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Tetraphenylarsonium Trichloride

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Abstract

$[As(C_6H_5)_4]Cl_3$, prepared by slow diffusion of Cl_2 into aqueous $[As(C_6H_5)_4]Cl$, crystallizes in space group $I\bar{4}$, $a = b = 17{\cdot}410\,(4)$, $c = 14{\cdot}751\,(3)$ Å, $Z = 8$, $D_c = 1{\cdot}454$ Mg m^{-3}, $\mu(\mathrm{Cu}\ K\alpha) = 5{\cdot}497$ mm^{-1} at 294 K. The structure ($R = 0{\cdot}038$ for 1570 reflexions) approximates $I\bar{4}c2$ with a pseudo twofold rotation axis passing through the central atom of the essentially linear Cl_3^- ion. The pseudosymmetry is discussed in detail. Intraionic Cl···Cl distances are 2·305 (3) and 2·227 (4) Å, with the closest interionic Cl···Cl distance being 3·979 (4) Å.

Introduction

This structure is the first known X-ray determination of the Cl_3^- ion. The crystal structures of compounds involving trihalide ions are of interest in that whenever site symmetry allows an asymmetry of the trihalide ion, statistically meaningful asymmetry is observed (Runsink, Swen-Walstra & Migchelsen, 1972). For some compounds, *e.g.* $[As(C_6H_5)_4]Br_3$, different crystalline forms have either symmetric (Bogaard, Peterson & Rae, 1979) or asymmetric (Ollis, James, Ollis & Bogaard, 1976) trihalide ions. This is also found for $[N(C_2H_5)_4]I_3$ (Migchelsen & Vos, 1967). The symmetric form of $[As(C_6H_5)_4]Br_3$ has space group $P2/c$ and asymmetry of the tribromide ion would be possible in the space group Pc. A small deviation from symmetry would be very difficult to detect by X-ray diffraction (Rae, 1975), as neither any extra reflexions nor any change in Laue symmetry would be observed. This is also true for the isomorphous crystal structures $[As(C_6H_5)_4]I_3$ (Runsink, Swen-Walstra & Migchelsen, 1972), $[P(C_6H_5)_4]Br_2I$ (Müller, 1979) and $[P(C_6H_5)_4]Br_3$ (Bogaard & Rae, 1981). In contrast, the symmetric form of $[N(C_2H_5)_4]I_3$ has space group $Cmca$, and asymmetry of the I_3^- ion would cause the destruction of the symmetry element 2 parallel to **a**. Extra reflexions should then be observed, but can be missed experimentally. In both structures the loss of symmetry creates an imaginary component for the structure factors which will have little effect on the magnitude of all but the weakest data.

It is of great interest therefore that in $[As(C_6H_5)_4]Cl_3$ there is a distortion away from higher symmetry but one which is readily detectable and refinable as it changes the diffraction from $I4/mmm$ to $I4/m$ and only one quarter of the data has a contribution from the As atom.

Experimental

A crystal $0{\cdot}069 \times 0{\cdot}052 \times 0{\cdot}120$ mm between parallel faces (001), $(00\bar{1})$, (100), $(\bar{1}00)$, (010), $(0\bar{1}0)$ was grown by slow diffusion of Cl_2 into an aqueous solution of $[As(C_6H_5)_4]Cl$. The crystal was coated in methyl α-cyanoacrylate to minimize decomposition during data collection. Unit-cell dimensions and intensities for 2372 independent reflexions were obtained at 294 K on a computer-controlled Siemens AED diffractometer using Cu $K\alpha$ radiation. Data were corrected for absorption and decomposition effects. Decomposition was minimal.

Solution and refinement

Systematic absences and diffraction symmetry allowed space groups $I4$, $I\bar{4}$ and $I4/m$, while the diffraction symmetry approximated $I4/mmm$. A three-dimensional Patterson function gave four As atoms consistent with four different special positions of symmetry $\bar{4}$ in $I\bar{4}$: $0,0,0$; $\tfrac{1}{2},\tfrac{1}{2},0$; $0,\tfrac{1}{2},\tfrac{1}{4}$; $\tfrac{1}{2},0,\tfrac{1}{4}$. A Fourier function based on these atoms and using h odd, k odd, $l = 4n + 2$ and h even, k even, $l = 4n$ data only (all with phase $\alpha_{hkl} = 0$) gave a map of approximately $F4/mmm$ symmetry in the subcell $a,b,c/2$. This pseudosymmetry necessitated the selection of a linear trichloride ion among ghosted images of this ion. The choice of one of these ghosts in space group $I\bar{4}$ selected an origin and enantiomorph for the crystal. The choice of enantiomorph was shown to be wrong in the final refinement cycle; the parameters listed are for the correct choice. The C atoms were located from a further electron density map. Refinement was by least squares using weights determined by counting statistics. An isotropic extinction parameter $R^* = (e^2/mc^2V)\lambda^3r^*$ was refined in the final cycle where the modified $F_c^* = k|F_c|(1 +$

