The Chemistry of Uranium. Part 20.† Tetraphenylphosphonium Pentachloro-oxouranate(VI): Crystal Structure and Bonding Characteristics

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The crystal structure of the title complex has been determined from three-dimensional *X*-ray diffraction data collected on a four-circle automatic diffractometer. The complex crystallises in space group *P*4/*n*, with $a = b = 13.264(5)$, $c = 7.621(5)$ Å, and $Z = 2$. The structure has been solved by Patterson and Fourier methods and refined to a final *R* of 0.024. The structure consists of octahedral anions and of cations with $\bar{4}$ (S_4) symmetry, both ions forming linear stacks parallel to *c*: U–O is 1.76(1) Å, four Cl atoms form an equatorial plane with U–Cl 2.536(2) Å, while the axial U–Cl bond, *trans* to U–O, is 2.433(4) Å. The results are discussed in relation to structural data for similar actinoid complexes with metal oxidation states IV—VI; strong evidence is adduced that the bonding in such complexes is predominantly ionic in character and strongly influenced by ligand–ligand repulsion.

TETRAPHENYLPHOSPHONIUM PENTACHLORO-OXOURANATE(VI) is a new type of uranium(VI) chloro-oxo-complex which has recently [1] been prepared and characterised by spectroscopic methods. The molecular structure and bond lengths are of interest from two points of view. First, with regard to the complex itself, it was observed [1] that the lower U–O stretching frequency, compared with that in $[UO_2Cl_4]^{2-}$, suggests weaker uranium–oxygen

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† Part 19: J. G. H. du Preez, J. W. Gonsalves, and P. J. Steenkamp, *Inorg. Chim. Acta*, 1977, **21**, 167.

[1] K. W. Bagnall and J. G. H. du Preez, *J.C.S. Chem. Comm.*, 1973, 820.

bonding, whereas the opposite is indicated by the somewhat lower rate of chlorination. Furthermore, the rate of bromination of $[UOCl_5]^-$ with anhydrous HBr, as well as the fact that the $[UO(Cl)Br_4]^-$ salt could be isolated,[1] suggests that one stronger U–Cl bond exists. Secondly, more accurate structural data on complexes containing the $UOXCl_4$ chromophore (X = O or Cl) for the oxidation states IV, V, and VI of uranium have recently become available (Table 5). Comparison of the bond lengths in $[UOCl_5]^-$ with those in the above complexes and in the $[PaOCl_5]^{2-}$ ion [2] should lead to a better understanding of the nature and extent of the interactions between the uranium, oxygen, and chloride ions in complexes of uranium having the above oxidation states.

Although these interactions are discussed more fully below, some preliminary remarks are appropriate. The nature of the bonding in linear dioxouranium(VI) species has received considerable attention for more than two decades, and while an essentially ionic bonding model has been considered by some workers [3] the bonding has generally been interpreted in terms of covalent models.[4] Accurate structural data on the $[UOCl_5]^-$ ion could provide decisive information on the nature of the U–O bond since this is the first example of an oxouranium(VI) complex in which one of the uranyl oxygen atoms has been replaced by a different atom. If (as may be expected) the structure of this anion is similar to that of $[PaOCl_5]^{2-}$, *i.e.* consisting of an equatorial square-planar MCl_4 and linear O=M–Cl systems, then the two *trans*-orientated axial ligands, which differ appreciably in electronegativity and charge density, should be sensitive to the nature of the bonding. If the bonding is covalent to a considerable extent, one would expect the '*trans* effect' [5] to be operative and to result in a relative lengthening of the axial U–Cl bond. On the other hand, a contraction of this bond can best be interpreted in terms of a predominantly ionic bonding model in which ligand–ligand repulsion plays an important part.

