Crystal and Molecular Structure of Tetraphenylarsonium Aquotetrachlorohydroxotellurate(IV)

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The structure of the title compound has been determined by single-crystal *X*-ray diffraction using diffractometer data and refined to a final *R* of 5·1%. Crystals are monoclinic, $a = 18{\cdot}71 \pm 0{\cdot}03$, $b = 7{\cdot}31 \pm 0{\cdot}02$, $c = 19{\cdot}29 \pm 0{\cdot}03$ Å, $\beta = 92{\cdot}03 \pm 0{\cdot}05°$, with $Z = 4$, space group either $C2/c$ or Cc. The structure has been refined in both space groups and a chemically similar structure obtained although the evidence favours a disordered model in the centrosymmetric space group $C2/c$. Tetraphenylarsonium ions, whose bond lengths and angles agree well with earlier studies, are present. The anion consists of a square pyramidal $[TeCl_4O]$ group with an apical oxygen atom but it is not possible to distinguish between the $[TeCl_4(OH)]^-$ and $[TeCl_4O]^{2-}$ formulations [Te–Cl 2·484(2), Te–O 1·74(1) Å]. Adjacent anions are weakly linked through water molecules interacting with the Te and O (or OH) groups to form an infinite chain structure.

THERE is considerable interest in the stereochemistry of compounds of the main-group elements with a formal lone-pair of electrons, which may be stereochemically active or inactive. Whereas the $[TeF_5]^-$ ion is a discrete square pyramid in $KTeF_5$,[1] the $[TeCl_5]^-$ ion in the compound $[PCl_4][TeCl_5]$ has been shown by two independent *X*-ray studies [2,3] to contain a polymeric anion with each tellurium atom being approximately octahedrally co-ordinated. The factors which promote this polymerisation are at present not clear and we thought it important to know whether changing the $[PCl_4]^+$ for a larger cation would radically alter the anion structure. A recent n.q.r. study on the hexachlorotellurate(IV) ion indicated that changes in the cation had little effect on its structure.[4] Inspection of the literature showed few, if any, compounds apparently containing the $[TeCl_5]^-$ ion and we examined the system $Ph_4AsCl/TeCl_4$ in an attempted synthesis of $[TeCl_5]^-$.

On carefully concentrating an equimolar mixture of tetraphenylarsonium chloride and tellurium tetrachloride in methylene dichloride, colourless crystals were isolated in low yield. The composition was eventually established as $[Ph_4As]TeCl_4(OH)(H_2O)$ by a combination of elemental analysis and the *X*-ray structure determination where the oxygen atoms presumably arise from either the reagents and/or the solvent. Further concentration of the solution gave a precipitate of the known yellow $[Ph_4As]_2TeCl_6$.[5,6] No other tellurium-containing species were isolated from the reaction mixture. Very recently the $[Te_3Cl_{13}]^-$ ion has been established from the reaction between triphenylmethyl chloride and tellurium tetrachloride.[7]

No other compounds of the type $[Ph_4As]TeCl_4(OH)(H_2O)$ have been established previously and we report now our *X*-ray results on this unusual structure.

EXPERIMENTAL

Synthesis of Compound and Analysis.—Tellurium tetrachloride was prepared from tellurium and chlorine.[8] Tetraphenylarsonium chloride (Schuchardt) and methylene dichloride were reagent grade. To a boiling solution of $TeCl_4$ in methylene dichloride was added an equimolar quantity of Ph_4AsCl dissolved in a small volume of the same solvent. A clear yellow solution formed immediately and on slow cooling in a stoppered vessel deposited, in small yield, colourless needle crystals (*A*) (m.p. 211—213 °C). On some occasions no crystals formed, and solvent was then distilled off before cooling, but if too much were removed yellow crystals of $[Ph_4As]_2TeCl_6$ were deposited (m.p. *ca.* 285 °C).