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Table 1. *Atomic parameters*

(*a*) Fractional atomic coordinates ($\times 10^4$) and $U_{\rm eq}$ [$=\frac{1}{3}(U_{11} + U_{22} + U_{33})$] with e.s.d.'s in parentheses

	x	y	z	$U_{\rm eq}$ (Å$^2 \times 10^3$)
Cl(1)	2455·4 (1·4)	3365·9 (1·6)	3775·6 (1·9)	84 (1)
Cl(2)	2056·4 (1·1)	2952·4 (1·1)	5184·2 (1·6)	65 (1)
Cl(3)	1651·9 (1·8)	2504·9 (1·7)	6515·2 (2·0)	100 (1)
As(1)	5000	5000	5000	39 (1)
As(2)	0	0	5000	45 (1)
As(3)	0	5000	2500	42 (1)
As(4)	5000	0	2500	42 (1)
C(11)	5102 (4)	4118 (4)	4225 (5)	42 (3)
C(12)	5792 (5)	3966 (5)	3823 (6)	57 (3)
C(13)	5843 (5)	3347 (6)	3236 (7)	75 (4)
C(14)	5205 (6)	2926 (5)	3037 (7)	75 (4)
C(15)	4511 (5)	3097 (5)	3421 (6)	65 (3)
C(16)	4443 (4)	3696 (5)	4040 (6)	50 (3)
C(21)	83 (4)	871 (4)	4220 (5)	47 (3)
C(22)	678 (4)	1381 (5)	4274 (6)	54 (3)
C(23)	713 (5)	1996 (5)	3674 (6)	58 (3)
C(24)	156 (5)	2091 (5)	3025 (6)	61 (3)
C(25)	−439 (5)	1576 (6)	2976 (7)	71 (4)
C(26)	−485 (5)	970 (5)	3561 (6)	68 (4)
C(31)	404 (4)	4203 (4)	1746 (5)	47 (3)
C(32)	1112 (5)	3883 (5)	1951 (6)	54 (3)
C(33)	1382 (5)	3286 (5)	1417 (7)	65 (3)
C(34)	949 (6)	3011 (5)	694 (6)	64 (3)
C(35)	238 (6)	3327 (5)	512 (7)	68 (4)
C(36)	−30 (5)	3922 (5)	1024 (6)	56 (3)
C(41)	4179 (4)	335 (4)	3268 (6)	47 (3)
C(42)	3818 (4)	1027 (4)	3121 (6)	52 (3)
C(43)	3221 (5)	1245 (5)	3688 (7)	68 (4)
C(44)	2989 (5)	778 (6)	4379 (7)	69 (4)
C(45)	3345 (5)	74 (5)	4527 (6)	67 (4)
C(46)	3937 (5)	−160 (5)	3961 (6)	58 (3)
H(12)	6257	4280	3968	
H(13)	6347	3218	2951	
H(14)	5242	2485	2604	
H(15)	4046	2780	3277	
H(16)	3937	3818	4324	
H(22)	1085	1311	4743	
H(23)	1149	2368	3710	
H(24)	182	2531	2594	
H(25)	−850	1646	2503	
H(26)	−919	593	3520	
H(32)	1425	4081	2471	
H(33)	1895	3059	1558	
H(34)	1144	2578	310	
H(35)	−74	3128	−4	
H(36)	−545	4150	884	
H(42)	3988	1367	2616	
H(43)	2962	1749	3594	
H(44)	2555	941	4780	
H(45)	3177	−270	5037	
H(46)	4194	−664	4059	