EXPERIMENTAL

Crystal Data.—$C_{24}H_{20}Cl_5OPU$, $M = 770.7$, Tetragonal, $a = b = 13.264(5)$, $c = 7.621(5)$ Å, $U = 1\,340.8$ Å^3, $D_c = 1.924$ g cm^{-3}, $Z = 2$, $D_m = 1.916$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 63.2 cm^{-1}, space group $P4/n$ (C_{4h}^3).

Collection of Intensity Data.—Deep orange-red crystals of the title complex were grown by slow cooling of the reaction mixtures described previously.[1] As the complex is sensitive to atmospheric moisture, crystals were mounted on fibres which were sealed into Lindemann glass capillaries in the dry-box. Two sets of intensity data were collected (see Table 1 and next section). The spherical crystal for data set 2 (μR 0.63) was ground under nitrogen in a Hilger and Watts crystal grinder to a sphericity of ±10% in order to obviate absorption corrections. Absorption corrections, by the Gaussian-grid method of Busing and Levy [6] which was adapted for Weissenberg geometry in program WASP,[7] were made for 512 sampling points in the crystal used for collecting data set 1. Both sets were corrected for Lorentz and polarization effects. The observable limits of intensity were taken as $F = 3\sigma(F)$ and $I = 1.65\sigma(I)$ for data sets 1 and 2 respectively. Structure factors above these limits were used in the structural analysis, those in data set 1 being further reduced to the number in Table 1 by excluding those with h or $k > 9$. Only data set 1 revealed any significant fluctuations or trends in the intensities of the monitor reflections, and appropriate corrections were applied. Accurate unit-cell dimensions were obtained by least-squares analysis of the setting angles obtained on the four-circle diffractometer for 25 high-order reflections.

TABLE 1

Intensity collection data

	Data set 1	Data set 2
Crystal size (mm)	0.13 × 0.13 × 0.48	sphere, diameter 0.20
Diffractometer	Stoe Stadi II (two-circle)	Philips PW 1100 (four-circle)
Radiation	Mo–K_α	Mo–K_α
Monochromator	graphite crystal	bent graphite crystal
Scan mode	ω-step scan	ω—2θ (continuous), 0.04° s^{-1}
Scan width	variable	1.2°
Reflections measured	2 540	980
Reflections used	1 630	764

Structure Determination.—Oscillation, Weissenberg, and precession photographs revealed that the crystal symmetry is apparently tetragonal, the only systematically absent reflections being ($hk0$) for $h + k$ odd. Although the a and b axes were identical and the cell angles 90°, the conditions for four-fold tetragonal symmetry $I(hkl) = I(\bar{k}hl)$ were not strictly obeyed, nor could the further condition $I(hkl) = I(khl)$, which applies to $4/mmm$ Laue symmetry (and which would allow distinction between the two possible space groups $P4/n$ and $P4/nmm$), be established with certainty. In view of the uranium atom's dominating contribution to the X-ray scattering, and since the deviations from the above conditions were small, these were regarded as at least partly due to absorption effects in the relatively large crystals used. The space group with least restrictive symmetry, $P4/n$, was therefore tentatively assumed. The correctness of this choice was borne out by the subsequent Patterson synthesis and structural analysis.

Using data set 1, the co-ordinates of the non-hydrogen atoms were determined by conventional heavy-atom methods (three-dimensional Patterson and electron difference synthesis). However, during the subsequent least-squares refinement some undesirable features emerged: the positional and thermal parameters of the oxygen atom, and to a lesser extent those of atom Cl(1), tended to become unstable. For example, they were unduly sensitive to the type of weighting scheme employed, and also to the introduction of layer-line scale factors; in addition there was strong correlation between these scale factors and the values of the constants used in the formula for artificial least-squares weights. This pointed to residual systematic errors which evidently exerted an enhanced effect on these atoms (situated on the four-fold axes) in view of the small

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[2] D. Brown, C. T. Reynolds, and P. T. Moseley, *J.C.S. Dalton*, 1972, 857.

[3] N. W. Alcock, *J.C.S. Dalton*, 1973, 1616.

