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## The Crystal Structure of Ammonium Thorium(IV) Octafluoride, $(\text{NH}_4)_4\text{ThF}_8^*$

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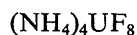
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Crystals of  $(\text{NH}_4)_4\text{ThF}_8$  are triclinic, space group  $P\bar{1}$ , with  $a=8.477$  (10),  $b=8.364$  (8),  $c=7.308$  (7) Å,  $\alpha=88^\circ 23'$  (3'),  $\beta=96^\circ 5'$  (3'),  $\gamma=106^\circ 20'$  (3'),  $Z=2$ ,  $D_x=3.06$ ,  $D_m=3.08$  g.cm<sup>-3</sup>. Each thorium atom has nine fluorine neighbors at an average distance of 2.38 Å; the polyhedron is a distorted trigonal prism with the three equatorial fluorine ions approximately normal to the face centers. The polyhedra are joined into infinite chains paralleling the  $b$  axis by sharing two edges in each polyhedron. The remaining fluoride ion is not involved in the coordination sphere of thorium; the closest thorium atom to this fluoride ion is at a distance of 4.98 Å. This fluoride ion is coordinated to five ammonium ions which are in approximately a square pyramidal configuration.

### Introduction

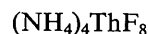
The tetravalent actinide fluorides of Pa, U, Np, Pu, and Am form with ammonium fluoride an isostructural series of complex compounds having the formula  $(\text{NH}_4)_4\text{MF}_8$ . The corresponding cerium(IV) compound has also been found to be isostructural (Penneman & Rosenzweig, 1969). Of these, the structure of



has been determined in detail (Rosenzweig & Cromer, 1968). It is monoclinic, space group  $C2/c$ , and contains

isolated  $[\text{UF}_8]^{4-}$  polyhedra in the form of distorted square antiprisms.

Recently a compound of thorium tetrafluoride and ammonium fluoride was prepared which has X-ray powder diffraction and optical properties distinctly different from those of the  $(\text{NH}_4)_4\text{UF}_8$  prototype, even though chemical analysis established the formula as  $(\text{NH}_4)_4\text{ThF}_8$ . Crystals of  $(\text{NH}_4)_4\text{UF}_8$  clearly show monoclinic symmetry; however, those of  $(\text{NH}_4)_4\text{ThF}_8$  have habits and optical properties which suggest triclinic symmetry. Consideration of intensities and cell constants estimated from precession photographs showed that the thorium-thorium distance is much shorter in



\* This work performed under the auspices of the U.S. Atomic Energy Commission.

than the U-U distance in  $(\text{NH}_4)_4\text{UF}_8$ ; this suggested a chain structure in  $(\text{NH}_4)_4\text{ThF}_8$  rather than isolated  $\text{MF}_8^{4-}$  groups. A preliminary report on the structure has been presented by Penneman, Ryan & Rosenzweig (1968).

### Experimental

Lath-shaped crystals of  $(\text{NH}_4)_4\text{ThF}_8$  showing oblique extinction result when a 45 wt.% (saturated) ammonium fluoride solution is stirred for several hours at room temperature with freshly precipitated  $\text{ThF}_4$ . Larger crystals, adequate for single-crystal investigation, result when a warm solution is allowed to cool slowly. Excess  $\text{NH}_4\text{F}$  floats on the denser aqueous solution and is readily removed by centrifugation. Methyl alcohol can be used to remove any  $\text{NH}_4\text{F}$  from the surfaces of the crystals. Chemical analysis gave: Th (as  $\text{ThO}_2$ ), 50.9%;  $\text{NH}_3$  (Kjeldahl), 14.84%; and F, 32.8%; calculated percentages for  $(\text{NH}_4)_4\text{ThF}_8$ : Th, 50.86%;  $\text{NH}_3$ , 14.93%; and F, 33.3%. A single crystal was selected and cut to a length suitable for examination by X-ray methods. The approximate dimensions of the resulting crystal were  $0.029 \text{ mm} \times (0.065 \text{ mm})^2$ . The crystal was mounted and aligned along the  $b^*$  axis and was coated

with Fluorolube to arrest an apparent slow decomposition which took place upon contact of the material with air.

Precession photographs taken with  $\text{Mo } K\alpha$  radiation showed the intensities to be strong when  $k=2n$  and weak when  $k=2n+1$ , indicating the heavier atoms to be half a unit cell apart in the  $b$  direction. The room-temperature cell constants obtained by a least-squares treatment based on 27 Debye-Scherrer lines, measured with  $\text{Cu } K\alpha_1$  ( $\lambda=1.5405$ ) radiation, are  $a=8.477(10)$ ,  $b=8.364(8)$ ,  $c=7.308(7)$  Å,  $\alpha=88^\circ 23'(3')$ ,  $\beta=96^\circ 5'(3')$ , and  $\gamma=106^\circ 20'(3')$ . The calculated density with  $Z=2$  is  $3.06 \text{ g.cm}^{-3}$ ; the density measured by flotation methods was  $3.08 \text{ g.cm}^{-3}$ .

