bond-strength calculation (Zachariasen, 1978) results in values for Σ's of 4·31, 4·37 and 4·23 for the valences of Th(1), Th(2) and Th(3) respectively. This means that the Th—O bond lengths in each coordination sphere are slightly shorter than would be expected for an ideal Th^{4+}.

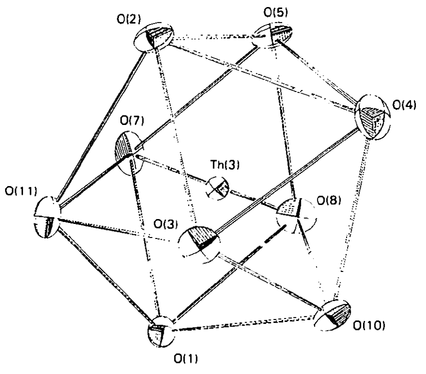

Fig. 1. Tricapped trigonal prismatic environment of Th(3).

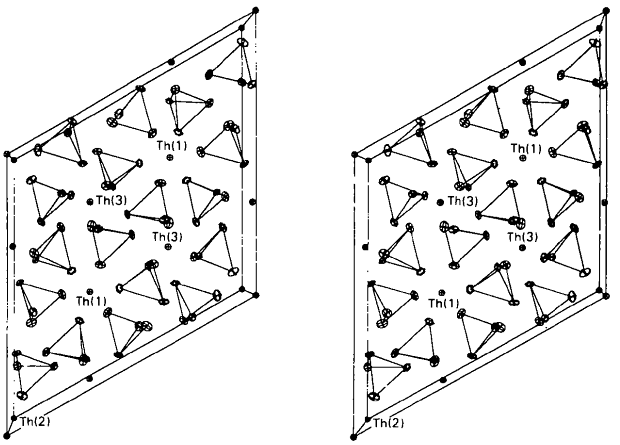

Fig. 2. Packing diagram for $Th(MoO_4)_2$ showing the molybdenum tetrahedra and thorium coordination ([010] vertical, [100] horizontal).

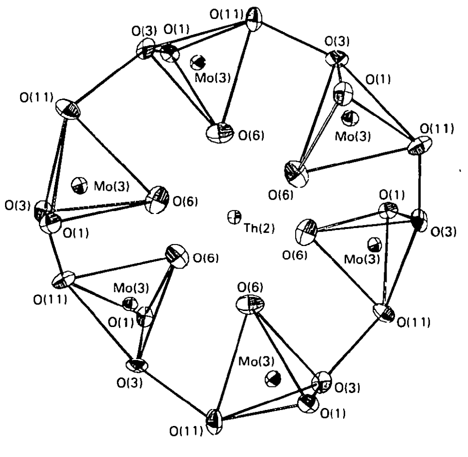

Fig. 3. Octahedral thorium environment of Th(2).

Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}(Å^2)
Th(1)	0·666667	0·333333	0·49737 (14)	1·16
Th(2)	0·0	0·0	0·0	1·10
Th(3)	0·33355 (3)	0·33376 (3)	0·75254 (7)	1·00
Mo(1)	0·26593 (8)	0·43560 (8)	0·23649 (18)	1·19
Mo(2)	0·59886 (8)	0·10214 (7)	0·25623 (19)	1·18
Mo(3)	0·23209 (8)	0·16591 (8)	0·26109 (19)	1·18
O(1)	0·0275 (8)	0·2401 (8)	0·4847 (16)	1·69
O(2)	0·4332 (7)	0·1139 (8)	−0·0028 (16)	1·62
O(3)	0·7520 (7)	0·0121 (8)	0·0667 (16)	1·87
O(4)	0·6322 (9)	0·0827 (9)	0·0082 (19)	2·40
O(5)	0·4869 (6)	0·0313 (6)	0·2896 (14)	1·71
O(6)	0·9196 (7)	0·0406 (7)	0·2109 (14)	2·46
O(7)	0·3069 (8)	0·4043 (8)	0·4521 (17)	2·41
O(8)	0·6592 (9)	0·0857 (9)	0·4584 (16)	2·20
O(9)	0·2901 (6)	0·5453 (6)	0·2874 (14)	2·07
O(10)	0·1535 (6)	0·3661 (7)	0·2160 (16)	2·29
O(11)	0·3021 (7)	0·1231 (6)	0·2395 (15)	2·27
O(12)	0·6220 (7)	0·2126 (6)	0·2810 (14)	2·35

Table 2. *Selected distances* (Å)