[4] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, p. 1089.

[5] Ref. 4, p. 667.

[6] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

[7] J. F. de Wet and M. Jones, unpublished work.

number of anisotropically refinable parameters for these special positions: z, $U_{11} = U_{22}$, U_{33}. It was therefore decided to collect a second, more accurate, set of intensity data in which absorption errors were eliminated as far as possible.

Full-matrix least-squares refinement was resumed with data set 2, starting with the previous positional parameters but refining thermal parameters anew. For a model with anisotropic U, O, Cl, and P atoms, and isotropic phenyl C atoms constrained to refine as a rigid body with idealised benzene geometry, three cycles with unit weights gave R 0.030; the quantity minimised was $\Sigma w\Delta^2$ where $\Delta = |F_o| - |F_c|$. Another three cycles followed in which the C atoms were released to refine anisotropically, phenyl H atoms with common isotropic thermal parameter being added artificially, and each riding on its parent C atom. Using weights proportional to $1/\sigma^2(F_o)$, R converged to 0.024. A final difference synthesis in which the hydrogen scattering contributions were omitted gave no peaks >0.4 e Å^{-3} other than those of the H atoms, which reappeared at their refined positions. Errors due to absorption or decomposition were now negligible, as was demonstrated by analysis of $\langle w\Delta^2 \rangle$ (Δ as above), sampled as a function of $|F_o|$, $(\sin\theta)/\lambda$, and elapsed time during data collection; no trends were noticeable. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22225 (7 pp.).* Scattering factors were calculated analytically,[8] those of U and Cl being corrected for anomalous dispersion.[9] Except for the absorption corrections on data set 1, all the computations were made with the program system SHELX.[10] Final atomic parameters are listed in Table 2.

TABLE 2

Final positional (× 10^4) parameters with estimated standard deviations in parentheses

Atom	x	y	z
U	2 500(0)	2 500(0)	1 790(1)
Cl(1)	2 500(0)	2 500(0)	−1 403(4)
Cl(2)	951(2)	1 379(2)	1 805(2)
O	2 500(0)	2 500(0)	4 093(12)
P	7 500(0)	2 500(0)	0(0)
C(1)	7 421(5)	3 583(5)	1 409(8)
C(2)	6 662(5)	4 264(6)	1 263(10)
C(3)	6 616(6)	5 064(7)	2 496(13)
C(4)	7 317(6)	5 126(7)	3 783(11)
C(5)	8 091(6)	4 439(7)	3 937(10)
C(6)	8 145(6)	3 660(6)	2 750(9)
H(2)	6 107 *	4 196	234
H(3)	6 014	5 608	2 396
H(4)	7 271	5 738	4 714
H(5)	8 647	4 508	4 967
H(6)	8 748	3 115	2 850

* Hydrogen atoms have positional estimated standard deviations equal to those of the parent C atoms on which they ride. All have a common 10^3 $U_{\text{iso.}} = 86(12)$ Å^2.

RESULTS AND DISCUSSION

Description of the Structure.—The structure (Figure 1) consists of alternate stacks of anions and cations parallel to c. The $\bar{4}$ (S_4) symmetry of the cation and differences in co-ordination environment at the O and Cl(1) apices of the $[UOCl_5]^-$ octahedron give rise to the observed space-group symmetry. This unusual mode of packing, involving linear chains of ions with like charge sign, has also been observed in the structure of $[PPh_4][WOCl_5]$ which is very similar, but not identical, to that of the title complex.[11] The stability of this structure is more readily understood if (*i*) the low charge density due to the distribution of a single unit charge over such large ions and (*ii*) the various interionic approach distances are taken into account. The large number of anion contacts with positively charged cation H atoms (32 are generated from the eight contacts listed in Table 3 by four-fold rotation) tend to screen the anions from each other, so that the repulsion arising from two anion–anion contacts (Table 3) is probably more than compensated for. On the other hand, the structure and stacking period of the $[PPh_4]^+$ cations is such that interplanar separations of