Intensities of all reflections with  $2\theta \leq 40^\circ$  were measured by means of a single-crystal orienter on a General Electric XRD-5 diffraction unit with the use of  $\text{Mo } K\alpha$  radiation, Zr-Y balanced filters, a take-off angle of  $5^\circ$ , the stationary-crystal-and-counter mode and a counting time of 20 seconds with each filter. The intensity of a standard reflection was measured after every 50 measurements and was not found to vary significantly from its mean value during the course of the data collection. Of the 1,306 reflections measured, 1,193 were observed according to the criterion  $[I-B] \geq 3[I+B]^{1/2}$  where  $B$  is the sum of the background as measured at the reflection with the Y filter and the average of the

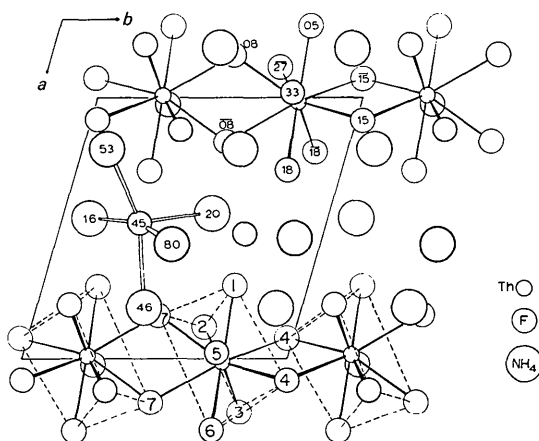


Fig.1 Projection of the structure along the  $c$  axis.

Table 1. Fractional coordinates and associated least squares errors

	$x$	$\sigma$	$y$	$\sigma$	$z$	$\sigma$
Th	0.9926	(1)	0.2486	(1)	0.9902	(1)
F(1)	0.2790	(14)	0.2808	(14)	0.9531	(15)
F(2)	0.1184	(14)	0.3479	(14)	0.2695	(13)
F(3)	0.7884	(15)	0.1161	(14)	0.1793	(15)
F(4) <i>a</i>	0.0824	(15)	0.0243	(13)	0.1524	(14)
F(5)	0.0180	(14)	0.2758	(13)	0.6732	(14)
F(6)	0.2680	(15)	0.7861	(15)	0.1805	(15)
F(7) <i>a</i>	0.8664	(14)	0.4619	(13)	0.0753	(14)
F(8)	0.4817	(15)	0.2986	(15)	0.4497	(15)
N(1)	0.4427	(22)	0.5601	(22)	0.2019	(21)
N(2)	0.4599	(21)	0.1034	(22)	0.1612	(21)
N(3)	0.8073	(23)	0.4065	(21)	0.4590	(21)
N(4)	0.8060	(23)	0.9046	(22)	0.4708	(22)

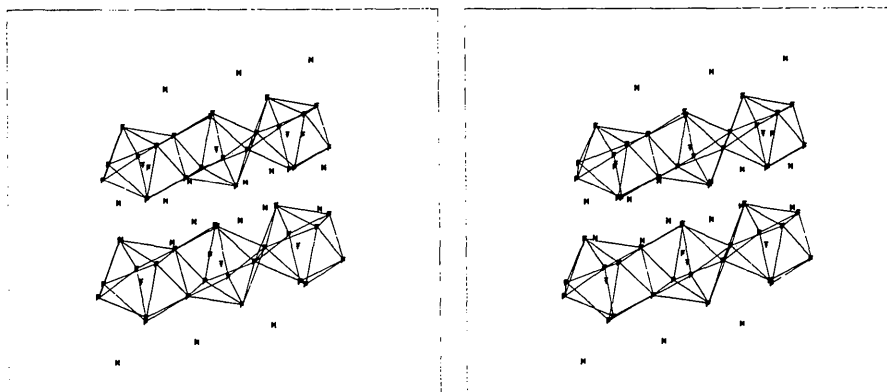


Fig.2. Stereo view of the structure showing the coordination polyhedra.

background measured at the same  $2\theta$  setting but with  $\chi$  and  $\phi$  offset. The absorption correction was made, assuming the crystal to be bounded by 6 planes, by the Busing & Levy (1957) method with Burnham's (1962) program modified for single-crystal-orienter geometry (Larson, Cromer & Roof, 1964). The linear absorption coefficient is  $221.6 \text{ cm}^{-1}$  and the calculated transmission varied from 0.282 to 0.550 with the 8-point Gaussian integration procedure.

