Tetrachlorobis(triethylarsine Oxide)uranium(IV): UCl₄.2(TEASO)

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Abstract. [UCl₄{OAs(C₂H₅)₃}₂], UCl₄As₂O₂C₁₂H₃₀, M = 736. Monoclinic, $P2_1/n$, a = 13·67 (1), b = 11·24 (1), c = 7·705 (5) Å, β = 103·2 (1)°, U = 1152 Å³, D_c = 2·128 g cm⁻³, Z = 2, μ(Mo $K\alpha$) = 99·9 cm⁻¹. R = 0·042 for 1631 observed data; U, As and two Cl atoms anisotropic and H atoms included. The two OAs(C₂H₅)₃ ligands are *trans* coordinated to the U in the square-planar UCl₄ group. U–Cl 2·66, 2·67; U–O 2·16, As–O 1·71 Å; mean As–C 1·92 Å; U–O–As 154°.

Introduction. Recent studies have shown that arsine oxide ligands are stronger oxygen donors than their P analogues, and are especially effective in replacing Cl⁻ ions in the coordination sphere of UCl₄ (du Preez, Edge, Gibson, Rohwer & van Vuuren, 1976). Previous crystallographic work has shown that the species UCl₄.2L, L = substituted phosphine oxide, may be *trans* for L = HMPA (de Wet & Darlow, 1971) and PTPA (Nassimbeni, 1975) or *cis* for L = TPPO (Bombieri, Brown & Graziani, 1975). [UCl₄{OAs(C₂H₅)₃}₂] was the first arsine oxide complex of UCl₄ to be reported (Lane & Venanzi, 1969) and it was of interest to determine whether the stronger U–O interaction would have any detectable effect on the U–Cl and U–O lengths.

Suitable crystals were supplied by Professor J. G. H. du Preez. They were moisture-sensitive, and had to be sealed in capillaries. Data were collected from a crystal 0·15 × 0·30 × 0·15 mm on a Philips four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·7107 Å) for θ between 3 and 25°. The ω–2θ scan technique was used; the scan width was 1·0°, the scan time was 33 s and the background was counted for 33 s for each peak. Of the 2133 reflexions measured, 1631 were classed as observed, $I > 1.65\sigma(I)$. Three reflexions were used as standards and their intensities remeasured after every 60 reflexions; no decomposition was detected. The intensities were corrected for Lorentz and polarization effects only. A temperature-sharpened

Patterson map confirmed that the U atom was at 0,0,0 and gave the coordinates of the As atom. The Cl, O and C atoms were found in the subsequent Fourier map. The structure was refined by block-diagonal least squares with U, As and two Cl atoms anisotropic, O and six C atoms isotropic. When R reached 0·044, a difference map clearly showed electron density in regions where the H atoms could be expected. The 15 H atoms were included in the structure factor calculations and the parameters of the heavy atoms refined to convergence; final R = 0·042 for 1631 observed

Table 1. *Atomic coordinates and thermal parameters*

(*a*) Fractional atomic coordinates and isotropic thermal parameters*

	x	y	z	B (Å²)
U	0·0	0·0	0·0	
As	0·2083 (1)	0·0961 (1)	0·3831 (1)	
Cl(1)	0·0401 (2)	0·2208 (2)	−0·0853 (3)	
Cl(2)	−0·1297 (2)	0·0895 (2)	0·1775 (4)	
O	0·1205 (4)	0·0174 (6)	0·2339 (8)	3·25 (13)
C(1)	0·2745 (7)	0·2024 (9)	0·2533 (13)	3·64 (20)
C(2)	0·3225 (8)	0·1358 (11)	0·1176 (15)	4·92 (27)
C(3)	0·3018 (7)	−0·0163 (9)	0·5156 (13)	3·73 (21)
C(4)	0·3853 (8)	0·0476 (10)	0·6533 (15)	4·54 (25)
C(5)	0·1405 (8)	0·1858 (10)	0·5332 (14)	4·37 (24)
C(6)	0·0857 (9)	0·2926 (11)	0·4514 (16)	5·31 (28)
H(11)	0·330	0·245	0·345	
H(12)	0·225	0·260	0·185	
H(21)	0·355	0·195	0·055	
H(22)	0·265	0·095	0·030	
H(23)	0·370	0·080	0·185	
H(31)	0·330	−0·060	0·430	
H(32)	0·260	−0·070	0·575	
H(41)	0·430	−0·015	0·720	
H(42)	0·350	0·090	0·735	
H(43)	0·420	0·105	0·590	
H(51)	0·190	0·210	0·650	
H(52)	0·095	0·130	0·580	
H(61)	0·055	0·330	0·540	
H(62)	0·035	0·265	0·345	
H(63)	0·135	0·345	0·415	

* All H atoms were assigned B = 6·0 Å².

