

Structure of Bis(ammonium) Hexanitratoplutonium(IV) and Bis(ammonium) Hexanitratothorium(IV)

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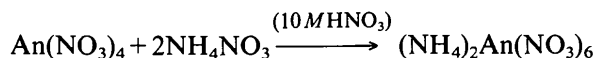
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Abstract. $[\text{NH}_4]_2[\text{Pu}(\text{NO}_3)_6]$, $M_r = 650.11$, monoclinic, $P2_1/n$, $a = 8.162$ (3), $b = 6.809$ (2), $c = 13.089$ (4) Å, $\beta = 91.34$ (3)°, $V = 727.2$ (4) Å³, $Z = 2$, $D_x = 2.969$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 5.5252$ mm⁻¹, $F(000) = 604$, $T = 295$ (1) K, $R = 0.037$ for 845 observed reflections [$I > 2\sigma(I)$]. $[\text{NH}_4]_2[\text{Th}(\text{NO}_3)_6]$, $M_r = 640.13$, monoclinic, $P2_1/n$, $a = 8.321$ (3), $b = 6.890$ (3), $c = 13.097$ (4) Å, $\beta = 91.55$ (3)°, $V = 750.6$ (4) Å³, $Z = 2$, $D_x = 2.832$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 10.3972$ mm⁻¹, $F(000) = 596$, $T = 295$ (1) K, $R = 0.0463$ for 809 observed reflections [$I > 2\sigma(I)$]. The two complexes are isostructural. The actinide atom lies on a symmetry centre [at $2(a)$]. It is twelve coordinated by O atoms which belong to six bidentate nitrate ions. The coordination polyhedron is an irregular icosahedron with An—O distances ranging from 2.454 (6) to 2.516 (5) Å and 2.545 (6) to 2.608 (5) Å, respectively, for Pu and Th. The connection between the $[\text{An}(\text{NO}_3)_6]^{2-}$ anions and the $[\text{NH}_4]^+$ cations is realized through a three-dimensional network of hydrogen bonds.

Introduction. Nitrate complexes of the actinide elements are known to play an important role in the separation chemistry of these elements. While tetravalent actinides were known to form hexanitratates in high nitric acid concentrations (Brown, 1973) no structural information on these complexes was available in the literature before we reported the structure of bis(tetraethylammonium) hexanitratouranium(IV) (Rebizant, Apostolidis, Spirlet, Andreetti & Kanellakopoulos, 1988). In an effort to understand and to improve the existing separation processes, novel hexanitrate complexes of plutonium and thorium have been synthesized and characterized by three-dimensional X-ray diffraction.

It should be mentioned that up to now only very few structure determinations on single crystals of Pu complexes have been made.

Experimental. The title complexes have been synthesized by reaction of actinide tetranitrate with ammonium nitrate in stoichiometric proportions in a 10 M nitric acid solution:



Single crystals suitable for X-ray structure determination were obtained by slow evaporation of the solution. They were sealed in thin-walled glass capillaries under nitrogen.

Intensity data were recorded on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation, using θ – 2θ scans. Calculations were performed with SDP programs (Enraf–Nonius, 1986). Atomic scattering factors and anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). For the Pu complex, the specimen was $0.30 \times 0.25 \times 0.20$ mm. Cell parameters were refined by least squares from 25 reflections in the range $8 < 2\theta < 44^\circ$. Systematic absences were found to be consistent with space group $P2_1/n$. 1891 reflections [$I > \sigma(I)$] were measured in the range $4 < 2\theta < 45^\circ$, corresponding to 949 unique reflections ($R_{\text{int}} = 0.028$). Intensities of three standard reflections were measured at 30 min intervals and an anisotropic decay correction was applied to the data (total decay 1.2%). Intensities were corrected for Lorentz–polarization effects and empirical absorption corrections applied (relative transmission factors 79.44 to 99.94%). Structure solved by direct methods, Fourier techniques and full-matrix least-squares refinement [function minimized $\sum(\Delta F)^2$]. Last cycles of

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refinement, carried out with unit weights (weighting scheme which gave the best agreement factors), were made on 845 independent reflections with $F^2 > 2\sigma(F^2)$ (index range h 0/+8, k 0/+7, l -13/+13). Anisotropic thermal parameters were calculated only for the Pu atom. H atoms were not included in the refinement. A secondary-extinction coefficient refined to $g = 2.99 \times 10^{-7} \{F_c = F_c/[1 + g(F_c)^2 Lp]\}$. Final agreement factors were $R = 0.037$, $wR = 0.058$ and $S = 4.4$. Final $(\Delta/\sigma)_{\max} < 0.01$. Max. and min. heights in the final difference Fourier map were 1.75 and $-1.28 \text{ e } \text{Å}^{-3}$, respectively.