$[Ph_4As]_2TeCl_6$ [5,6] was prepared by mixing Ph_4AsCl and $TeCl_4$ (2 : 1 mole ratio) in hot methylene dichloride, when the yellow crystalline compound was precipitated [Found: Cl, 19·4 (mean). Calc. for $[Ph_4As]_2[TeCl_6]$: Cl, 19·22%, m.p. 281—286 °C). By use of dry-box procedures the colourless crystals (*A*) were separated from the mother liquor, pumped *in vacuo*, and subsequently analysed for Cl, Te, and the Ph_4As^+ ion by techniques described later. The results obtained on two separate preparations are shown in Table 1. The atomic ratios of Ph_4As : Te : Cl is 1 : 1 : 4. The unaccounted for elements must carry a single negative charge and the analytical evidence favours a compound containing both OH^- and H_2O, rather than only the hydroxo-ion.

TABLE 1

Analyses (%)

	Cl	Te	Ph_4As	Remainder
Found [prep. (1)]	20·8	18·65	55·85	4·7
Found [prep. (2)]	20·45	18·3	54·8	6·40
Calc. for $[Ph_4As][TeCl_5]$	25·76	18·54	55·70	0·00
Calc. for $[Ph_4As]TeCl_4(OH)(H_2O)$	20·62	18·56	55·74	5·08
Calc. for $[Ph_4As]TeCl_4(OH)$	21·18	19·05	57·23	2·54

Subsequent experiments on the reagent Ph_4AsCl established unambiguously that it is approximately the monohydrate (Found: Cl, 8·15. Calc. for Ph_4AsCl: Cl, 8·46. Calc. for Ph_4AsCl,H_2O: Cl, 8·12%); the i.r. spectrum (Nujol and hexachlorobutadiene mull) showed an intense band at *ca.* 3500 cm^{-1}. This no doubt is the origin, at least in part, of the oxygen content of compound (*A*).

The analyses for the three components were performed on the same weighed sample (*ca.* 0·05 g). After hydrolysis with NaOH solution (10 ml, 2M), the solution was made up to 100 ml (1M in NaOH). Aliquot portions (10 ml) of this

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[1] A. J. Edwards and M. A. Mouty, *J. Chem. Soc.* (*A*), 1969, 703; S. H. Mastin, R. R. Ryan, and L. B. Asprey, *Inorg. Chem.*, 1970, **9**, 2100.

[2] P. H. Collins and M. Webster, *Acta Cryst.*, 1972, **B28**, 1260.

[3] B. Krebs, B. Buss, and W. Berger, *Z. anorg. Chem.*, 1973, **397**, 1.

[4] T. B. Brill and W. A. Welsh, *J.C.S. Dalton*, 1973, 357.

[5] D. M. Adams and D. M. Morris, *J. Chem. Soc.* (*A*), 1967, 2067.

[6] M. L. Unland, *J. Chem. Phys.*, 1968, **49**, 4514.

[7] B. Krebs and V. Paulat, *Angew Chem. Internat. Edn.*, 1973, **12**, 666.

[8] J. F. Suttle and C. R. F. Smith, *Inorg. Synth.*, 1950, **3**, 140.

solution were used for the subsequent determinations. Chlorine was estimated by potentiometric titration against standard silver nitrate after acidification with nitric acid. Tellurium(IV) was estimated spectrophotometrically as the $[TeCl_6]^{2-}$ ion at 295 nm in *ca.* 5M-hydrochloric acid. Tellurium dioxide was used to set up the calibration graph and to verify Beer's Law for the system, and a tellurium analysis for $TeCl_4$ gave good agreement with the theoretical value. The tetraphenylarsonium ion was estimated spectrophotometrically using the bands at 263 and 270 nm, and a calibration graph constructed by use of tetraphenylarsonium chloride. Experimental conditions were carefully standardised during the analyses and qualitative and quantitative spectra recorded on Unicam SP 800 and SP 500 spectrometers. Attempts to estimate tellurium(IV) colorimetrically using ammonium pyrrolidine dithiocarbamate [9] were unsatisfactory.