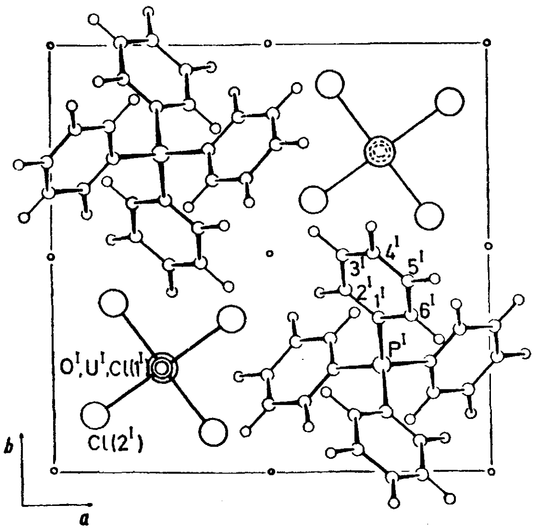

FIGURE 1 Projection of the unit cell of $[PPh_4][UOCl_5]$ down the c axis. Numbered atoms (element symbol omitted for carbon atoms) refer to the asymmetric unit (Table 2)

TABLE 3

Closest non-bonded distances (Å) in the vicinity of the $[UOCl_5]^-$ anion

(*a*) Anion–anion contacts [a]

O ··· Cl(1^{VIII}) [b] 3.43 (and its equivalent, Cl(1) ··· O^{IX})

(*b*)

O ··· H(3^{II})	3.56	Cl(2) ··· H(3^{V})	3.36
Cl(1) ··· H(3^{II})	3.28	Cl(2) ··· H(4^{IV})	3.21
Cl(2) ··· H(2^{V})	3.29	Cl(2) ··· H(4^{VI})	3.29
Cl(2) ··· H(2^{VII})	3.08	Cl(2) ··· H(5^{IV})	3.12

[a] The first atoms (no superscripts) refer to those in symmetry position I.

[b] Symmetry equivalents:

I x, y, z (see Table 2, Figure 1)
II $1 - x, 1 - y, \bar{z}$
III $1 - y, -\frac{1}{2} + x, 1 - z$
IV $-\frac{1}{2} + y, 1 - x, 1 - z$
V $-\frac{1}{2} + x, -\frac{1}{2} + y, \bar{z}$
VI $-\frac{1}{2} + x, -\frac{1}{2} + y, 1 - z$
VII $\frac{1}{2} - x, \frac{1}{2} - y, z$
VIII $x, y, 1 + z$
IX $x, y, 1 - z$

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

[8] D. T. Cromer and J. B. Mann, *Acta Cryst.*, **A24**, 321.

[9] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[10] G. M. Sheldrick, University Chemical Laboratory, Cambridge.

[11] J. F. de Wet, unpublished work.

ca. 4.55 Å are maintained between the phenyl rings. The repulsion at these intercationic distances is evidently also low, particularly since the positive charge is likely to be localised largely at the 20 peripheral H atoms. It is noteworthy that, for its stability in the solid state, the $[UOCl_5]^-$ anion is apparently strongly dependent on the size as well as the $\bar{4}$ symmetry of the $[PPh_4]^+$ cation; attempts to induce crystallisation with other cations have not been successful.[1] In contrast, other large similar anions are not so selective: $[PaOCl_5]^{2-}$ forms a salt with $[NEt_4]^+$; $[WOCl_5]^-$ with both $[PPh_4]^+$ and $[PPh_3(CH_2Ph)]^+$; $[UCl_6]^-$ with the latter cation; and $[UCl_6]^{2-}$ with $[PEtPh_3]^+$.*

