Contribution from the Department of Chemistry, Texas A&M University,
College Station, Texas 77843

Structure of Tetraphenylarsonium Tetrachloroferrate(III)

F. ALBERT COTTON* and CARLOS A. MURILLO

Received February 25, 1975 AIC50140B

The crystal structure of tetraphenylarsonium tetrachloroferrate, $As(C_6H_5)_4[FeCl_4]$, has been accurately determined in a three-dimensional X-ray diffraction study. The compound crystallizes in the tetragonal space group $I\bar{4}$ with unit cell dimensions $a = 13.158$ (5) Å and $c = 7.161$ (3) Å; with $V = 1239.8$ Å^3 and $Z = 2$, the calculated density is 1.555 g cm^{-3}. Using 796 reflections in the range $0° < 2\theta \leq 60°$ (Mo Kα radiation) for which $I > 3\sigma(I)$ the structure refined to final values of the discrepancy indices, defined in the usual way, of $R_1 = 0.026$ and $R_2 = 0.035$. The conformation of the rings in the $AsPh_4^+$ ion is such that it has crystallographically demanded S_4 symmetry. This is also true for the $[FeCl_4]^-$ ion. An important feature in this compound is that none of the C–C–C angles in the phenyl rings deviates significantly from 120° including C(2)–C(1)–C(6). The $[FeCl_4]^-$ ion is tetragonally distorted and has Fe–Cl bond lengths of 2.182 (1) Å.

Introduction

Considerable interest has been developing in the structural features of different EPh_4 species for which the C–C–C angles at the carbon atom bound to the E atom are smaller than 120° when E is B,[1] C,[2] Si,[3] or Ge,[4] as well as in the case of $Sn(C_6F_5)_4$.[5] This trend was beginning to look general for all EPh_4 species although the range in E–C distance was quite large, varying from 1.553 Å in CPh_4 to 1.954 Å in $GePh_4$, and this range can be broadened if $Sn(C_6F_5)_4$ is considered since the distance Sn–C is 2.164 Å in this case. The literature contains several structure determinations in which the $AsPh_4^+$ ion is involved but the accuracy of these determinations is insufficient for the sort of analysis we wish to conduct, except, possibly, in one case,[6] where a low-temperature determination indicated that the C–C–C angle in question might exceed 120° by 1.4–1.9°. We concluded that an accurate determination of the structure of the tetraphenylarsonium ion was necessary to our general analysis of the structural properties of Ph_4E species and sought a compound well suited to the purpose. Since an early study,[7] though of very limited accuracy, had revealed that $Ph_4As[FeCl_4]$ has a simple, symmetrical structure, in which both the cation and the anion are crystallographically constrained to have S_4 ($\bar{4}$) symmetry, we elected to reexamine and refine this structure.

An added motivation for studying this particular compound was to provide another accurate structure for the $[FeCl_4]^-$ ion, since several previous measurements showed a variation in bond lengths and differing degrees of angular distortion. The earlier report[7] on $Ph_4As[FeCl_4]$ indicated a pronounced flattening of the tetrahedron along one S_4 axis.

We report here a structure analysis of $Ph_4As[FeCl_4]$ which provides dimensions accurate enough to deal with the questions which have just been mentioned. With regard to the Ph_4As^+ ion, the C(2)–C(1)–C(6) angle is found to be scarcely, if at all, different from 120°. It is, in fact, slightly larger than that. In this respect, then, Ph_4As^+ differs from all other Ph_4E species previously subjected to accurate structure determination. The $[FeCl_4]^-$ ion in this compound is indeed appreciably distorted. The Fe–Cl bond distance is in excellent agreement with the most accurate of the previously reported values, that in $PCl_4[FeCl_4]$.[8]

Experimental Section

Ferric chloride was dissolved in 8 *M* hydrochloric acid and set in a diffusion apparatus with a fine-porosity frit separating it from a solution of tetraphenylarsonium chloride in 8 *M* HCl. Two days later, large yellow crystals appeared on both sides of the frit.

Crystallographic Procedures. A long tetragonal crystal was cut to the dimensions 0.192 × 0.194 × 0.479 mm, mounted on a glass fiber with the longest dimension nearly parallel to the axis of the goniometer head, and examined on a Syntex $P\bar{1}$ four-circle automatic diffractometer.