For the Th complex, the specimen was $0.35 \times 0.30 \times 0.25 \text{ mm}$. Cell parameters were refined by least squares from 25 reflections in the range $10 < 2\theta < 40^\circ$. 1956 reflections [$I > \sigma(I)$], corresponding to 982 unique reflections ($R_{\text{int}} = 0.053$), were measured in the range $4 < 2\theta < 45^\circ$. Intensities of three standard reflections were measured at 30 min intervals and an anisotropic decay correction was applied to the data (total decay 1.1%). Intensities were corrected for Lorentz-polarization effects; empirical absorption corrections applied (relative transmission factors 33.31 to 99.91%). Structure solved by direct methods and Fourier techniques, and full-matrix least-squares refinement [function minimized $\sum(\Delta F)^2$] showed that the complex was isostructural with the ammonium hexanitrate complex of plutonium. Last cycles of refinement, carried out with unit weights (weighting which gave the best R factors), were made on 809 independent reflections with $F^2 > 2\sigma(F^2)$ (index range h 0/+8, k 0/+7, l -14/+13). Anisotropic thermal motion was applied only to the Th atom. H atoms were not included in the refinement. A secondary-extinction coefficient refined to $g = 9.82 \times 10^{-7}$. Final agreement factors were $R = 0.046$, $wR = 0.055$ and $S = 4.166$. Final $(\Delta/\sigma)_{\max} < 0.01$. Max. and min. heights in the final difference Fourier map were 2.11 and $-1.45 \text{ e } \text{Å}^{-3}$, respectively.

Discussion. Final atomic coordinates for the two complexes of Pu and Th are given in Table 1.* Corresponding distances and angles are listed in Table 2. The structure of the hexanitratoplutonium anion is illustrated in Fig. 1. The crystal packing is illustrated by Fig. 2. In the hexanitrate anion, the actinide atom is surrounded by 12 O atoms which belong to the six bidentate nitrate ligands. As the actinide ion lies on a centre of symmetry [$2(a)$], there are three symmetrically independent nitrate ions. The actinide-bonded O atoms are at the corners of an

Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors with e.s.d.'s in parentheses

$$B_{\text{eq}} = (1/3)\sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Pu complex				
Pu	0.000	0.000	0.000	1.40 (2)*
N(1)	-0.039 (2)	-0.255 (2)	0.177 (1)	1.9 (3)
N(2)	-0.278 (2)	0.245 (2)	0.054 (1)	1.8 (3)
N(3)	0.216 (2)	0.271 (2)	0.111 (1)	2.5 (3)
O(1)	0.074 (1)	-0.277 (2)	0.1166 (9)	2.3 (2)
O(2)	-0.068 (2)	-0.374 (2)	0.244 (1)	3.0 (3)
O(3)	-0.129 (1)	-0.106 (2)	0.1636 (8)	1.9 (2)
O(4)	-0.394 (1)	0.357 (2)	0.0632 (9)	2.6 (2)
O(5)	-0.292 (1)	0.087 (2)	0.0007 (9)	2.1 (2)
O(6)	-0.137 (1)	0.277 (2)	0.0893 (9)	2.5 (2)
O(7)	0.184 (1)	0.287 (2)	0.0161 (9)	2.3 (2)
O(8)	0.299 (2)	0.386 (2)	0.1616 (9)	2.7 (2)
O(9)	0.150 (1)	0.123 (2)	0.1536 (9)	2.6 (2)
N(4)	-0.028 (2)	0.235 (3)	0.339 (1)	3.3 (3)
Th complex				
Th(1)	0.000	0.000	0.000	1.30 (1)
N(1)	-0.036 (2)	-0.262 (2)	0.181 (1)	2.2 (3)*
N(2)	-0.283 (2)	0.249 (2)	0.052 (1)	2.2 (3)*
N(3)	0.219 (1)	0.279 (2)	0.1142 (9)	1.5 (2)*
O(1)	0.073 (1)	-0.284 (2)	0.1204 (9)	2.3 (2)*
O(2)	-0.065 (1)	-0.379 (2)	0.248 (1)	3.2 (3)*
O(3)	-0.127 (1)	-0.107 (2)	0.1671 (8)	2.0 (2)*
O(4)	-0.397 (1)	0.356 (2)	0.061 (1)	3.2 (3)*
O(5)	-0.296 (1)	0.091 (2)	-0.003 (1)	3.1 (3)*
O(6)	-0.146 (1)	0.282 (2)	0.0919 (8)	1.6 (2)*
O(7)	0.189 (1)	0.292 (2)	0.0196 (8)	1.8 (2)*
O(8)	0.303 (1)	0.391 (2)	0.1612 (9)	2.5 (2)*
O(9)	0.151 (1)	0.132 (2)	0.1568 (9)	2.4 (2)*
N(4)	-0.035 (2)	0.232 (2)	0.338 (1)	2.9 (3)*

