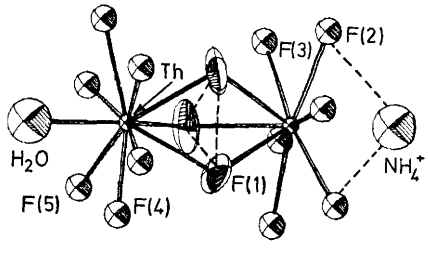
Structure of the Dimer in Ammonium Tri-μ-fluoro-bis(hexafluorothorate) Hydrate

By R. A. PENNEMAN and R. R. RYAN

(*University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico* 87544)

Summary Single-crystal *X*-ray analysis of $(NH_4)_7Th_2F_{15}$,-H_2O shows that the structure contains a dimer, the first reported for the actinide fluorides.

ISOTROPIC crystals ($n = 1{\cdot}448$) obtained on cooling (from 125°) a solution of ThF_4 in *ca.* 40% aqueous NH_4F have a molar refractivity of 40·0 ml; this is closer to 42·0 ml for $(NH_4)_4ThF_8$ than to 34·2 ml for $(NH_4)_3ThF_7$. Chemical analysis gives a NH_3/Th mol ratio of 3·5/1. That the molar refractivity exceeds the value expected for the anhydrous $(NH_4)_{3\cdot5}ThF_{7\cdot5}$ can be accounted for by the formula $7(NH_4F),2ThF_4,H_2O$ which also gives the correct density of 2·98 g ml for $Z = 4$. Precession photos established that the space group is $P2_13$. The lattice constant, $a = 12{\cdot}573$-(1), and intensity data were obtained using a Picker 4-circle automated diffractometer and Mo-K_α radiation; 1636 reflections were measured yielding 919 unique reflections. Corrections for absorption and anomalous dispersion were included in the usual manner.[1] The positions of thorium atoms on the 3-fold axis were deduced from structure factor plots and the three bridging fluorine atoms between them were located with the aid of a projected Fourier (suggested to us by W. H. Zachariasen). The three bridging fluorines in the triangular plane [0·5858, 0·4523, 0·4602(15)] refined with anisotropic temperature factors, showing highly restricted motion toward the two thorium atoms and greater motion normal to this direction.



The two independent thorium atoms on the cube diagonal, at $x, x, x = 0{\cdot}4114$ and 0·5933(1) nearly establish a pseudo centre of symmetry at 1/2, 1/2, 1/2. This psuedo centre causes difficulty in refinement of some light atoms. How-

ever, Fourier maps phased on the two thorium and bridging fluorine atoms show additional light-atom positions further along the body diagonal at 0·7076(7) and 0·3030(16) and *two* atoms (obviously nitrogens by their distance from thorium) in the general positions (12-fold sets) 0·249, 0·350, 0·112(2), and 0·695, 0·598, 0·911(2). The remaining six fluorines per thorium appear as an equatorial ring of electron density surrounding each thorium atom, essentially in a plane perpendicular to the three-fold axis. It was possible to locate half of the fluorines in each ring which were not centrosymmetrically related to a counterpart fluorine in the other ring: 0·413, 0·510, 0·247(1·8) and 0·553, 0·383, 0·290(2). At this point, the R factor was 0·09, with 6 of the 12 fluorines located. In order to refine the remaining fluorine atoms, it was necessary to restrain the approach distance of a pair of fluorines in each ring. A full refinement including the rest of the ring fluorines at 0·433, 0·686, 0·645(3), and 0·526, 0·565, 0·766(2) yielded a chemically reasonable structure. The R factor is 0·063 with the two thorium atoms and the three shared fluorines having anisotropic thermal parameters and the rest isotropic parameters. The Figure shows the unusual fluorine co-ordination. In the dimeric unit, each thorium shares a small triangular ring of three fluorines and is located in a puckered equatorial ring of six fluorines. Each of these six-membered fluorine rings is capped by either a water molecule or an ammonium ion, located on the three-fold axis. The remaining 24 ammonium ions in the lattice are co-ordinated to fluorines in the dimeric unit at reasonable distances for hydrogen bonding.

Some bond distances (Å) are: Th(1)–Th(2) = 3·962(2); H_2O–Th(1) = 2·36(4); Th(1)–3F(1) = 2·31(2); –3F(4) = 2·37(3); –3F(5) = 2·39(2); Th(2)–3F(1) = 2·45(2); –3F(2) = 2·37(3); –3F(3) = 2·39(3).

One-, two-, and three-dimensional polymers as well as isolated fluoro-anions containing thorium are known. However, among the actinide fluorides this structure contains the only established dimeric fluoride unit

This work was performed under the auspices of the U.S. Atomic Energy Commission. The authors would like to thank I. K. Kressin for some preparative and analytical work, and Dr. Allen C. Larson for his distance restraint program.

(*Received*, 30*th October* 1972; *Com.* 1844.)

[1] R. A. Penneman, R. R. Ryan, and I. K. Kressin, *Acta Cryst.*, 1971, **B27**, 2279.