The Novel Structure of $(NH_4)_4ThF_8$

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CHEMICAL analysis, and *X*-ray studies, show that $(NH_4)_4ThF_8$ is isostoicheiometric, but not isostructural, with the compounds $(NH_4)_4MF_8$ (M = Pa, U, Np, Pu, and Am) formed by the succeeding five actinides.[1] In the monoclinic series, typified by $(NH_4)_4UF_8$, the actinide is 8-co-ordinated in a distorted antiprism arrangement.[2] In triclinic $(NH_4)_4ThF_8$, however, the thorium is 9-co-ordinated and one fluorine in the structure is not involved in a Th–F bond.

High co-ordination numbers are common with the actinides and lanthanides, often exceeding the stoicheiometric fluoride : actinide ratio in a given compound by sharing fluorides. Examples are: $RbPaF_6$, $(NH_4)_2CeF_6$, 8-co-ordinated;[3] K_2PaF_7 and Li_4UF_8, 9-co-ordinated.[4] However, we believe that $(NH_4)_4ThF_8$ represents the first case where a higher co-ordination number is achieved by sharing fluorides, with exclusion of a fluoride from the co-ordination sphere of the actinide. Thorium is the largest of the tetrapositive actinides, and is therefore the most likely to achieve 9- rather than 8-co-ordination. The monomeric MF_8^{4-} goes over to polymeric 9-fold co-ordination in the $(NH_4)_4MF_8$ series at thorium(IV). In the actinide tetrafluoride–alkali fluoride series, **4 : 1** (XF : MF_4) complexes are extremely rare while the 3 : 1 ratio is widely found.[5] Since 9-fold co-ordination could be achieved in a compound of composition $(NH_4)_3ThF_7$, the 4 : 1 stoicheiometry is unexpected in the thorium fluoride–ammonium fluoride system.

Acicular crystals of $(NH_4)_4ThF_8$ result when a 45% (w/w) (saturated NH_4F solution) ammonium fluoride solution is stirred for several hours at room temperature with freshly precipitated ThF_4. Larger crystals result when a warm solution is allowed to cool slowly. Excess of NH_4F floats on the denser aqueous solution and is readily removed (centrifuge). Methyl alcohol can be used to remove any NH_4F from the surfaces of the $(NH_4)_4ThF_8$ needles.

Crystals of $(NH_4)_4ThF_8$ are triclinic with unit cell dimensions $a = 8{\cdot}59$, $b = 8{\cdot}41$, $c = 7{\cdot}33$ Å, $\alpha = 88°\ 28'$, $\beta = 95°\ 46'$, $\gamma = 106°\ 49'$; space group $P\bar{1}$, $Z = 2$, $D_c = 3{\cdot}0$.

Three-dimensional X-ray diffraction data were collected by use of a single crystal orienter on a G.E. XRD-5. The relative positions of the thorium atoms were deduced from the Patterson function. A difference Fourier phased on the refined thorium positions showed the positions of the remaining atoms, and the structure has been refined by full matrix least-squares to $R = 4{\cdot}2\%$.

In $(NH_4)_4UF_8$ the average U–F distance is 2·28 Å, with a range of 2·27 to 2·33 Å. In $(NH_4)_4ThF_8$ thorium has nine fluorine neighbours at an average distance of 2·40 Å, with a range of 2·28 to 2·47 Å. The fluorine co-ordination polyhedron around the thorium is distorted from a tricapped trigonal prism of ideal D_{3h} symmetry. The remaining fluorine lies approximately 5·04 Å from its nearest thorium neighbour. This F, which is not bonded to thorium, is surrounded by five N-atoms in approximately a square pyramidal configuration with an average N. . . . F distance of 2·74 Å.

Differential thermal analysis shows that NH_4F is lost from $(NH_4)_4ThF_8$ less readily than from $(NH_4)_4UF_8$. The peak of the first endotherm of $(NH_4)_4UF_8$ occurs at 180°: that of $(NH_4)_4ThF_8$ occurs at 205°.

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