(*b*) Anisotropic thermal motion of the $\mathrm{Cl_3^-}$ ion ($\times 10^3$), including values of $\langle u^2 \rangle$ along the Cl—Cl—Cl direction (direction cosines: 0·313, 0·313, −0·897)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Bond
Cl(1)	61 (1)	97 (2)	95 (2)	2 (1)	5 (2)	21 (2)	78 (2)
Cl(2)	52 (1)	65 (1)	78 (2)	8 (1)	−6 (1)	−7 (1)	83 (2)
Cl(3)	113 (2)	104 (2)	85 (2)	38 (2)	20 (2)	11 (2)	80 (2)

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Trichloride ion

Cl(1)—Cl(2)	2·305 (3)	Cl(1)—Cl(2)—Cl(3)	177·45 (15)
Cl(2)—Cl(3)	2·227 (4)		

Tetraphenylarsonium ion

	Phenyl 1	Phenyl 2	Phenyl 3	Phenyl 4
As—C(1)	1·921 (7)	1·910 (8)	1·914 (7)	1·914 (8)
C(1)—C(2)	1·366 (10)	1·366 (10)	1·386 (10)	1·376 (10)
C(2)—C(3)	1·387 (12)	1·389 (11)	1·388 (11)	1·387 (11)
C(3)—C(4)	1·360 (12)	1·374 (11)	1·390 (12)	1·366 (13)
C(4)—C(5)	1·369 (13)	1·371 (12)	1·382 (12)	1·389 (13)
C(5)—C(6)	1·395 (11)	1·363 (12)	1·364 (11)	1·389 (11)
C(6)—C(1)	1·388 (10)	1·400 (11)	1·393 (11)	1·401 (11)
As—C(1)—C(2)	119·6 (6)	122·6 (6)	119·3 (6)	121·0 (6)
As—C(1)—C(6)	117·6 (6)	117·5 (6)	120·0 (6)	117·9 (6)
C(1)—C(2)—C(3)	118·6 (8)	119·7 (8)	118·6 (8)	119·2 (8)
C(2)—C(3)—C(4)	120·0 (9)	120·5 (7)	120·6 (8)	120·5 (8)
C(3)—C(4)—C(5)	121·1 (8)	119·2 (8)	120·0 (8)	120·7 (8)
C(4)—C(5)—C(6)	120·4 (8)	121·3 (9)	120·0 (9)	119·7 (9)
C(5)—C(6)—C(1)	117·2 (8)	119·4 (7)	120·3 (8)	118·7 (8)
C(6)—C(1)—C(2)	122·6 (7)	119·8 (8)	120·6 (7)	121·1 (8)
C(1)—As—C(1)^a	107·0 (4)	106·1 (5)	108·8 (5)	107·5 (5)
C(1)—As—C(1)^b	110·7 (2)	111·2 (2)	109·8 (2)	110·5 (2)

(*a*) Carbon atoms related by a twofold axis parallel to **c**.
(*b*) Carbon atoms not related by a twofold axis.

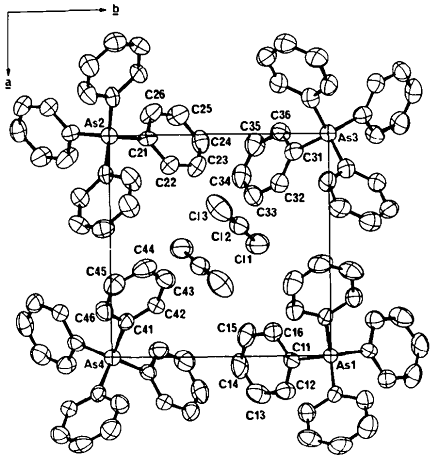

Fig. 1. Part of the unit cell of $[\mathrm{As(C_6H_5)_4}]\mathrm{Cl_3}$, viewed down **c**, showing four of the eight monocations lying on $\bar{4}$ axes and two of the eight trichloride monoanions lying in general positions for $I\bar{4}$ symmetry. The asymmetric unit shown has side $a/2$. I-centering causes cations to be separated by $c/2$ but only cations with z(As) < 0·5 are shown.

$2r^* |F_c|^2 \delta)^{-1/4}$, $\delta = (e^2/mc^2 V)^2 \; (\lambda^3/\sin 2\theta) \; [(1 + \cos^4 2\theta)/(1 + \cos^2 2\theta)]\bar{T}$ and $\bar{T}$ is the mean path length in the crystal (Larson, 1970). A value of $R^* =$ 0·00033 (9) was obtained. H atoms were incorporated with their unrefined atomic coordinates determined from the known geometry of the phenyl groups and with their thermal parameters held to be the same as those of the C atoms to which they were attached.