Axial photographs, θ–2θ and ω scans of several intense reflections, showed that the crystal was of good quality with satisfactory mosaicity. A peak width at half-height of 0.3° was found. Cell constants and an orientation matrix for the tetragonal unit cell were determined from least-squares refinement of the setting angles of 15 computer-centered reflections in the range $25° < 2\theta < 34°$. The tetragonal cell parameters at 21 ± 1° are $a = 13.158$ (5) Å, $c = 7.161$ (3) Å, and $V = 1239.8$ (9) Å^3. With mol wt 581.0, the calculated density for $Z = 2$ is 1.555 g cm^{-3}. The pattern of systematic absences indicated, as previously reported,[7] that the space group is $I\bar{4}$.

Data were collected at 21 ± 1° using graphite-monochromatized Mo Kα radiation and θ–2θ scans varying from 4 to 24°/min, depending on the intensity of the reflection. A total of 835 independent reflections were collected in the range $0° < 2\theta$(Mo Kα) $\leq 60°$ with a scan range from 0.9° below the Kα_1 peak to 0.9° above the Kα_2 peak. From these reflections, 796 with $I > 3\sigma(I)$ were retained as observed data. Three standard reflections measured at intervals of 100 scans were stable. With a linear absorption coefficient for this compound of 24.6 cm^{-1} and the crystal dimensions, the calculated transmission factors for the minimum and maximum path lengths are 0.660 and 0.595 and the average is 0.623. An absorption correction was applied.

Solution and Refinement of the Structure.[9] To begin, the atomic positions reported by Zaslow and Rundle[7] were used in three cycles of least-squares refinement. This resulted in agreement factors of $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.32$ and $R_2 = (\sum w(|F_o - F_c|^2/\sum wF_o^2))^{1/2} = 0.38$ and an error in an observation of unit weight of 10.1. Most of the temperature factors were of unreasonable magnitudes.

A least-squares cycle refining only the temperature factors of the atoms in special positions was done and gave $R_1 = 0.38$ and $R_2 = 0.42$. Following this, a difference Fourier synthesis revealed all but one of the nonhydrogen atoms. The position of the missing carbon atom was calculated. Several cycles of full-matrix least-squares refinement with isotropic thermal parameters resulted in agreement factors $R_1 = 0.088$ and $R_2 = 0.124$.

After three more cycles of refinment using anisotropic thermal parameters, a difference Fourier map revealed the positions of the hydrogen atoms. Final full-matrix least-squares refinement of the nonhydrogen atoms anisotropically and the hydrogen atoms isotropically, using a factor p of 0.06 in the weighting expression, led to R values of 0.027 and 0.037 with an error in an observation of unit weight of 1.01. At this point, there were two hydrogen atoms that refined to chemically unreasonable positions. They were moved to calculated positions with a distance of 1.00 Å from the carbon atom and C–C–H angles of 120°. Two more cycles of full-matrix least-squares refinement were carried out, which caused these hydrogen atoms to move back to the old positions.

At this point, an absorption correction was applied and two more cycles of full-matrix least-squares refinement gave the final positional and thermal parameters, none of which change by more than 1 esd from the previous refinement neglecting that correction. The final residuals were $R_1 = 0.026$ and $R_2 = 0.035$, with an error in observation of unit weight of 0.98.

A final analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$ showed no unusual trends in $\sum w(|F_o| - |F_c|)^2$ as a function of reflection number, $\lambda^{-1} \sin \theta$, or various classes of indices.

Since $I\bar{4}$ is a noncentrosymmetric space group, there are two enantiomeric forms. The absolute configuration of the crystal structure