Crystals for *X*-ray examination were grown from methylene dichloride and mounted in capillaries under glove-box conditions.

Crystal Data.—$C_{24}H_{23}AsCl_4O_2Te$, $M = 687{\cdot}8$, Monoclinic, $a = 18{\cdot}71 \pm 0{\cdot}03$, $b = 7{\cdot}31 \pm 0{\cdot}02$, $c = 19{\cdot}29 \pm 0{\cdot}03$ Å, $\beta = 92{\cdot}03 \pm 0{\cdot}05°$, $U = 2636{\cdot}6$ Å^3, $D_m = 1{\cdot}73 \pm 0{\cdot}02$ (by flotation), $Z = 4$, $D_c = 1{\cdot}732$ g cm^{-3}. Systematic absences: $h + k = 2n + 1$ for hkl, and $l = 2n + 1$ for $h0l$, consistent with space groups *Cc* (No. 9) or *C2/c* (No. 15). $\mu(\text{Cu-}K_\alpha) = 148{\cdot}3$ and $\mu(\text{Mo-}K_\alpha) = 29{\cdot}0$ cm^{-1}.

Preliminary cell dimensions, diffraction symmetry, and systematic absences were obtained from Weissenberg and precession photographs. For data collection, a crystal (max.) 0·5 × (min.) 0·1 mm was mounted about the *b* axis in a Lindemann glass capillary (0·3 mm diam.). Data were collected by use of a General Electric XRD 6 manual diffractometer in the stationary-crystal–stationary-counter mode with zirconium-filtered Mo-radiation, take-off angle 3°). Counting for 10 s, 2324 independent reflections were recorded up to 2θ (max.) 50°. A general background was measured as a function of 2θ by offsetting ω by $\pm 1°$ from a number of observed reflections, and was subtracted from the measured peak intensity to give the corrected intensity, $I_{\text{corr.}}$. 457 Reflections having $I_{\text{corr.}} < 1{\cdot}2 \times$ background were considered unobserved.[10] Three medium-intensity reflections were monitored and used as standards to correct for the observed deterioration (*ca.* 7%) in the diffracted intensities. Lorentz and polarisation factors were applied together with an absorption correction by the method of de Meulenaer and Tompa.* Scattering factors for neutral atoms were taken from ref. 11 and a dispersion correction [11] for tellurium, arsenic, and chlorine was applied in the structure-factor calculations.

Structure Determination.—Examination of the three-dimensional Patterson function gave plausible positions for the tellurium and arsenic atoms. In space group *Cc*, two general positions were occupied, while in space group *C2/c* the tellurium was in position 4(*c*) and the arsenic in 4(*e*). Apart from the different choice of origin, these two solutions were the same and the structure solution was investigated in both space groups.

(*a*) *Space group Cc.* A structure-factor calculation based on the Te and As positions, followed by an electron-density synthesis, revealed four chlorine atoms. On adding these into the model, repetition of this procedure gave the position of 24 carbon atoms associated with the tetraphenylarsonium group. Because of the insensitivity of the chemical analysis to the oxygen content of the molecule it was not clear at this stage whether we were looking for one or two oxygen atoms per molecule, although the chemical analysis and density measurements favoured two oxygen atoms.

One cycle of least-squares refinement [unit weights, fixed carbon atoms, refinement of scale factors and heavy atom (Te, As, Cl) positional and isotropic thermal parameters] reduced *R* to 16·8% and further refinement to include the carbon atoms (positional and isotropic thermal parameters) reduced *R* to 12·8% with reasonable temperature factors. An electron-density map calculated from this model showed only four small unaccounted peaks. The absorption correction was applied at this stage.