Scattering curves and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). A final $R_1(F)$ value for the 1570 reflexions with $I > 3\sigma$ was 0·042 for the incorrect choice of enantiomorph and 0·038 for the correct choice.* Atomic coordinates and their standard deviations, and Cl-atom anisotropic thermal parameters are given in Table 1. Bond lengths and angles are given in Table 2. The contents of the asymmetric unit cell are shown in Fig. 1.

Description of the structure

The tetraphenylarsonium and trichloride ions stack in columns parallel to **c**. The Cl_3^- ions run zigzag and end-to-end about 2_1 screw axes parallel to **c** in the space between stacks of $As(C_6H_5)_4^+$ ions separated by $c/2$. The Cl_3^- ion is almost linear [Cl—Cl—Cl angle 177·5 (2)°] and is asymmetric [2·227 (4), 2·305 (3) Å]. A Cl···Cl approach distance of 3·979 (4) Å between Cl_3^- ions is close to the van der Waals diameter for Cl.

The structure closely approaches $I\bar{4}c2$ symmetry. The symmetry operator $\frac{1}{2} + x, \frac{1}{2} - y, z$ of $I\bar{4}c2$ operates on phenyl ring 2 to approximate ring 1. The symmetry operator $y, x, \frac{1}{2} - z$ of $I\bar{4}c2$ operates on phenyl ring 4 to approximate ring 3. Atomic coordinates of rings 2 and 4 so transformed have a mean displacement of 0·44 Å from the actual coordinates of the corresponding atoms of rings 1 and 3. The symmetry operation $\frac{1}{2} - y, \frac{1}{2} - x, 1 - z$ of $I\bar{4}c2$ very nearly superposes the Cl_3^- ion on itself, interchanging Cl(1) and Cl(3). This pseudosymmetry does not restrict least-squares refinement in any way as the independent observation of equivalents of F_{hkl} and $F_{\bar{h}kl}$ resolves the asymmetry, the Fourier transform of $\rho(x,y,z) - \rho(\bar{x},y,\frac{1}{2} + z)$ being $F_{hkl} - (-1)^l F_{\bar{h}kl}$ (Rae, 1975).

However, the observed difference between $|F_{hkl}|$ and $|F_{khl}|$ may be lost should the crystal be twinned. Though this was not so in our case, it was decided to test the ability of least-squares refinement to detect such an occurrence. An artificial data set was created for this purpose.

The 1570 reflexions with $I > 3\sigma$ were used to form a data set of 683 reflexions $|F_{hkl}(\text{new})| = \frac{1}{2}(|F_{hkl}|^2 + |F_{khl}|^2)^{1/2}$. The value of $\sum(|F_{hkl}| - |F_{khl}|)/\sum(|F_{hkl}| + |F_{khl}|)$ is 0·12 for the 529 reflexion pairs for which F_{hkl} is not equivalent to F_{khl}. The F_{hkl}(new) and a model of ordered isotropic atoms in $I\bar{4}c2$ yields an unweighted $R_1(F)$ of 0·078 on refinement. A disordered $I\bar{4}c2$ structure, refined using rigid phenyl groups and constrained least squares (Rae, 1976) to control covariance problems, yields an unweighted $R_1(F)$ of 0·075. In each case refinement was commenced from the atomic parameters of the final refinement cycle of $I\bar{4}$. It is seen that, although the incorrect structural models in $I\bar{4}c2$ would have yielded an $R_1(F)$ value acceptable for publication, refinement using a twinned-crystal model would have halved the final value of $R_1(F)$. This choice of model would be preferred even more if the 75% of data with no As contribution were considered.

Müller (1980) has listed a number of preferred space groups for tetraphenylphosphonium and tetraphenylarsonium salts based on parallel stacking of cations. The packing of cations in the $[As(C_6H_5)_4]Cl_3$ structure agrees with Müller's concepts. However, the space group has four times the unit-cell volume of the seven space groups of $I\bar{4}$ symmetry listed by Müller. The As atom arrangement in the smaller cell (**a**′,**b**′,**c**′) is maintained but the cell volume is quadrupled by changing to axes $\mathbf{a} = \mathbf{a}' + \mathbf{b}'$, $\mathbf{b} = \mathbf{b}' - \mathbf{a}'$, $\mathbf{c} = 2\mathbf{c}'$.

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* Lists of structure factors, all anisotropic thermal parameters and *T* values have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36007 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.