Table I. Positional and Thermal Parameters for $As(C_6H_5)_4[FeCl_4]^a$

Atom	Wy-koff nota-tion	x	y	z	β_{11} or B_{iso}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	c	0.0	0.5	0.25	0.00443 (4)	β_{11}	0.0211 (2)	0.0	0.0	0.0
Cl	g	0.1337 (1)	0.4600 (1)	0.4145 (2)	0.00819 (8)	0.00702 (7)	0.0375 (4)	−0.00125 (6)	−0.0080 (1)	0.0036 (1)
As	a	0.0	0.0	0.0	0.00300 (2)	β_{11}	0.0144 (1)	0.0	0.0	0.0
C(1)	g	0.1070 (2)	0.0457 (3)	0.1581 (4)	0.0032 (1)	0.0042 (2)	0.0132 (6)	−0.0001 (1)	−0.0002 (2)	−0.0008 (3)
C(2)	g	0.1376 (3)	0.1466 (3)	0.1579 (6)	0.0049 (2)	0.0040 (2)	0.0206 (8)	0.0001 (2)	−0.0012 (4)	−0.0004 (3)
C(3)	g	0.2148 (3)	0.1766 (3)	0.2760 (7)	0.0050 (2)	0.0056 (2)	0.0266 (10)	−0.0014 (2)	−0.0018 (4)	−0.0026 (4)
C(4)	g	0.2606 (3)	0.1072 (4)	0.3941 (7)	0.0053 (2)	0.0083 (3)	0.0232 (10)	−0.0004 (2)	−0.0037 (4)	−0.0028 (5)
C(5)	g	0.2295 (3)	0.0068 (4)	0.3954 (7)	0.0061 (3)	0.0081 (3)	0.0217 (10)	0.0003 (2)	−0.0039 (5)	0.0022 (5)
C(6)	g	0.1522 (3)	−0.0240 (3)	0.2775 (6)	0.0056 (2)	0.0050 (2)	0.0200 (8)	0.0001 (2)	−0.0021 (4)	0.0019 (4)
H(2)	g	0.101 (3)	0.192 (3)	0.060 (5)	3.5 (9)					
H(3)	g	0.229 (3)	0.242 (4)	0.281 (7)	3.7 (10)					
H(4)[b]	g	0.316	0.130	0.479	5.0					
H(5)	g	0.263 (4)	−0.045 (4)	0.454 (7)	4.6 (11)					
H(6)[b]	g	0.128	−0.096	0.278	5.0					

[a] All values include estimated standard deviations in parentheses. The anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Calculated positions.

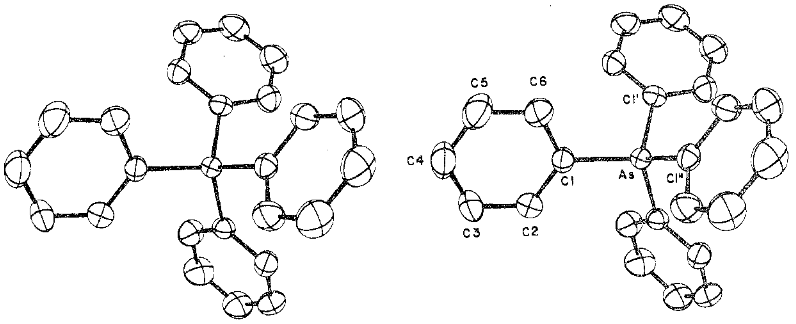

Figure 1. ORTEP stereoview of the $As(C_6H_5)_4$ ion. The atom-numbering scheme used in all tables is defined. The atoms are represented by 50% probability thermal ellipsoides.

was checked via the transformation of all atomic coordinates from (x, y, z) to $(-x, -y, -z)$ and refinement of parameters as before. The least-squares refinement led to convergence with substantially increased residuals of $R_1 = 0.052$ and $R_2 = 0.072$. Clearly, the original coordinates (x, y, z) were the correct ones, and the results of the latter refinement were discarded. A list of the $|F_o|$ and final $|F_c|$ values is available, as explained in the paragraph at the end of the paper concerning supplementary material.

Results

The positional and thermal parameters for the crystallographically independent atoms are listed in Table I. The arsenic and the iron atoms lie on the special positions 0, 0, 0 and 0, $^1/_2$, $^1/_4$, respectively, where the crystallographic symmetry is $\bar{4}$ for each of them. Thus, the four phenyl rings as well as the chlorine atoms are crystallographically equivalent. Figure 1 presents a stereoscopic view of the $AsPh_4^+$ ion with hydrogen atoms omitted for clarity. It also defines the numbering scheme. Interatomic distances are listed in Table II and bond angles in Table III. The least-squares plane for the phenyl ring is given by the equation $-8.876X + 2.793Y + 5.063Z + 0.0163 = 0$, where X, Y, and Z are fractional coordinates measured along the unit cell edges. The carbon atoms deviate very slightly from this plane. The deviations in 0.001 Å for C(1) to C(6), respectively, are −6, 4, 0, −2, 1, 4. The arsenic atom lies 0.016 Å from the plane.