### Solution and refinement of the structure

The calculated Patterson map could be interpreted in space group  $P\bar{1}$  with the use of two different models for the heavy atoms. In one model the thorium atoms were at the centers of symmetry 0, 0, 0 and 0,  $\frac{1}{2}$ , 0; in the other they were in general positions with  $x \approx 0$ ,  $y \approx \frac{1}{4}$ , and  $z \approx 0$ . The thorium-thorium distance, in either case, indicates a thorium fluoride chain in the  $b$  direction. Since no reasonable structure could be imagined with the thorium atoms on centers of symmetry, the second model was chosen for a first try. Since the normal equations based on the thorium positions alone are singular at 0,  $\frac{1}{4}$ , 0, there are four different starting models for the least-squares calculation, *i. e.*  $x$  positive or negative,  $y$  greater than or less than  $\frac{1}{4}$ ,  $z$  positive or negative, with one of the choices arbitrary. The refinement resulting in thorium coordinates 0.992, 0.248, 0.994 gave a lower  $R$

( $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ) value of 0.17 and a significantly better weighted residual than the other three models.

Two cycles of difference Fourier syntheses followed by least-squares calculations revealed the positions of the remaining twelve atoms. At this point seven of the twelve light atoms could be considered as fluorine atoms because of their proximity to the thorium atoms. Of the remaining five atoms, one had a negative temperature factor when refined with the use of nitrogen scattering factors. When fluorine scattering factors were used for this atom, its temperature factor converged to a reasonable value with a significant reduction in the weighted residual.

The full-matrix least-squares refinement of all non-hydrogen positions, with Larson's (1968) program, was carried out until the shift in all parameters was less than 1% of their standard deviations. The quantity minimized was  $\Sigma \omega_i (F_o - KF_c)_i^2$  where  $\omega_i$  is the weight based on counting statistics. Scattering factors given in *International Tables for X-ray Crystallography* (1962) were used for fluorine and nitrogen atoms. Cromer & Waber's (1965) scattering factors and Cromer's (1965) anomalous dispersion terms were used for thorium. Free-atom scattering factors were used in the refinement except for the last cycle when N, F<sup>-</sup> and Th<sup>4+</sup> factors were used. No significant improvement was effected by the use of valence-state scattering factors. The final  $R$

Table 2. Anisotropic temperature factors ( $\times 10^4$ ) as defined by  $\exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Th	42 (1)	33 (1)	53 (2)	20 (2)	42 (2)	-8 (2)
F(1)	65 (22)	85 (23)	129 (26)	46 (37)	80 (38)	-49 (37)
F(2)	70 (22)	101 (23)	63 (22)	71 (37)	28 (35)	-60 (34)
F(3)	80 (23)	57 (21)	147 (27)	48 (36)	140 (40)	67 (36)
F(4)	99 (23)	25 (19)	85 (23)	26 (34)	5 (36)	-18 (32)
F(5)	59 (21)	30 (19)	106 (24)	16 (32)	47 (35)	36 (32)
F(6)	81 (24)	98 (24)	125 (26)	102 (39)	-64 (39)	-38 (38)
F(7)	54 (21)	42 (20)	110 (24)	22 (33)	63 (35)	-10 (33)
F(8)	54 (22)	114 (26)	140 (28)	-20 (39)	97 (39)	-101 (40)
N(1)	52 (32)	105 (36)	68 (34)	35 (55)	89 (53)	-33 (53)
N(2)	49 (33)	98 (36)	90 (35)	45 (56)	53 (55)	-80 (54)
N(3)	79 (35)	59 (33)	82 (35)	20 (56)	65 (57)	-20 (52)
N(4)	71 (34)	75 (35)	92 (36)	13 (57)	87 (58)	15 (54)

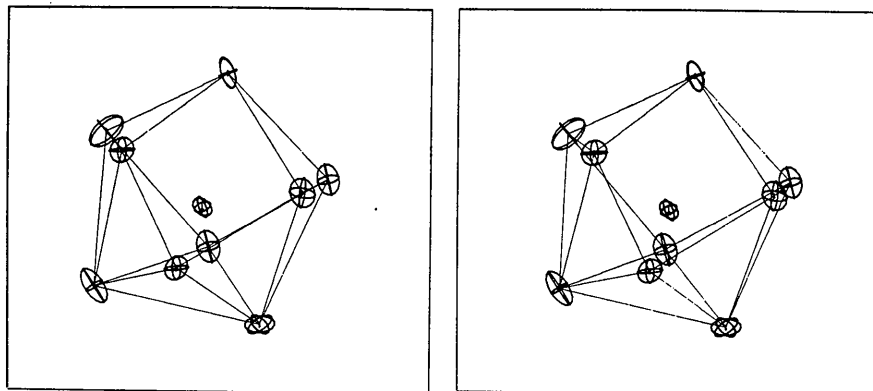


Fig. 3. Stereo view of a coordination polyhedron.



