Chemical Communications

(The Journal of the Chemical Society, Section D)

NUMBER 23/1971 8 DECEMBER

Chemistry of the Uranyl Group. Preparation and Crystal and Molecular Structure of Bis-(*NN*-diethyl diselenocarbamate)dioxo(triphenylarsine oxide)uranium(VI), $UO_2[Et_2NCSe_2]_2Ph_3AsO$

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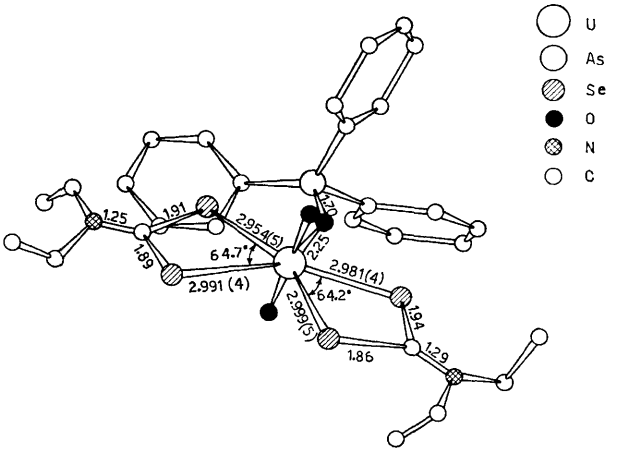
Summary Two complexes of formula $UO_2(Et_2NCSe_2)_2{\cdot}L$ ($L = Ph_3PO$ or Ph_3AsO) have been prepared; the arsine oxide derivative is a pentagonal-bipyramidal complex, the four selenium atoms and the ligand oxygen atom lying in the plane normal to the uranyl group.

THE uranyl ion forms a variety of complexes with oxygen-donor anionic ligands. The preparation and properties of uranyl diethyl dithiocarbamate complexes with triphenylphosphine oxide and triphenylarsine oxide as neutral ligands have been reported;[1] in these molecules the anionic groups are chelated to the uranium through the sulphur atoms. Furlani *et al.*[2] pointed out that the chemical behaviour of selenium in transition-metal diethyl diselenocarbamate complexes is similar to that of sulphur. In order to see if this occurs also for the uranyl compounds, the corresponding diethyl diselenocarbamate derivatives with the above mentioned neutral ligands were prepared. Crystalline precipitates of $UO_2(Et_2NCSe_2)_2Ph_3PO$ and $UO_2(Et_2NCSe_2)_2Ph_3AsO$ were obtained by reaction of $UO_2(NO_3)_2,6H_2O$ in methanol with the required amount of potassium diethyl diselenocarbamate in water–dioxan solution[3] and adding successively a methanolic solution of appropriate ligand. $UO_2(Et_2NCSe_2)_2Ph_3PO$ has m.p. 252°; $UO_2(Et_2NCSe_2)_2Ph_3AsO$ has m.p. 245°. Satisfactory elemental analyses were obtained. The crystals of the arsenic derivative, grown from acetone solution, were suitable for *X*-ray analysis.

The molecular and crystal structure was determined by single-crystal *X*-ray methods. The monoclinic, $P2_1/n$ unit cell of dimensions $a = 18{\cdot}589(5)$, $b = 9{\cdot}141(3)$, $c = 21{\cdot}329(6)$ Å, $\beta = 111°52'(2)$, $V = 3363$ Å^3, contains four molecular units of formula $UO_2(Et_2NCSe_2)_2Ph_3AsO$; D_m (flotation) $= 2{\cdot}10$, $D_x = 2{\cdot}12$ g cm^{-3}. The intensities of 4307 independent reflections were recorded on a Siemens A.E.D. out to the value of $\theta = 60°$ using nickel-filtered



FIGURE

Cu-K_α radiation. The structure was solved by standard methods, and least-squares refinement on the 3927 non-zero reflections has reached a conventional R factor of 0·10. Isotropic temperature factors were used for all but the U, As, and Se atoms.

Each uranium atom can be considered to be in a pentagonal-bipyramidal environment. As shown in the Figure, in which the most significant bond distances are reported, the linear uranyl group (O–U–O angle = 178°) is perpendicular to the equatorial plane in which the four selenium atoms of the two anionic groups and the oxygen atom of the ligand occupy the corners of an irregular pentagon. The U–O (uranyl) distances are 1·76(2) Å, and 1·77(2) Å. The four U–Se–C angles lie in the range 88—91°, the two Se–U–O angles are 79° and 81°, respectively, and the sum of the five angles subtended by the uranium atom in the equatorial plane is 360°. The U–O–As angle is 157°. These values are in good agreement with the corresponding values found in $UO_2(Et_2CNS_2)_2Ph_3AsO$, and $UO_2(Et_2CNS_2)_2Ph_3PO$ which are isostructural. Notable dimensional features are the four U–Se bond distances (mean value 2·98 Å), and the relatively short U–O(ligand) distance of 2·25(3) Å, the corresponding values in the above sulphur derivative with arsine oxide being 2·84(1) Å and 2·30(2) Å.

We thank Mrs. M. Magnabosco and Mr. F. Benetollo for helpful assistance in data reduction.

(*Received, August 4th,* 1971; *Com.* 1350.)

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