A number of calculations were undertaken to establish which, if any, of the unassigned Fourier peaks should be regarded as genuine oxygen atoms. One peak [O(1)] at *ca.* 1·96 Å from the tellurium atom was considered to be an oxygen atom on the basis of its position, peak-height, and behaviour on least-squares refinement. Inclusion of this atom in the refinement reduced *R* to 9·2% and a subsequent electron-density synthesis showed only one unaccounted peak which was taken as the second oxygen atom [O(2)]. In space group *C2/c* the tellurium atoms would occupy sites of $\bar{1}$ symmetry but there was no evidence for a second oxygen atom centrosymmetrically related to O(1). An empirical weighting scheme was derived from a plot of $\overline{|\Delta F|}$ *vs.* $\bar{F}_o$ for various ranges of F_o [$w(\text{obs.}) = 1/(A + BF_o^2 - CF_o)$; $A = 4{\cdot}75$, $B = 4{\cdot}0 \times 10^{-5}$, $C = 7{\cdot}0 \times 10^{-4}$; $w(\text{unobs.}) = 0{\cdot}81 \times w(\text{obs.})$]. Further refinement [179 parameters; calc. weights, scale factors, positional parameters for all atoms (fixing only the *x* and *z* co-ordinate for Te), isotropic carbon and oxygen atoms, anisotropic thermal parameters for chlorine, arsenic and tellurium atoms] reduced *R* to a final value of 5·1%. No hydrogen atoms were included in the structure-factor calculations. Inspection of the correlation matrix derived from the least-squares routines showed, as might be expected, large correlation coefficients (0·8—0·9) between the corresponding parameters of the pseudo-centrosymmetrically related chlorine atoms. Similarly the carbon atoms related by the approximate two-fold axis passing through the arsenic atom and parallel to *b* show large (*ca.* 0·75) correlation coefficients. The origin of this effect is clearly the space-group ambiguity since the correlated atoms are just those which would be symmetry related in the higher symmetry group *C2/c*. We experienced no difficulty with the least-squares refinement program (CRYLSQ) except that the isotropic temperature factor for two pseudo-symmetry-related carbon atoms showed marked oscillations from cycle to cycle although the other refined parameters showed low shift-to-error values indicating satisfactory convergence. A number of authors have experienced similar problems with pseudo-symmetry and space-group ambiguities.[12,13] The bulk of the scattering material in the

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* Using the program ABSCOR in ref. 10(*b*).

[9] C. A. Watson, Monograph, No. 74, Hopkin and Williams, 1971.

[10] (*a*) G. J. Palenik, *Acta Cryst.*, 1972, **B28**, 1633; (*b*) '*X*-Ray '63' system of programs,

[11] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[12] J. D. Lee and M. W. R. Bryant, *Acta Cryst.*, 1969, **B25**, 2497; B. Van Dijk and G. J. Visser, *ibid.*, 1971, **B27**, 846; H. Einspahr and J. Donohue, *ibid.*, p. 846; J. D. Lee, *ibid.*, p. 847.

[13] L. K. Templeton and D. H. Templeton, *Acta Cryst.*, 1971, **B27**, 1678.

cell is approximately centrosymmetric and therefore choosing the enantiomorph may present difficulties. The least-squares calculation was repeated for the enantiomorphic structure and gave a small decrease in the unweighted and weighted R factors (see Table 2).

TABLE 2

Comparisons of selected bond lengths (Å) and angles (°) in space groups *Cc* and *C*2/*c*

(*a*) Distances	*Cc* (1st enantiomorph)	*Cc* (2nd enantiomorph)	*C*2/*c*
Te–Cl(1)	2·466(10)	2·457(10)	2·484(2)
Te–Cl(2)	2·490(10)	2·476(10)	2·483(2)
Te–Cl(3)	2·472(10)	2·487(10)	*
Te–Cl(4)	2·505(10)	2·514(09)	*
Te–O(1)	1·740(12)	1·736(12)	1·741(11)
Te–O(2)	2·912(23)	2·914(25)	2·886(15)
O(1)–O(2)^{II}) †	3·020(26)	3·015(27)	3·042(19)
(*b*) Angles			
O(1)–Te–Cl(1)	89·1(5)	89·4(5)	89·9(4)
O(1)–Te–Cl(2)	90·2(5)	91·3(4)	90·6(4)
O(1)–Te–Cl(3)	90·3(5)	89·2(5)	89·4(4) *
O(1)–Te–Cl(4)	90·9(5)	90·3(4)	90·2(4) *
R (observed only)	5·09$_6$	5·04	5·12%
R'	5·30	5·26	5·43%
No. of refined parameters	179	179	108

* Cl(1) and Cl(4) are related by the centre of symmetry in space group *C*2/*c* and similarly for atoms Cl(2) and Cl(3). † See footnote to Table 5.

