The Structure of the Eight-co-ordinate Complex Tetramethylammonium Uranyl Tris-diethyldithiocarbamate

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INFORMATION concerning the bonding between the heavy elements and sulphur donor atoms is very limited, and in particular, no structural information is available. We now report the crystal and molecular structure of tetramethylammonium uranyl tris-diethyldithiocarbamate $[Me_4N][UO_2 \cdot 3dtc]$. This complex was first prepared by Zingaro.[1] We have repeated the synthesis in anhydrous methanol, and by controlled precipitation under nitrogen obtained single crystals which were used in this study.

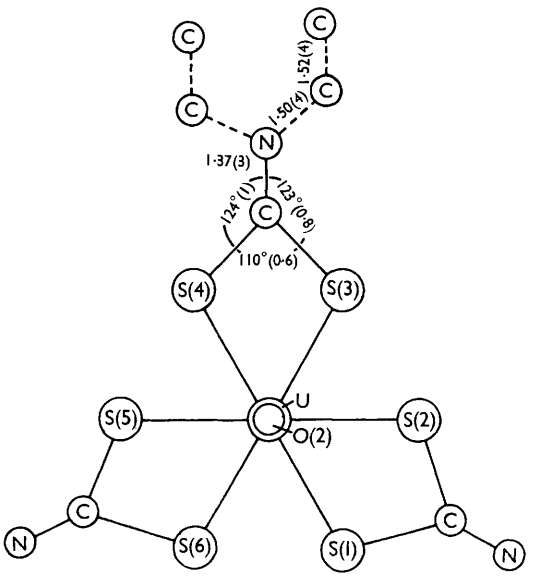

FIGURE. *The co-ordination around the uranium atom. O(2) is below the plane and is not shown. Estimated standard deviation is given in parentheses.*

The crystals of $[Me_4N][UO_2 \cdot 3dtc]$ are orthorhombic with cell dimensions $a = 19{\cdot}03$, $b = 17{\cdot}21$, $c = 9{\cdot}41$ Å, $U = 3083$ Å^3, $Z = 4$. Systematic absences for $0k1$, $k + 1 = 2n + 1$, and for $h0l$, $h = 2n + 1$, are consistent with space groups $Pna2_1$ and $Pnam$. Intensities of 1200 non-zero reflections were estimated visually from equi-inclination Weissenberg photographs using Zr-filtered Mo-K_α radiation. Using Howells[2] method we concluded the space group to be $Pna2_1$. The position of the uranium and the six sulphur atoms were obtained readily from a three-dimensional Patterson map. All carbon and nitrogen atoms were then placed by successive-difference Fourier synthesis. Several cycles of least-squares refinement of positional, scale, and thermal parameters converged to an R factor of 14·0%. The refinement is being continued.

The configuration about the uranium atom as seen along the uranyl axis is shown in the Figure. The uranyl group is linear (the O–U–O angle is $178{\cdot}8 \pm 0{\cdot}5°$), and the U–O(1) and U–O(2) bond lengths are $1{\cdot}72 \pm 0{\cdot}04$ Å and $1{\cdot}69 \pm 0{\cdot}05$ Å respectively. The six sulphur atoms are arranged hexagonally around the uranium atom with an average U–S bond length of $2{\cdot}80 \pm 0{\cdot}01$ Å. The six sulphur atoms are not coplanar but they are staggered with respect to the plane which contains the uranium atom and perpendicular to the uranyl axis. The atoms S(1), S(3), and S(5) are 0·30, 0·25, and 0·23 Å above this plane, and the atoms S(2), S(4), and S(6) are 0·17, 0·26, and 0·20 Å below it. The average S–U–S angle is $73{\cdot}5 \pm 0{\cdot}5°$. The fact that the six sulphur donor atoms are not coplanar may be attributed to steric factors. In contrast, six oxygen donor atoms have been shown to be coplanar, as for example in $Na(UO_2)(OAc)_3$.[3] The dimensions of the diethyldithiocarbamate group are similar to other complexes containing this ligand.[4] The average angles and bond lengths for the diethyldithiocarbamate ligand are shown in the Figure.

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