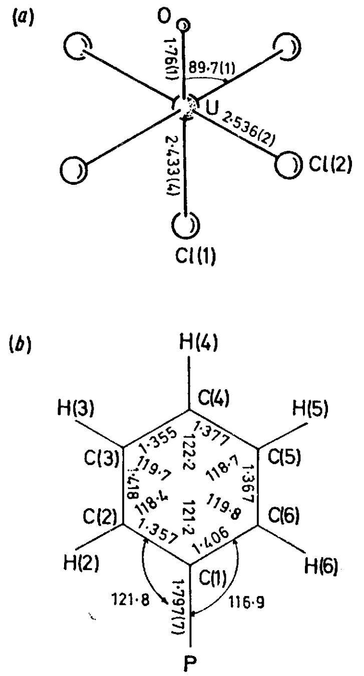

FIGURE 2 Schematic representations of (*a*) the $[UOCl_5]^-$ anion and (*b*) the $[PPh_4]^+$ cation, with bond lengths and angles (estimated standard deviations in parentheses). C–H bond lengths were artificially fixed at 1.08 Å

Bond lengths and angles are given in Figure 2; in addition, the C(1)–P–C′(1) angle [C′(1) being a symmetry-related atom attached to the same P atom] is 107°. In the cation the phenyl C atoms are coplanar to within 0.003 Å (Table 4). The P atom is nearly in the same plane as these atoms, so that the inequality in the C–C–P bond angles (Figure 2) represents an in-plane distortion about C(1). This results in a shift of H(4) by 0.2Å from its symmetrical position, probably in order to achieve closer equality in the approach distances of Cl(2) to the $H(4^{IV})$ and $H(4^{VI})$ atoms (Table 3).

Nature of the Bonding.—The structural information on certain classes of actinoid halogeno-oxo-complexes which has recently become available reveals a number of significant features which, in our opinion, provide evidence that the bonding around the actinoid atom is highly ionic in character and strongly influenced by ligand–ligand repulsion. We refer to complexes with metal oxidation states IV—VI, oxygen-donor ligand complexes of U^{IV} of the type $UX_4{\cdot}2L$ (X = Cl or Br), and particularly to those containing the $UOXCl_4$ (X = O or Cl) chromophore.

TABLE 4

Equation[a] of the best mean plane through the phenyl group and deviations (Å) from the plane (in square brackets)

$$0.574\,1X + 0.560\,6Y - 0.596\,8Z = 7.6938$$

[P[b] −0.1100, C(1) 0.0003, C(2) −0.0011, C(3) 0.0024, C(4) −0.0028, C(5) 0.0019, C(6) −0.0007]

[a] Referred to a right-handed orthogonal system (in Å) with *Z* parallel to *c* and *Y* parallel to *a**. [b] Not included in the least-squares calculation.

First, whereas the U=O bond lengths † are equal in the $[UOCl_5]^-$ and $[UO_2Cl_4]^{2-}$ ions (1.76 Å), the U–Cl bond lengths in the latter (2.67 Å) are longer than those in $[UOCl_5]^-$ (axial 2.43 and equatorial 2.54 Å). Secondly, the data on uranium(IV) complexes with the UO_2Cl_4 chromophore point to an inverse relation between the U–O and U–Cl bond lengths, which respectively decrease and increase (Table 5) with increasing donor strength [12] of the neutral ligand, *i.e.* in the sequence PPh_3O, $PPh(NMe_2)_2O$, $P(NMe_2)_3O$, and $AsEt_3O$. [Although the trend is perhaps not apparent between adjacent members in the series, it is quite obvious between the end members (L = $AsEt_3O$ and PPh_3O or $P(NMe_2)_3O$.] Also, for complexes with a common ligand [*e.g.* $P(NMe_2)_3O$] replacement of chloride by the weaker donor bromide results in significant shortening of the U–O bond (2.23 to 2.19 Å). We note that in all these complexes, with the exception of that with the weakest ligand (PPh_3O), the oxygen atoms are situated *trans* to each other. Thirdly, comparison of the bond lengths in $[UOCl_5]^-$ with those in $[PaOCl_5]^{2-}$ is of particular significance. The axial bond lengths are very similar (M=O 1.76 and 1.74, and M–Cl 2.43 and 2.42 Å, respectively), but the equatorial M–Cl bond length is appreciably shorter in $[UOCl_5]^-$ (2.54 as against 2.64 Å for $[PaOCl_5]^{2-}$). If one assumes that the same comparison is valid for $[UOCl_5]^{2-}$, reasonable since its M–O and M–Cl stretching frequencies are very similar [1] to those of $[PaOCl_5]^{2-}$, then the change in oxidation state from U^V to U^{VI} appears to result in a significant contraction of the equatorial U–Cl bond. Furthermore, the values of the bond lengths illuminate the extent of the interactions in these two complexes. Thus, in both complexes the axial bonds have lengths which are characteristic of U^{VI}: that of M=O corresponds to the average value for many uranyl complexes, and specifically for the $[UO_2Cl_4]^{2-}$ ion, and that of M–Cl to the value in UCl_6 (2.47 Å). But whereas the equatorial U–Cl bond length in $[UOCl_5]^-$ is comparable to