(*b*) *Space group C*2/*c*. A similar analysis in space group *C*2/*c* was undertaken. Tellurium is on a centre of symmetry $(\frac{1}{4},\frac{1}{4},0)$ and arsenic on a two-fold axis $(0,y,\frac{1}{4})$. The chlorine and carbon atoms were readily located and least-squares refinement [100 variables, calculated weights, atom positional parameters, atom isotropic (C) and anisotropic (Cl, As, Te) thermal parameters] reduced R to 7·9%. The same weighting scheme was used and an examination of ΔF as a function of sin θ and F_0 showed no gross abnormalities. An electron-density synthesis showed two additional peaks ascribed to oxygen atoms. Various models with ordered and disordered oxygen atoms were explored and the model in which both oxygen atoms were present with population parameters of 0·5 was found to give the markedly lowest R factor of 5·1% on refinement. Low shift-to-error values in the full-matrix least-squares analysis indicated satisfactory convergence and an electron-density synthesis on the final parameters gave peak electron densities of 4·5—6·5 eÅ^{-3} for carbon and 2·7 and 2·5 eÅ^{-3} for oxygen atoms O(1) and O(2). A final difference electron-density synthesis showed no prominent features on the map, particularly where atoms are located, and in addition showed a number of small peaks (0·3—0·6 eÅ^{-3}). The position of ten of these was found to be in the correct position for hydrogen atoms bonded to the carbon atoms of the phenyl rings and their peak heights were consistent with this interpretation.[14] A few other small peaks were observed close to the oxygen atoms but these did not allow a clear decision on the hydrogen positions. No hydrogen atoms were included in the structure-factor calculation.

(*c*) *Comparison of structure solutions*.—In gross chemical terms the structural solutions found for the two space

TABLE 3

Final positional (×10^4) and isotropic thermal (×10^3) parameters with standard deviations in parentheses (space group *C*2/*c*)

	x/a	y/b	z/c	U/Å^2
Te	2500	2500	0	
Cl(1)	1427(1)	3617(4)	0593(1)	
Cl(2)	3002(1)	1347(4)	1126(1)	
O(1) *	2912(6)	4608(16)	0142(6)	59(3)
O(2) *	2581(7)	6443(21)	0011(7)	113(4)
As	0	4961(1)	2500	
C(11) †	0281(4)	6505(10)	1761(4)	45(2)
C(12)	0819(5)	7794(12)	1913(4)	58(2)
C(13)	1034(5)	8957(14)	1383(5)	70(3)
C(14)	0712(5)	8804(14)	0718(5)	68(3)
C(15)	0180(5)	7536(13)	0578(5)	63(2)
C(16)	−0044(4)	6348(12)	1103(4)	54(2)
C(21)	4236(4)	8400(10)	2197(4)	41(2)
C(22)	3575(4)	8520(11)	2505(4)	50(2)
C(23)	3028(5)	7330(13)	2269(4)	60(2)
C(24)	3155(5)	6023(13)	1770(5)	65(2)
C(25)	3833(5)	5910(13)	1474(5)	65(2)
C(26)	4371(5)	7102(12)	1692(4)	60(2)

* Population parameter of 0·5. † Carbon atoms are numbered C(ij); i = 1,2 and refers to the ith phenyl ring, j = 1—6 and refers to the carbon atoms of the ith ring numbered cyclically.