Table 1 (*cont.*)

(*b*) Anisotropic thermal motion parameters (× 10⁵). The expression is exp $[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
U	263 (2)	483 (4)	1191 (9)	−69 (7)	22 (7)	86 (14)
As	277 (5)	430 (8)	960 (19)	12 (12)	2 (15)	−38 (22)
Cl(1)	452 (15)	528 (22)	1773 (58)	−95 (30)	321 (48)	279 (58)
Cl(2)	562 (18)	795 (26)	2149 (65)	123 (37)	983 (55)	30 (71)

data.* Weighting was proportional to $1/\sigma(F)$. Scattering factors for neutral atoms were used (*International Tables for X-ray Crystallography*, 1962); that of U was corrected for anomalous dispersion. Final positional and thermal parameters are given in Table 1, bond lengths and angles in Table 2: estimated standard deviations are given in parentheses.

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

(a) Bond lengths and angles

U——Cl(1)	2·66 (1)	Cl(1)–U——Cl(2)	88·5 (5)
U——Cl(2)	2·67 (1)	Cl(2)–U——O	90·5 (5)
U——O	2·16 (1)	Cl(1)–U——O	88·0 (5)
O——As	1·71 (1)	U——O——As	154 (1)
As——C(1)	1·91 (2)	O——As—C(1)	108 (1)
As——C(3)	1·92 (2)	O——As—C(3)	107 (1)
As——C(5)	1·92 (2)	O——As—C(5)	108 (1)
C(1)–C(2)	1·54 (3)	As——C(1)–C(2)	112 (2)
C(3)–C(4)	1·54 (3)	As——C(3)–C(4)	111 (2)
C(5)–C(6)	1·48 (3)	As——C(5)–C(6)	116 (2)

(b) Important intramolecular non-bonded contacts

Cl(1)···C(1)	3.65	Cl(2) ···C(6)	3·95
Cl(1)···C(2)	3·92	Cl(2)′···C(2)	3·97

(c) Shorter intermolecular contacts

	Unit-cell translation	
Cl(1)···C(3)ⁱⁱ	–	3·61
Cl(1)···C(4)ⁱⁱ	–	3·87
C(1)····Cl(1)ⁱ	–	3·66
C(1)····Cl(2)ⁱ	–	3·97
C(2)····Cl(1)ⁱ	–	3·69
C(4)····C(6)ⁱ	–	3·67
C(5)····Cl(2)ⁱ	–	3·98
Cl(1)···C(5)	0,0,–1	3·51
Cl(1)···C(6)	0,0,–1	3·84
C(3)····C(1)ⁱⁱ	0,–1,0	3·75

Equivalent positions

Superscript

None	x	y	z		(ii)	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
(i)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$					

Discussion. The molecule is centrosymmetric. The four Cl atoms are bonded to the U in a square plane and the two TEASO ligands are *trans* coordinated to the U (Fig. 1). The bond lengths and angles are similar to those observed in the related compounds UCl₄.2(TPPO) and UCl₄.2(PTPA) in both of which U–Cl is 2·61 to 2·63 Å and U–O is 2·23 to 2·24 Å. The U–Cl lengths are surprisingly close to the 2·65, 2·66 Å found in [UO₂Cl₄]²⁻ (Sipio, Tondello, Pelizzi, Ingletto & Montenero, 1974). In UCl₄.2(TEASO) the lengthening of the U–Cl bonds appears to be accompanied by a real shortening of the U–O bond because the As–O bond is significantly longer than the 1·644 Å found in
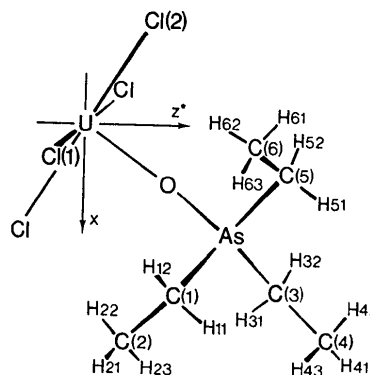
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* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31593 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Fig. 1. A projection down y showing the numbering system.

OAs(C₆H₅)₃.H₂O (Ferguson & Macaulay, 1969). All these observations are consistent with a stronger U–O interaction than is observed in the phosphine oxide complexes.

The C₂H₅ groups in the TEASO ligand are folded in an irregular manner which is best illustrated by comparing the torsion angles O–As–C(1)–C(2) 57°, –C(3)–C(4) 179°, –C(5)–C(6) 76°. Two ethyl groups are folded against the UCl₄ plane [Table 2(b); C(2) and C(6)] while the third stands away from it. This seems to reduce the packing density resulting in a mean volume of over 27 Å³ per non-hydrogen atom in UCl₄.2(TEASO) compared with 25 Å³ in UCl₄.2(HMPA) and 24 Å³ in UCl₄.2(PTPA).

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