The Crystal Structures of Eight-co-ordinate (Tetrakis-*NN*-diethyldithiocarbamate) Complexes

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Summary The crystal structures of thorium tetrakis-(*NN*-diethyldithiocarbamate) and of tetraethylammonium neptunium tetrakis-(*NN*-diethyldithiocarbamate) have been determined.

THE preparation and unit-cell dimensions of quadrivalent actinide tetrakis-(*NN*-diethyldithiocarbamate) complexes of the type M dtc_4 (M = Th, U, Np, and Pu) and of tervalent actinide and lanthanide complexes of the type NEt_4M dtc_4 (M = La–Lu except Pm, Np, and Pu) have recently been reported.[1–3] I.r. spectral studies have indicated that the *NN*-diethyldithiocarbamate groups are probably bidentate, implying an eight-co-ordinate environment for the central metal atom. Since the co-ordination of eight sulphur atoms to a metal has not previously been recorded it seemed worthwhile investigating the structures of Th dtc_4 and NEt_4Np dtc_4.

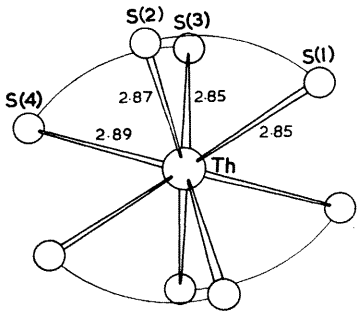

FIGURE 1. *The co-ordination polyhedron in* Th dtc_4 *viewed down the crystallographic two-fold axis.*

The complexes were prepared as previously described[2,4] and were recrystallised from anhydrous benzene [Th dtc_4] or methylene dichloride [NEt_4Np dtc_4]. Th dtc_4 is monoclinic, space group $C2/c$, $a = 19{\cdot}16$, $b = 11{\cdot}74$, $c = 16{\cdot}11$ Å, $\beta = 116.42°$, $Z = 4$ and $D_c = 1{\cdot}687$ g.cm.$^{-3}$; NEt_4Np dtc_4 is monoclinic, space group $P2_1/c$, $a = 11{\cdot}68$, $b = 20{\cdot}49$, $c = 16{\cdot}11$ Å, $\beta = 116{\cdot}5°$, $Z = 4$, $D_c = 1{\cdot}532$ g.cm.$^{-3}$. Three dimensional *X*-ray data were collected by the equi-inclination Weissenberg technique using Cu-K_α radiation ($\lambda = 1{\cdot}5418$ Å). The intensities were estimated visually and after application of the usual geometrical corrections 1209 and 1263 nonzero intensities were obtained for Th dtc_4 and NEt_4Np dtc_4, respectively. The metal co-ordinates were deduced from Patterson syntheses and the co-ordinates of the light atoms from subsequent Fourier syntheses. Refinement by full-matrix least-squares has reduced the residuals to 0·112 for Th dtc_4 and 0·117 for NEt_4Np dtc_4. Refinement is being continued.

The configuration of the sulphur atoms around the thorium atom is shown in Figure 1 and the configuration about the neptunium atom in Figure 2. In the thorium complex the sulphur atoms are arranged as a distorted dodecahedron. However, the co-ordination polyhedron in the neptunium complex is different from any previously observed eight-co-ordinate polyhedron. It is best regarded as an almost plane pentagonal arrangement of five sulphur atoms, S(1)—(5), with one sulphur atom, S(6), located below, and the remaining two, S(7) and S(8), above, this plane. The neptunium atom is slightly above the plane of the five sulphur atoms.

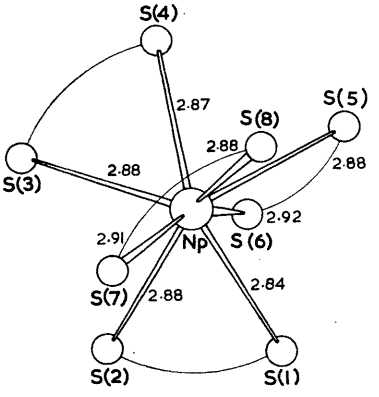

FIGURE 2. *The co-ordination polyhedron in* NEt_4Np dtc_4.

The mean Th–S and Np–S distances are 2·86 and 2·89 Å, respectively; the remaining interatomic distances do not differ significantly from those reported for other *NN*-diethyldithiocarbamate complexes.[5] The mean M–S distances are very similar to the mean U–S distance (2·80 Å) recently reported[6] for the complex NMe_4UO_2 dtc_3.

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