Table 4. Pertinent interatomic distances and standard deviations

Th—F(1)	2.41 (1) Å	F(2)—F(4) <i>a</i>	2.79 (2) Å
Th—F(2)	2.26 (1)	F(2)—F(7) <i>a</i>	2.81 (2)
Th—F(3)	2.34 (1)	F(2)—F(7) <i>b</i>	2.94 (2)
Th—F(4) <i>a</i>	2.42 (1)	F(3)—F(4) <i>a</i>	2.83 (2)
Th—F(5)	2.35 (1)	F(3)—F(4) <i>b</i>	3.15 (2)
Th—F(6)	2.36 (1)	F(3)—F(6)	2.76 (2)
Th—F(7) <i>a</i>	2.45 (1)	F(3)—F(7) <i>a</i>	2.88 (2)
Th—F(4) <i>b</i>	2.45 (1)	F(4) <i>a</i> —F(4) <i>b</i>	2.48 (2)
Th—F(7) <i>b</i>	2.44 (1)	F(4) <i>a</i> —F(5)	2.74 (2)
F(1)—F(2)	2.95 (2)	F(4) <i>a</i> —F(6)	2.86 (2)
F(1)—F(4) <i>a</i>	2.80 (2)	F(5)—F(6)	2.66 (2)
F(1)—F(5)	2.84 (2)	F(5)—F(7) <i>a</i>	2.79 (2)
F(1)—F(7) <i>b</i>	2.76 (2)	F(6)—F(7) <i>a</i>	3.73 (2)
F(1)—F(4) <i>b</i>	3.42 (2)	F(6)—F(7) <i>b</i>	2.74 (2)
F(2)—F(3)	2.94 (2)	F(7) <i>a</i> —F(7) <i>b</i>	2.54 (2)

The eighth fluorine atom, F(8), is not involved in the thorium coordination sphere, being 4.98 Å from its nearest thorium neighbor. This fluorine atom has five nitrogen atom neighbors at an average distance of 2.72 Å (range 2.65–2.87 Å), which form a much distorted square pyramid. Its nearest fluorine neighbor is at a distance of 3.35 Å.

Though the ninefold coordination of Th<sup>4+</sup> is to be expected on the basis of the ratio of the thorium to fluorine ionic radii, to the best of our knowledge this is the first actinide fluoride complex in which a fluorine atom is not included in the coordination sphere of the heavy metal ion. One might expect that the composition of this material would best be described by writing the formula as (NH<sub>4</sub>)<sub>3</sub>ThF<sub>7</sub>.NH<sub>4</sub>F and that the first NH<sub>4</sub>F

would be relatively easy to lose. However, it is found that the first NH<sub>4</sub>F loss from (NH<sub>4</sub>)<sub>4</sub>ThF<sub>8</sub> (which is also the first endotherm above room temperature) occurs at an even higher temperature (205°) than it does from (NH<sub>4</sub>)<sub>4</sub>UF<sub>8</sub> (180°). In this latter compound all fluorine atoms are involved in the coordination of the U<sup>4+</sup>.

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## The Crystal Structure of 1-*p*-Nitrobenzeneazo-2-naphthol (Para Red) from Overlapped Twin-Crystal Data

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The crystal structure of the red pigment known as Para Red has been determined by the use of photographic X-ray methods. The crystals are monoclinic, space group *Pb*, with two molecules per unit cell. The dimensions of the unit cell at room temperature are  $a = 3.797 \pm 0.002$ ,  $b = 27.036 \pm 0.006$ ,  $c = 7.199 \pm 0.002$  Å,  $\gamma = 115^\circ 13' \pm 1'$ . The structure was solved first in projection and then in three dimensions but failed to refine properly. It was found that the crystals suffered from pseudo-merohedral twinning of small obliquity and that the reflexions from the two individuals overlapped at room temperature. The overlapped data were subsequently used successfully in three methods of least-squares refinement, each method having certain advantages. With structure amplitudes corrected for twinning, the final *R* value was 0.13. The almost planar molecules were arranged end-to-end in zigzag fashion.

#### Introduction

Para Red (paranitroaniline red), 1-*p*-nitrobenzeneazo-2-naphthol, C<sub>16</sub>H<sub>11</sub>N<sub>3</sub>O<sub>3</sub>, was one of the first of the syn-

thetic organic dyes and pigments, the Para Red process for dyeing being developed in 1880 (Venkataraman, 1952, p. 4). It is currently used as a paint pigment. The structural formula was known to be