TABLE 4

Heavy-atom anisotropic temperature factors * (×10^4), with standard deviations in parentheses (space group *C*2/*c*)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Te	705(5)	557(5)	496(19)	137(4)	131(4)	75(4)
Cl(1)	692(14)	824(17)	687(23)	117(13)	165(11)	−33(13)
Cl(2)	779(15)	792(16)	555(22)	87(13)	−2(11)	106(12)
As	375(5)	462(6)	436(19)	0 †	5(4)	0 †

* In the form: $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^*\cos\gamma^* + 2U_{13}hla^*c^*\cos\beta^* + 2U_{23}klb^*c^*\cos\alpha^*)]$. † Constrained to be zero by the atom site symmetry (H. A. Levy, *Acta Cryst.*, 1956, **9**, 679).

TABLE 5

Pertinent bond lengths (Å) and angles (°), with standard deviations in parentheses (space group *C*2/*c*)

(*a*) Anion			
Te–Cl(1)	2·484(2)	Cl(1)–Te–Cl(2)	89·8(1)
Te–Cl(2)	2·483(2)	Cl(1)–Te–Cl(2^{I})	90·3(1)
Te–O(1)	1·74(1)	O(1)–Te–Cl(1)	89·9(4)
Te–O(2)	2·89(2)	O(1)–Te–Cl(2)	90·6(4)
O(1)–O(2^{II})	3·04(2)	O(1)–Te–Cl(1^{I})	89·4(4)
		O(1)–Te–Cl(2^{I})	90·2(4)
(*b*) Cation			
As–C(11)	1·907(7)	C(11)–As–C(21)	110·4(3)
As–C(21)	1·905(7)	C(11)–As–C(11^{III})	107·4(3)
		C(21)–As–C(21^{III})	106·4(3)
		C(11^{III})–As–C(21)	111·1(3)
C(11)–C(12)	1·40(1)	C(21)–C(22)	1·39(1)
C(12)–C(13)	1·40(1)	C(22)–C(23)	1·41(1)
C(13)–C(14)	1·40(1)	C(23)–C(24)	1·38(1)
C(14)–C(15)	1·38(1)	C(24)–C(25)	1·41(1)
C(15)–C(16)	1·41(1)	C(25)–C(26)	1·39(1)
C(16)–C(11)	1·39(1)	C(26)–C(21)	1·39(1)

Atoms superscripted are related by a symmetry operation to those with no superscript. Atoms with superscripts I and II are related by a centre of symmetry (at $\frac{1}{4},\frac{1}{4},0$ and $\frac{1}{4},\frac{3}{4},0$ respectively), and those with III by the two-fold axes passing through the arsenic atom $(0,y,\frac{1}{4}$ and $\frac{1}{2},\frac{1}{2}+y,\frac{1}{4})$.

(*c*) Equations for the least-squares plane through the carbon atoms of the phenyl rings (where x, y, and z are the fractional coordinates in direct space)

Plane (*a*): C(11)—(16) $13·141x - 4·868y - 5·327z = -3·737$
Plane (*b*): C(21)—(26) $5·062x - 4·772y + 13·456z = 1·100$

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[14] G. H. Stout and L. H. Jensen, '*X*-Ray Structure Determination,' Macmillan, New York, 1968.

groups are very similar and Table 2 shows some pertinent bond lengths and angles for the two space groups. In such situations Hamilton[15] has suggested the use of statistical tests based on the *R* factor ratio for the two space groups. Comparing the second enantiomorph in *Cc* with *C*2/*c* using either the weighted or unweighted *R* factors indicates that at better than the 25% significance level the space group *C*2/*c* is preferred.

Final positional and thermal parameters for the analysis in *C*2/*c*, together with the standard deviations derived from the least-squares analysis, are shown in Tables 3 and 4. Table 5 lists chemically interesting bond lengths and angles. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21012 (3 pp.).*

All calculations except for the absorption correction were carried out on an ICL 1906A computer at Harwell, using the *X*-ray system of programs devised by J. M. Stewart.