Th(1)—O(9)	2·305 (9)	Mo(1)—O(9)	1·785 (9)
Th(1)—O(12)	2·298 (9)	Mo(2)—O(12)	1·782 (9)
Th(2)—O(6)	2·292 (9)	Mo(3)—O(6)	1·800 (10)
Th(3)—O(1)	2·437 (11)	Mo(3)—O(1)	1·758 (10)
Th(3)—O(2)	2·449 (11)	Mo(1)—O(2)	1·746 (11)
Th(3)—O(3)	2·416 (11)	Mo(3)—O(3)	1·757 (10)
Th(3)—O(4)	2·430 (12)	Mo(2)—O(4)	1·748 (11)
Th(3)—O(5)	2·481 (9)	Mo(2)—O(5)	1·738 (9)
Th(3)—O(7)	2·420 (10)	Mo(1)—O(7)	1·740 (10)
Th(3)—O(8)	2·421 (12)	Mo(2)—O(8)	1·762 (12)
Th(3)—O(10)	2·477 (9)	Mo(1)—O(10)	1·733 (10)
Th(3)—O(11)	2·488 (9)	Mo(3)—O(11)	1·741 (10)

The structure of trigonal $Th(MoO_4)_2$ differs radically from that of the low-temperature orthorhombic uranium and thorium compounds of the same stoichiometry. The uranium structure contains six-coordinate molybdenum and eight-coordinate uranium and is best considered as a mixed oxomolybdate, since O atoms are present which bridge two U atoms or two molybdates. In contrast, the orthorhombic thorium compound is a molybdate which contains eight-coordinate thorium and tetrahedral molybdenum. In the high-temperature trigonal form reported here, the thorium becomes nine-coordinate and is identical to that of the analogous uranium compound (Serezkin *et al.*, 1974).

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The Structure of Ba_4PtO_6 from Time-of-Flight Powder Neutron Diffraction Data

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Abstract. Tetrabarium platinum(IV) hexaoxide, $M_r = 840{\cdot}45$, rhombohedral, $R\bar{3}c$, $a = 10{\cdot}2101\ (2)$, $c = 12{\cdot}6172\ (3)$ Å (hexagonal setting), $V = 1139{\cdot}08\ (5)$ Å^3, $Z = 6$, $D_x = 4{\cdot}42$ g cm^{-3}. Rietveld refinement using time-of-flight powder neutron diffraction data [TOF 40 000–120 000 μs, $T = 298$ K, $F(000) = 391{\cdot}98$ fm, 240 contributing reflections] resulted in $R_p = 5{\cdot}09$, $R_{wp} = 5{\cdot}79$ ($R_{\rm exp} = 5{\cdot}83$), $\chi^2 = 0{\cdot}99$. The structure of a new phase of Ba_4PtO_6, isostructural with Sr_4PtO_6 and rhombohedral Ca_4PtO_6, has been determined.

Introduction. In a study of the Ba—Pt—O phase diagram Schneider & McDaniel (1969) reported the existence of three phases, one which was unidentified, and the other two were Ba_4PtO_6 and a solid solution centred on $Ba_3Pt_2O_7$. Compositions in the solid solution have since been studied by other workers; the structure of $Ba_3Pt_2O_7$ has been determined (Haradem, Chamberland, Katz & Gleizes, 1977) and the composition $BaPtO_3$ has been examined (Gallagher, Johnson, Vogel, Wertheim & Schnettler, 1977).

The phase Ba_4PtO_6 was found to be hexagonal by Schneider & McDaniel, $a = 10{\cdot}064$, $c = 12{\cdot}663$ Å, and stable over the temperature range 1320–1490 K. The authors suggested that this phase could not be isostructural with the previously reported compound Sr_4PtO_6 which is rhombohedral, $R\bar{3}c$, $a = 9{\cdot}74$, $c = 11{\cdot}90$ Å (Randall & Katz, 1959), even though the unit cells were similar, as the available powder data could not be indexed on a rhombohedral unit cell. In the present work, powder neutron diffraction has been used to determine the structure of Ba_4PtO_6.

Experimental. A sample of Ba_4PtO_6 was prepared by the reaction of $BaCO_3$ and PtO_2. About 5 g of starting materials were mixed, ground and pressed into 13 mm diameter pellets. The pellets were placed in an alumina crucible lined with platinum foil and the sample was heated at 1370 K for 3 days. The sample was then quenched by tipping the crucible contents on to a thick aluminium plate. The pellets which had been in contact with the platinum foil had reacted with it, forming a brown material. All the brown material was carefully separated from the bulk of the sample, which was olive-green. The sample was then transferred to a desiccator to avoid sample hydrolysis. Our quenching procedure avoids the possibility of hydrolysis due to sample icing.

Powder X-ray data collected on the green material implied the presence of a single rhombohedral phase, $a = 10{\cdot}225\ (7)$, $c = 12{\cdot}642\ (8)$ Å, analogous to Sr_4PtO_6, rather than the hexagonal phase reported by Schneider & McDaniel (1969). Powder neutron data were then collected at the High Resolution Powder Diffractometer (HRPD) at ISIS

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