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* All the complexes of W and U were prepared in this laboratory by Dr. B. J. Gellatly (see also refs. and Table 5).

† All the bond lengths quoted in this section are summarised in Table 5 together with their standard deviations and literature references.

[12] J. G. H. du Preez, P. L. Gellatly, and H. E. Rohwer, *J. Inorg. Nuclear Chem.*, in the press.

that of U^{V}–Cl (2.49 Å) in $[PPh_3(CH_2Ph)][UCl_6]$, the corresponding bond length in the protactinium complex resembles that of U^{IV}–Cl (2.62 Å) in $[PEtPh_3]_2[UCl_6]$.

In the systems referred to above, the oxide has the highest charge density; a second negative ion would therefore be subjected to the least ligand–ligand repulsion when situated *trans* to it. This would account for the linear structure of the uranyl group, and, in derived linear systems such as those in $[UOCl_5]^-$, $[UOCl_5]^{2-}$, and $[PaOCl_5]^{2-}$, would permit a chloride ion replacing one of the oxide ions to approach the $M^{6(5)+}$ ion more closely than the equatorial Cl^- ions. Now, if the axial M–Cl (M = U or Pa) were predominantly covalent in nature, one might have expected an *increase* in bond length relative to the equatorial M–Cl bonds through the '*trans* effect', which is associated with the weakening of a bond *trans* to oxygen or fluorine.[5] These structural features (MO_2 linearity, contraction of axial M–Cl bonds) are not paralleled in comparable *d* transition-metal complexes, which display more pronounced covalent bonding. For example, in $[WO_2Cl_2(PPh_3O)_2]$ [13] and in the dichlorodioxo(pentane-2,4-dionato)tungstate(VI) anion,[14] and apparently in $Cs_2[WO_2Cl_4]$,[15] the oxygen atoms are *cis*. Furthermore, preliminary results [11] on $[PPh_4][WOCl_5]$ show that the axial and equatorial W–Cl bond lengths are very similar.

In addition to the above axial effect, ligand–ligand repulsion should also influence bonding distances in the planar equatorial system, acting in a way which involves the mutual interactions between axial and equatorial ligands. Thus, the stronger the metal–ligand interactions in the axial direction (which increase with greater charge density on these ligands) the greater will be the repulsion between axial and equatorial ligands. These effects should result in adjustments of the bonding distances which are complementary in an axial *versus* equatorial sense: a decrease in axial bond length(s) would be accompanied by an increase in equatorial bond lengths, and *vice versa*. Hence the increase in the equatorial U–Cl bond length in going from $[UOCl_5]^-$ to $[UO_2Cl_4]^{2-}$ and from $[UCl_4\{P(NMe_2)_3O\}_2]$ to $[UCl_4(AsEt_3O)_2]$. The effect is thus apparently operative even in the case of neutral oxygen-donor ligands which only possess a fractional negative charge on the oxygen atom. Furthermore, the similarity in the axial bond lengths of $[UOCl_5]^-$ and $[PaOCl_5]^{2-}$ (and, presumably, also of $[UOCl_5]^{2-}$), in spite of differences in metal oxidation state, can also be accounted for in terms of this model. In $[UOCl_5]^-$ the stronger interactions between the equatorial chloride ions and the more highly charged linear $[O=U-Cl]^{3+}$ system result, through ligand–ligand repulsion, in axial bond lengths which are relatively