DISCUSSION

Diagrams of the structure are presented in Figures 1 and 2. The arrangement of ligands around the tellurium atom shows four chlorine atoms lying in a square-planar arrangement with a tellurium oxygen bond (1·74 Å) perpendicular to the plane. This oxygen atom is disordered (in the space group *C*2/*c*) and the atoms thus form a disordered square-pyramidal group with an axial oxygen. As expected, for a disordered model, the bond angles involving the apical oxygen are close to 90° (see Table 5) and we are thus not able to comment on the value for any one $TeCl_4O$ group. The Te–Cl bond lengths can be compared with the mean of 2·44 for the terminal bonds in $PCl_5,TeCl_4$ [2] and 2·53 Å in octahedral *trans*-$TeCl_4$,2(tetramethylthiourea).[16] There are no directly comparable Te–O bond lengths in related molecules but the Te–O distances in a number of Te^{VI} oxides and hydroxides fall in the range 1·84—1·99 Å,[17-19] and in $[SeOCl_4]^{2-}$ (ref. 20) and $SeOCl_2$ the Se–O distance is 1·61 Å.

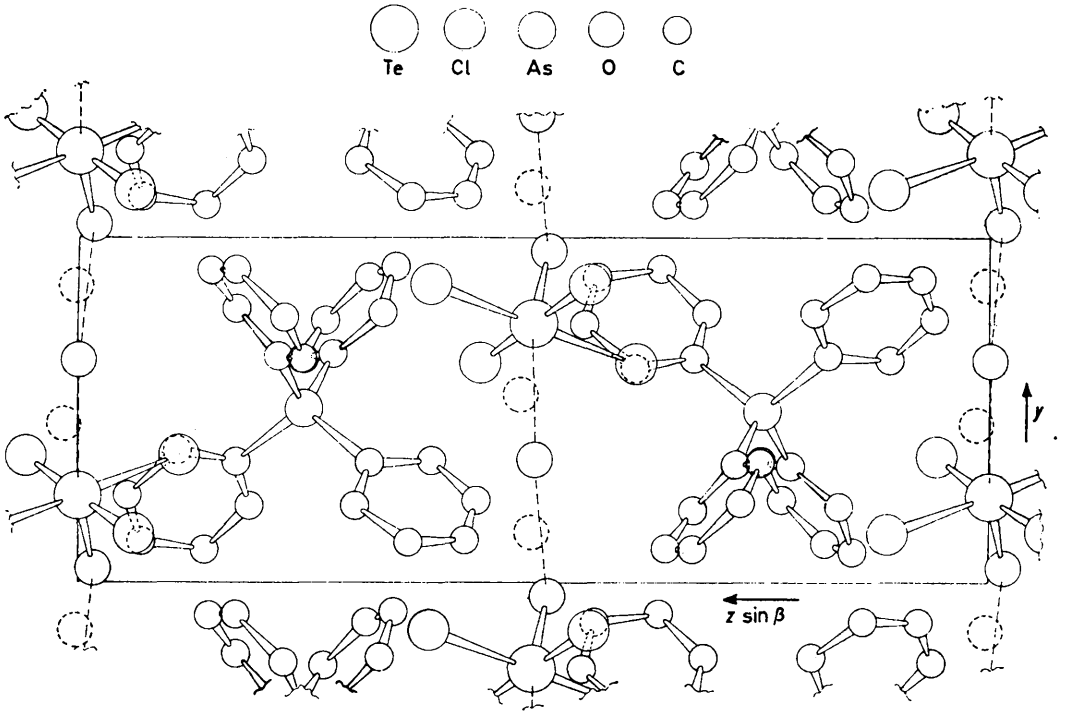

FIGURE 1 View of the unit cell looking in the −*x* direction (The ½,½,0 related positions have been omitted for clarity. Each disordered oxygen atom is shown as a full and dashed circle, the former making one and the latter the other chain. The long oxygen–oxygen and oxygen–tellurium distances are drawn with broken lines for the full-circle oxygen atoms only.)