The dimensions of the $[FeCl_4]^-$ ion agree, within the error limits, with those previously reported.[7] The Fe–Cl distance is 2.182 (1) Å compared to the previously determined value of 2.19 (3) Å. The earlier report indicated an appreciable tetragonal distortion such that two Cl–Fe–Cl angles were 114.5 (15)° while the other four were 107.0 (15)°. We find values which are more accurate than but in good agreement with these, namely, 114.6 (1) and 106.95 (5)°.

Table II. Interatomic Distances(A)[a]

Atoms	Distance	Atoms	Distance
Fe–Cl	2.182 (1)	C(6)–C(1)	1.387 (5)
As–C(1)	1.905 (3)	C(2)–H(2)	1.03 (4)
C(1)–C(2)	1.387 (5)	C(3)–H(3)	0.89 (5)
C(2)–C(3)	1.380 (6)	C(4)–H(4)	1.00
C(3)–C(4)	1.383 (7)	C(5)–H(5)	0.92 (5)
C(4)–C(5)	1.383 (7)	C(6)–H(6)	1.00
C(5)–C(6)	1.383 (6)		

[a] Numbers in parentheses are the estimated standard deviations in the last significant digit. Atoms are labeled as in Figure 1.

Table III. Bond Angles (deg)

Atoms[a]	Angle	Atoms	Angle
Cl–Fe–Cl'	114.6 (1)	As–C(1)–C(6)	118.3 (3)
Cl–Fe–Cl	106.95 (5)	C(1)–C(2)–H(2)	115 (2)
C(1)–As–C(1')	110.7 (1)	C(3)–C(2)–H(2)	125 (2)
C(1)–As–C(1'')	107.0 (2)	C(2)–C(3)–H(3)	117 (3)
C(2)–C(1)–C(6)	120.6 (3)	C(4)–C(3)–H(3)	122 (3)
C(1)–C(2)–C(3)	119.1 (4)	C(3)–C(4)–H(4)	120
C(2)–C(3)–C(4)	120.4 (4)	C(5)–C(4)–H(4)	120
C(3)–C(4)–C(5)	120.4 (4)	C(4)–C(5)–H(5)	125 (3)
C(4)–C(5)–C(6)	119.6 (4)	C(6)–C(5)–H(5)	115 (3)
C(5)–C(6)–C(1)	119.8 (4)	C(5)–C(6)–H(6)	120
As–C(1)–C(2)	121.1 (3)	C(1)–C(6)–H(6)	120

[a] Primed atoms are symmetry related to the corresponding unprimed atoms.

Discussion

In connection with the structures of Ph_4E molecules or ions, two main questions arise. They concern the conformation (i.e., the relative orientations of the ring planes, considered as having rotational freedom about the E–C(1) axes) and the deviations of the rings from regular hexagonal shape.

The conformation of the Ph_4As^+ ion in this compound has strictly S_4 ($\bar{4}$) symmetry. It has been generally recognized that an S_4 or D_2 configuration is likely to be preferred, though it is not yet clear how all the factors, including E–C distances and intermolecular interactions, will work out in any given case.[10] In the group 4 tetraphenyls,[2–5] crystallographically rigorous S_4 conformations are also found. In the vast majority of cases, however, there is no rigorous (crystallographic) symmetry and it is seldom easy to recognize with certainty whether the conformation approximates at all closely to any given idealized symmetry.[11]

With respect to the shape of the phenyl rings, there is no significant deviation from hexagonal symmetry. For the C–C distances this is completely obvious since the entire range of 0.009 Å from the shortest to the longest is only 1.5 times the average esd of an individual one. The angles vary slightly more relative to their esd's. However, the mean deviation from the average value (120.0°) is only 0.4° (with the largest individual deviation being 0.9°) while the esd's of individual angles are also 0.4°. This is the only example so far available in which there is no significant deviation from perfect hexagonal symmetry. In all other cases the angle at C(1) is significantly smaller (by 1–6°) than 120° and there are compensatory increases in others. A comparative discussion of the magnitudes and the possible significance of these distortions will be given elsewhere.