* Atoms refined anisotropically. The form of the anisotropic displacement parameter is $\exp\{-0.25[h^2 a^2 B(1,1) + k^2 b^2 B(2,2) + l^2 c^2 B(3,3) + 2hkaB(1,2) + 2hlacB(1,3) + 2klcbB(2,3)]\}$.

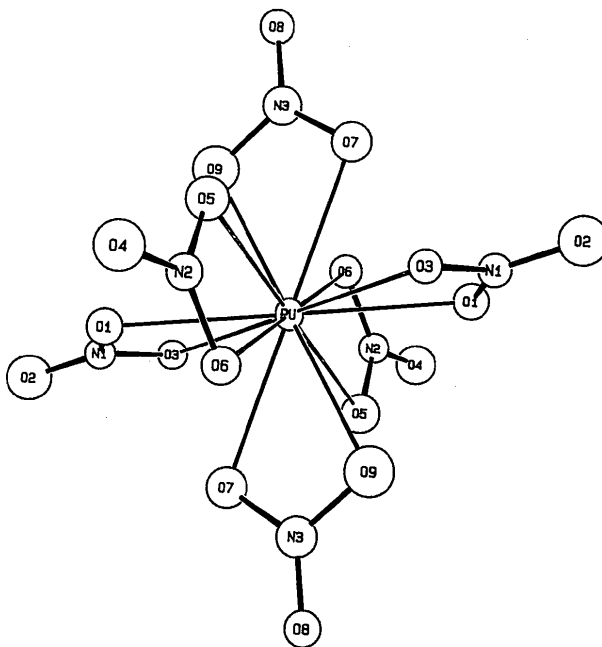


Fig. 1. View of the molecular structure with thermal ellipsoids at 50% probability level (ORTEP; Johnson, 1976).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54331 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Selected distances (Å) and angles (°) with *e.s.d.*'s in parentheses