The second (disordered) oxygen atom in the structure [O(2)] is 3·04 Å from the oxygen atom bound to the Te and 2·89 Å from an adjacent Te atom, the whole structure forming an infinite chain parallel to *b* (see Figure 2). The 3·04 Å O · · · O distance must be regarded as a rather long hydrogen bond[21,22] and the 2·89 Å distance may indicate a weak interaction between the oxygen and tellurium atoms.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full size copies).

[15] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.

[16] S. Husebye and J. W. George, *Inorg. Chem.*, 1969, **8**, 313.

[17] O. Lindqvist, *Acta Chem. Scand.*, 1970, **24**, 3178.

[18] O. Lindqvist, *Acta Chem. Scand.*, 1972, **26**, 4107.

[19] O. Lindqvist and M. S. Lehmann, *Acta Chem. Scand.*, 1973, **27**, 85.

[20] B. C. Wang and A. W. Cordes, *Inorg. Chem.*, 1970, **9**, 1643.

[21] G. C. Pimentel and A. L. McClellan, 'The Hydrogen Bond,' 1960, Freeman, San Francisco.

[22] W. C. Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids,' Benjamin, New York, 1968.

We cannot distinguish between the two formulations $[TeCl_4(OH)]^-(H_2O)$ and $[TeCl_4O]^{2-}H_3O^+$ and indeed because of (almost certain) hydrogen bonding between the oxygen atoms the distinction between these two may be somewhat artificial. The i.r. spectrum of the compound (4000—650 cm^{-1}) showed clear evidence for the presence of the tetraphenylarsonium group, but a clearly recognisable absorption in the OH stretching region was not apparent. It is known that the i.r. absorption spectra of hydrogen bonded systems are often broad and of low intensity.[23] In view of the large amount of scattering by heavy and not-so-heavy atoms, the hydrogen atoms observed in the difference electron-density synthesis were not considered adequate for the establishment of the appropriate formulation.

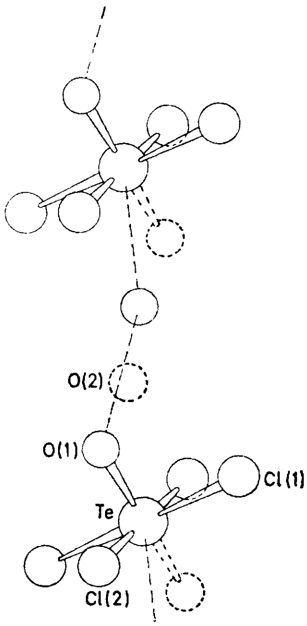

FIGURE 2 The anion and associated atoms (see caption to Figure 1)

The dimensions of the tetraphenylarsonium ion agree well with previous crystallographic studies on molecules containing this ion.[24-32] The mean C–C distances in the phenyl rings are 1·40 Å and the angles around the arsenic atom are close to the tetrahedral value. The ion is required to have two-fold symmetry, although it exhibits approximately S_4 point-group symmetry.

Tellurium(IV) in its compounds is capable of displaying or not displaying a stereochemically active lone-pair of electrons. Square-pyramidal arrangements have been found in $[TeF_5]^-$,[1] $[MeTeI_4]^-$,[33] and the polymeric chlorine-bridged $RTeCl_3$ ($R = CH_2{\cdot}CH_2Cl$)[34] whereas with six-co-ordinate species, *e.g.* $[TeCl_6]^{2-}$, octahedral symmetry is found in the solid state.[4,35] The trisoxalatoantimonate(III) ion[36] is one of the few well-defined six-co-ordinate species with a stereochemically active lone-pair and other less clear-cut examples in tellurium chemistry are known.[37] Indeed an alternative viewpoint of the present structure is to give the long Te–O interaction structural significance and regard the anion as involving six bonds to the central tellurium. A non-octahedral arrangement of these bonds arises on the Sidgwick–Powell model from the stereochemically active lone-pair of electrons on the central atom.

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