Finally, we note that the $[FeCl_4]^-$ ion has Fe–Cl distances of 2.182 (1) Å which is in excellent accord with the average value of 2.185 (2) Å in the $PCl_4[FeCl_4]$ salt. Since the latter has been recently used for comparison with $[FeCl_4]^{2-}$ in order to determine the dependence of the tetrahedral radius of the iron atom on oxidation state,[12] it is satisfying to have it confirmed to within the esd's. These two values agree satisfactorily with the mean value of 2.196 (9) Å in $Na[FeCl_4]$.[13] The only remaining literature value then is for the $[FeCl_4]^-$ ion in $[FeCl_2(DMSO)_4][FeCl_4]$,[14] in which the ion also has S_4 crystallographic symmetry, a compressed structure with angles (112.2 and 108.2°) similar to those here but an Fe–Cl distance of 2.162 (5) Å. The difference between this value and those in $Ph_4As[FeCl_4]$ and $PCl_4[FeCl_4]$, 0.022 Å, is about 4 times the sum of the esd's, which makes it of marginal significance.

Acknowledgment. We are grateful to Dr. D. M. Collins for some helpful discussions and to The Robert A. Welch Foundation for financial support under Grant No. A494.

Registry No. $Ph_4As[FeCl_4]$, 21279-18-5.

Supplementary Material Available. A list of F_o and F_c values will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all the supplementary material for papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number AIC50140B-10-75.

References and Notes

(1) (a) D. M. Collins, F. A. Cotton, B. A. Frenz, and C. A. Murillo, to be submitted for publication; (b) M. DiVaira and A. B. Orlandini, *J. Chem. Soc., Dalton Trans.*, 1704 (1972); (c) R. J. Sime, R. P. Dodge, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **10**, 537 (1971); (d) D. M Duggan and D. N. Hendrickson, *ibid.*, **13**, 1911 (1974).

(2) A. Robbins, G. A. Jeffrey, J. P. Chesick, J. Donohue, F. A. Cotton, B. A. Frenz, and C. A. Murillo, *Acta Crystallogr.*, in press.

(3) C. Glidewell and G. M. Sheldrick, *J. Chem. Soc. A*, 3127 (1971).

(4) P. C. Chieh, *J. Chem. Soc. A*, 3243 (1971).

(5) A. Karipides, C. Forman, R. Thomas, and T. Reed, *Inorg. Chem.*, **13**, 811 (1974).

(6) J. Runsink, S. Swen-Walstra, and T. Migchelson, *Acta Crystallogr., Sect. B*, **28**, 1331 (1972).

(7) B. Zaslow and R. E. Rundle, *J. Phys. Chem.*, **61**, 490 (1957).

(8) T. J. Kistenmacher and G. D. Stucky, *Inorg. Chem.*, **7**, 2150 (1968).

(9) The following computer programs were used: DATARED by Frenz for data reduction; AGNOST, used for the absorption correction, a modification by Frenz of Cohen's AGNOST; FAME, a program for calculating normalized structure factors by Dewar; JIMDAP, a version of Zalkin's Fourier program FORDAP as modified by Ibers; NUCLS, a full-matrix least-squares program by Ibers and Doedens, based on Busing and Levy's ORFLS program; RSCAN by Doedens for analysis of structure factors; ORTEP by Johnson for illustrations; ORFFE by Busing, Martin, and Levy, as modified by Brown, Johnson, and Thiessen for distances and angles; LIST by Snyder for listing structure factors for publication.

(10) M. G. Hutchings, J. D. Andose, and K. Mislow, *J. Am. Chem. Soc.*, in press.

(11) In the case of $RbBPh_4$[1a] the conformation is D_{2d}. A general survey of all published Ph_4E structures in which their approach to any of the higher idealized conformation symmetries (D_{2d}, S_4, D_2) is analyzed is in preparation by the present authors.

(12) J. W. Lauher and J. A. Ibers, *Inorg. Chem.*, **14**, 348 (1975).

(13) R. R. Richards and N. W. Gregory, *J. Phys. Chem.*, **69**, 239 (1965).

(14) M. J. Bennett, F. A. Cotton, and D. L. Weaver, *Acta Crystallogr.*, **23**, 581 (1967).