	Pu complex	Th complex
M—O(1)	2.495 (6)	2.574 (6)
M—O(3)	2.516 (5)	2.562 (5)
M—O(5)	2.454 (6)	2.545 (6)
M—O(6)	2.495 (6)	2.608 (5)
M—O(7)	2.483 (6)	2.563 (6)
M—O(9)	2.477 (6)	2.548 (6)
O(1)···O(3)	2.134 (8)	2.163 (8)
O(1)···O(5)	2.705 (8)	2.783 (9)
O(1)···O(6)	2.753 (8)	2.863 (7)
O(1)···O(7)	2.701 (8)	2.813 (8)
O(1)···O(9)	2.837 (9)	2.973 (9)
O(3)···O(5)	2.811 (8)	2.938 (8)
O(3)···O(6)	2.785 (8)	2.860 (8)
O(3)···O(7)	2.685 (8)	2.794 (8)
O(3)···O(9)	2.771 (8)	2.846 (8)
O(5)···O(6)	2.134 (8)	2.177 (8)
O(5)···O(7)	2.706 (8)	2.799 (9)
O(5)···O(9)	2.752 (8)	2.734 (9)
O(6)···O(7)	2.809 (8)	2.975 (7)
O(6)···O(9)	2.682 (8)	2.799 (7)
O(7)···O(9)	2.142 (8)	2.139 (8)
O(1)—M—O(3)	50.4 (2)	49.8 (2)
O(1)—M—O(3')	129.6 (2)	130.2 (2)
O(1)—M—O(5)	113.7 (2)	114.2 (2)
O(1)—M—O(5')	66.3 (2)	65.9 (2)
O(1)—M—O(6)	113.0 (2)	112.9 (2)
O(1)—M—O(6')	67.0 (2)	67.1 (2)
O(1)—M—O(7)	114.1 (2)	113.6 (2)
O(1)—M—O(7')	65.9 (2)	66.4 (2)
O(1)—M—O(9)	69.6 (2)	71.0 (2)
O(1)—M—O(9')	110.4 (2)	109.0 (2)
O(3)—M—O(5)	68.9 (2)	70.2 (2)
O(3)—M—O(6')	111.1 (2)	109.8 (2)
O(3)—M—O(6)	67.5 (2)	67.2 (2)
O(3)—M—O(6')	112.5 (2)	112.8 (2)
O(3)—M—O(7)	114.9 (2)	113.9 (2)
O(3)—M—O(7')	65.1 (2)	66.1 (2)
O(3)—M—O(9)	67.4 (2)	67.7 (2)
O(3)—M—O(9')	112.6 (2)	112.3 (2)
O(5)—M—O(6)	51.1 (2)	50.0 (2)
O(5)—M—O(6')	128.9 (2)	130.2 (2)
O(5)—M—O(7)	113.4 (2)	113.6 (2)
O(5)—M—O(7')	66.6 (2)	66.4 (2)
O(5)—M—O(9)	112.2 (2)	112.4 (2)
O(5)—M—O(9')	67.8 (2)	67.6 (2)
O(6)—M—O(7)	68.9 (2)	70.2 (2)
O(6)—M—O(7')	111.2 (2)	109.8 (2)
O(6)—M—O(9)	65.3 (2)	66.7 (2)
O(6)—M—O(9')	114.7 (2)	114.3 (2)
O(7)—M—O(9)	51.3 (2)	49.5 (2)
O(7)—M—O(9')	128.7 (2)	130.5 (2)

Symmetry code: (i) $-x, -y, -z$.

irregular icosahedron as illustrated in Fig. 3. This coordination geometry was previously observed around the U atom in the structure of bis(tetraethylammonium) hexanitratouranium(IV) (Rebizant, Apostolidis, Spirlet, Andreetti & Kanellakopoulos, 1988) in which the nitrate groups were found disordered with two possible orientations. It has also been observed and described for MgTh(NO₃)₆·8H₂O (Ščavničar & Prodić, 1965), [Th(NO₃)₃(PMe₃O)₄]₂[Th(NO₃)₆] (Alcock, Esperas, Bagnall & Hsian-Yun, 1978), [(C₁₀H₈N₂H)₃NO₃][Th(NO₃)₆] (Khan, Kumar & Tuck, 1984) and for (NH₄)₂Ce(NO₃)₆ (Beineke & Delgaudio, 1968). The O—O edge lengths vary

between 2.134 (8) and 2.837 (9) Å and between 2.139 (8) and 2.975 (7) Å, respectively, for the Pu and Th complexes. The distortions within the AnO₁₂ icosahedra are also reflected by the An—O bond distances and by the O—An—O angles (Table 2). In a regular icosahedron, the values of the O—An—O angles involving a particular oxygen would be 63.5° (five angles), 116.5° (five angles) and 180° (one angle).

The crystal packing (Fig. 2) shows a three-dimensional network of hydrogen bonds between ammonium ions and nitrate O atoms. These hydrogen-bond distances range from 2.95 (1) to 3.17 (1) Å in the Pu compound and from 2.93 (1) to 3.17 (1) Å in the Th compound. Some of the bonds are directed towards nitrate O atoms which are also bonded to the central actinide atom.

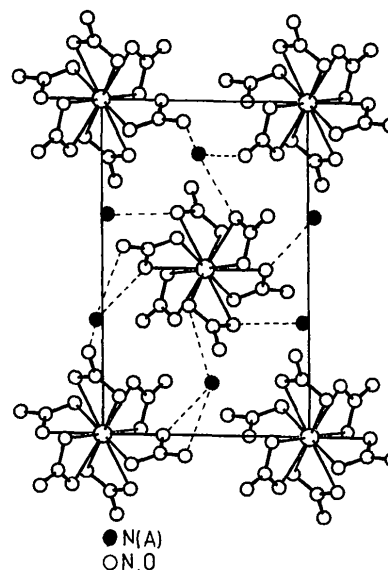
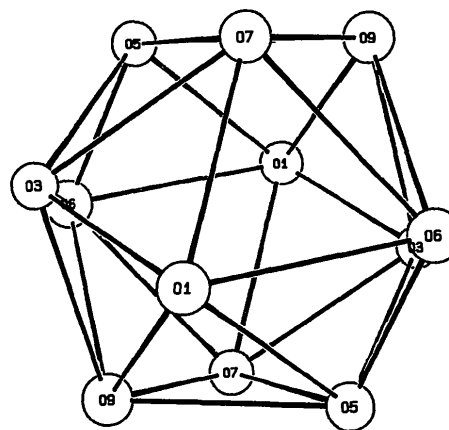
Fig. 2. The crystal structure as a projection along the *b* axis. *a* is horizontal from left to right.

