The Crystal and Molecular Structure of Acetate-bridged Uranyl Compounds

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RECENTLY we have prepared two new isomorphous and isostructural uranyl compounds with triphenyl derivatives of phosphorus and arsenic oxides, which are formulated as $[UO_2(AcO)_2Ph_3PO]_2$ and $[UO_2(AcO)_2Ph_3AsO]_2$.

The following data were established by *X*-rays (Cu-K_α), $C_{44}H_{42}O_{14}P_2U_2$, $M = 1332$, triclinic, $a = 8{\cdot}346(12)$, $b = 11{\cdot}022(16)$, $c = 13{\cdot}680(18)$ Å, $\alpha = 101°\ 50'(10')$, $\beta = 91°\ 12'(10')$, $\gamma = 109°\ 12'(10')$, $U = 1147$ Å^3, $D_m = 1{\cdot}91$, $Z = 1$, $D_c = 1{\cdot}93$ g.cm.$^{-3}$. Space group, $P1$ or $P\bar{1}$; the latter (No. 2) was bourne out by the analysis, and it implies that the dimeric molecule is centrosymmetric.

The intensities were recorded with the Weissenberg equi-inclination method (0*kl* through 4*kl*) and corrected for Lorentz, polarization and absorption. The structure was solved by the heavy-atom procedure and the refinement was carried out by the block-diagonal least-squares method using isotropic temperature factors. The *R* index was 12% for 1399 reflections. The Figure shows a perspective view of the dimer (the triphenylphosphine groups are summarised as PPh_3). The most significant bond lengths and angles are also reported.

The hepta-co-ordination is realized with the

TABLE

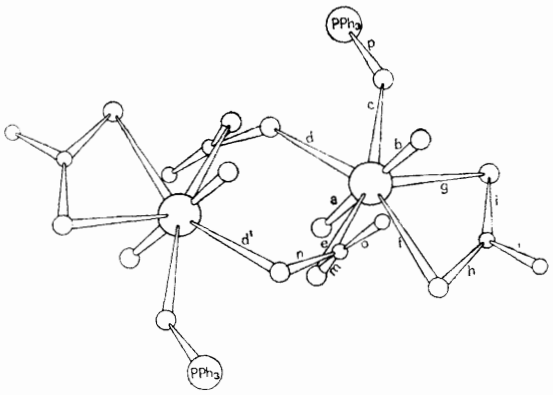
a	1·81 Å	$\sigma_{a,b}$	0·03 Å	∠ *ab*	177·3°	∠ *de*	79·0°
b	1·82			∠ *ac*	92·8	∠ *df*	155·2
c	2·37	$\sigma_{c,d,e,f,g}$	0·02	∠ *ad*	94·1	∠ *dg*	150·1
d	2·32			∠ *ae*	90·4	∠ *ef*	76·2
e	2·33	$\sigma_{h,i,m,n}$	0·04	∠ *af*	86·6	∠ *eg*	130·9
f	2·38	$\sigma_{l,o}$	0·05	∠ *ag*	87·0	∠ *fg*	54·7
g	2·37			∠ *bc*	89·2	∠ *fh*	97·5
h	1·29	σ_{p}	0·03	∠ *bd*	88·2	∠ *gi*	95·8
i	1·34			∠ *be*	88·6	∠ *hi*	112·0
l	1·42			∠ *bf*	90·8	∠ *hl*	126·6
m	1·36			∠ *bg*	91·8	∠ *il*	121·3
n	1·33			∠ *cd*	74·8	∠ *em*	121·2
o	1·46			∠ *ce*	152·9	∠ *mn*	101·8
p	1·48			∠ *cg*	76·0	∠ *mo*	121·0
				∠ *cf*	92·8	∠ *no*	126·0
				∠ *cp*	143·8	∠ *nd'*	143·3

The e.s.d. of the angles are generally $\sim\pm 2°$.

uranium atom at the centre of a pentagonal bipyramid formed by five oxygen atoms in the equatorial plane normal to the uranyl group. The bond angles to the uranium atom in the equatorial plane are 75°, except the chelate bond angle which is 54°. The angles in the different acetate groups and in the triphenyl phosphine are regular.

As for the As–O bond in $UO_2(NO_3)_2.2Ph_3AsO$,[1] the P–O bond is notably shorter than the sum of the covalent radii.

The compound is defined as *trans*-di-μ-acetato-bis-(dioxotriphenylphosphineoxideacetato)diuranium(VI). The presence of dimers was also recognized for both compounds by molecular weight and conductivity measurements in nitromethane and in 1,2-dichloromethane solutions.



FIGURE

(*Received, January 12th*, 1968; *Com.* 041.)

[1] U. Croatto, R. Graziani, C. Panattoni, B. Zarli, and G. Bombieri, to be published.