TABLE 5

Summary of bond lengths (Å) quoted in text, with estimated standard deviations in parentheses. Where quoted in the form $L \pm d(s)$, L is the mean length of chemically equivalent, but crystallographically distinct, bonds, d is the mean deviation, and s is the mean estimated standard deviation

		Complex	M = U or Pa		Ref.
			M–O	M–Cl	
(*a*) UO_2Cl_4 Chromophores					
(*i*)	U^{IV}	$[UCl_4(PPh_3O)_2]$	2.242(7) [a]	2.618 ± 0.009(4)	*b*
		$[UCl_4\{PPh(NMe_2)_2O\}_2]$	2.226(6) [c]	2.621 ± 0.008(4)	*d*
		$[UCl_4\{P(NMe_2)_3O\}_2]$	2.23(1) [c]	2.615 ± 0.001(5)	*e*
		$[UBr_4\{P(NMe_2)_3O\}_2]$	2.19(1) [c]		*f*
		$[UCl_4(AsEt_3O)_2]$	2.16(1) [c]	2.665 ± 0.005(10)	*g*
(*ii*)	U^{VI}	$[NEt_4]_2[UO_2Cl_4]$	1.76(2) [h]	2.668 ± 0.004(10)	*i*
		$[NEt_3H]_2[UO_2Cl_4]$	1.75(1) [h]	2.668 ± 0.005(5)	17
(*b*) $MOCl_5$ Chromophores (M = U or Pa)					
(*i*)	U^{V}	$[UCl_5(PPh_3O)]$	2.11(2)	2.47(1) [j] 2.488 ± 0.009(10) [k]	*l*
(*ii*)	Pa^{V}	$[NEt_4]_2[PaOCl_5]$	1.74(9) [h]	2.42(3) [j] 2.64 ± 0.05(5) [k]	2
(*iii*)	U^{VI}	$[PPh_4][UOCl_5]$	1.76(1) [h]	2.433(4) [j] 2.536(2) [k]	This work
(*c*) UCl_6 Chromophores					
(*i*)	U^{IV}	$[PEtPh_3]_2[UCl_6]$		2.624 ± 0.002(1) [m]	13
(*ii*)	U^{V}	$[PPh_3(CH_2Ph)][UCl_6]$		2.491 ± 0.011(7) [m]	13
(*iii*)	U^{VI}	UCl_6		2.51(4) [n] 2.41(4) [n] 2.47(4) [p]	*o*

[a] *cis* O atoms. [b] G. Bombieri, D. Brown, and R. Graziani, *J.C.S. Dalton*, 1975, 1873. [c] *trans* O atoms. [d] M. R. Caira and L. R. Nassimbeni, *J. Inorg. Nuclear Chem.*, 1977, **39**, 455. [e] J. F. de Wet and S. F. Darlow, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 1041; redetermined with improved precision by J. G. H. du Preez, B. J. Gellatly, G. Jackson, L. R. Nassimbeni, and A. L. Rodgers, *Inorg. Chim. Acta*, 1978, in the press. [f] Second ref. in footnote *e*. [g] P. Sommerville and M. Laing, *Acta Cryst.*, 1976, **B32**, 1541. [h] Uranyl-type oxygen. [i] C. Bois, Nguyen-quy Dao, and N. Rodier, *Acta Cryst.*, 1976, **B32**, 1541. [j] Axial bond. [k] Equatorial bond. [l] G. Bombieri, D. Brown, and C. Mealli, *J.C.S. Dalton*, 1976, 2025. [m] Equivalent bonds. [n] Three crystallographically equivalent bonds. [o] J. C. Taylor and P. W. Wilson, *Acta Cryst.*, 1974, **B30**, 1481. [p] Six crystallographically equivalent bonds.