Fig. 3. The coordination icosahedron.

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Single-Crystal Structure of BaSm₂S₄

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Abstract. Nonstoichiometric barium samarium sulfide, Ba_{1-x}Sm₂S_{4-x} ($x = 0.10$), $M_r = 549.43$, orthorhombic, *Pnma*, $a = 12.262$ (3), $b = 4.121$ (3), $c = 14.713$ (2) Å, $V = 743.5$ (6) Å³, $Z = 4$, $D_x = 4.91$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 218.74$ cm⁻¹, $T = 296$ K, $F(000) = 947.2$, $R = 0.027$, $wR = 0.037$ for 736 observed unique reflections [$I > 3\sigma(I)$]. X-ray single-crystal structure results confirm that the title compound crystallizes in a CaFe₂O₄-type structure, which is built up from edge-sharing, double octahedral, infinite chains. The structure also contains BaS₈ polyhedra, which can best be described as bicapped trigonal prisms (b.t.p). The two capping S(2) atoms adopt much longer Ba—S bond distances. This is attributed in part to the nonstoichiometry of the Ba and S(2) site. The same structure type is also adopted by other heavier rare-earth metal ternary sulfides and selenides, e.g., A(RE)₂Q₄ (Q = S and Se), where RE = Tb—Lu for A = Sr and RE = Nd—Lu for A = Ba.

Introduction. The combination of alkaline-earth (A) and rare-earth (RE) chalcogenides (Q) allows for the formation of a series of ternary compounds with a general formula of A(RE)₂Q₄, where A = Sr, Ba; RE = La—Lu, and Q = S, Se (Patrie, Golabi, Flahaut & Domange, 1964). These ternary rare-earth chalcogenide compounds appear in different structure types, e.g. CaFe₂O₄ (Decker & Kasper, 1957) and Th₃P₄ (Meisel, 1939). It is recognized that the coordination of the trivalent rare-earth cations, (RE)³⁺, governs the formation of each specific structure type. Patrie *et al.* have prepared a series of polycrystalline samples of ternary strontium and barium rare-earth

sulfides and selenides. They observed, using indexed powder X-ray diffraction patterns, that the ternary phases which incorporate rare-earth elements at the end of the lanthanide series possess the CaFe₂O₄-type structure. Due to a lack of a single crystal, no structure characterization has been made. We report the X-ray single-crystal structure of BaSm₂S₄, which provides the detailed atomic arrangements and bond interactions for the late series of the ternary rare-earth sulfides and selenides. Nonstoichiometry due to cation deficiency, found during the single-crystal investigation of Ba_{1-x}Sm₂S_{4-x}, is reported for the first time and is also discussed.

Experimental. *Synthesis and crystal growth.* Single crystals of BaSm₂S₄ were discovered in the reaction products formed during an attempt to synthesize the 'BaSmInS₄' analogue of CaYbInQ₄ (Q = S and Se) (Carpenter & Hwu, 1991) using a halide flux. For the preparation of the quaternary precursor a solid-state reaction, using the starting materials BaS (Aesar 99.9%), Sm (Aldrich 99.9%), In (Aldrich 99.98%), and S (Aldrich 99.99%) in a molar ratio of 1:1:1:3, was carried out. The reaction mixture was ground together under a blanket of nitrogen in a dry box and then loaded into a quartz reaction ampule, which was subsequently sealed under vacuum. The reaction mixture was heated stepwise to a final temperature of 1223 K, annealed at this temperature for two days, and then cooled to room temperature over a 24 h period. To prepare the flux, BaCl₂ (Mallinckrodt, reagent) and KCl (Baker, reagent) were dried under vacuum at approximately 473 K, weighed in a dry box, and ground together prior to use. The composition of the eutectic flux was BaCl₂:KCl ~ 28:72 mol % (m.p. 923 K) obtained

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