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[13] J. F. de Wet, M. R. Caira, and B. J. Gellatly, *Acta Cryst.*, 1978, in the press.

[14] M. G. B. Drew, G. W. A. Fowles, D. A. Rice, and K. J. Shanton, *J.C.S. Chem. Comm.*, 1974, 614.

[15] K. W. Bagnall, J. G. H. du Preez, B. J. Gellatly, and J. H. Holloway, *J.C.S. Dalton*, 1975, 1963.

increased to values which are characteristic of the lower oxidation state in $[PaOCl_5]^{2-}$ (or $[UOCl_5]^{2-}$).

Now that the available structural data have been shown to provide an acceptable basis for regarding the bonding in complexes of the actinoids with oxygen and chlorine to be predominantly ionic in character, it is still necessary to examine previous arguments against such bonding, particularly for the $[UO_2]^{2+}$ species. For example, in a recent study of the uranium oxalates Alcock[3] admitted that for uranyl complexes ' the view . . . that these structures are the result of essentially electrostatic packing around linear $[UO_2]^{2+}$ groups ' should be seriously considered; yet he regarded the variability in the U–O bond length and its inverse correlation with the ligand U–O bond lengths to be the strongest argument against an electrostatic model of this nature. However, the correlation referred to can, as we have shown above, be explained equally satisfactorily in terms of an essentially ionic model. Furthermore, it should be borne in mind, when comparing U–O bond lengths, that the extent of interaction between the uranium(VI) ion and the equatorial ligands will not only be a function of the charge density and electronegativity of these ligands but of the co-ordination number as well. Thus an increase in co-ordination number would result in a lengthening of the equatorial bond distances due to the relative increase in in-plane ligand repulsion. The accompanying decrease in axial bond lengths[3] can, in fact, be explained in electrostatic terms, namely in that the axial oxide ions now experience less repulsion from the equatorial ligands.

A further significant observation is that the uranyl U–O bond length can be influenced by the vicinity of other ions in the lattice, even if they are located too far away for significant covalent interaction with the uranyl oxygen atom.[16] For example, in the complex $[Cu(OH_2)_4][UO_2(HGeO_4)]_2$, one half of the uranyl oxygen atoms are approached by copper ions to a distance of 2.41 Å, resulting in a uranyl bond of 1.78 Å, whereas a bond length of 1.73 Å is observed for the bonds with the much more distant copper neighbours. Several further examples of this effect are quoted by these workers. Evidence for high ionicity in the U–Cl bond in $[UO_2Cl_4]^{2-}$ is also provided by the fact that an electrostatic effect such as hydrogen bonding (for example, by the $[NEt_3H]^+$ salt) is able to influence the Cl–U–Cl bond angles.[17] Besides electrostatic influences such as these, other factors may well have to be taken into account when comparing uranyl bond lengths: for example, the structure and stereochemistry of the ligands, and the nature, charge, and charge density of the donor atoms, *etc.*

In conclusion we note that evidence for highly ionic bonding character is to be found not only in complexes such as those discussed here but also in the general chemical behaviour of uranium. Three examples may be quoted. The absence of those organometallic compounds for which highly covalent bonding character is a requisite, such as carbonyl and arene complexes, whereas those which can be stabilised by ionic bonding (cyclopentadienide and cyclo-octatetraene complexes) are common. Also, uranium displays only a very weak tendency to form cyano-complexes.[18] And finally, the surprising thermal stability of uranyl carbonate, which decomposes at 500—600 °C.

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