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THE CRYSTAL STRUCTURE OF THE COMPLEX OF TRIPHENYLARSINE OXIDE WITH TETRACHLOROCATECHOL; AN ADDUCT STABILIZED BY CHELATING HYDROGEN BONDS

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SUMMARY

The 1/1 triphenylarsine oxide adduct of tetrachlorocatechol crystallizes in the orthorhombic space group *Pbca* with $a = 15.07 \pm 0.02$, $b = 18.82 \pm 0.03$, and $c = 16.53 \pm 0.02$ Å. An observed density of 1.58 g/cm^3 and calculated density of 1.62 g/cm^3 indicated the presence of 8 molecules per unit cell. 1219 reflections above background were collected with Cu-$K\alpha$ radiation using a manual diffractometer of Weissenberg geometry. The structure was solved by Patterson and Fourier techniques and refined by least squares methods (As, O, Cl anisotropic; C, H isotropic) to a conventional R of 0.070 and a weighted R of 0.041. The structure consists of triphenylarsine oxide and tetrachlorocatechol moieties hydrogen bonded together to give discrete monomeric adducts. The arsine oxide oxygen (O_{As}) is hydrogen bonded symmetrically to the two OH groups of the catechol with an $O–O_{As}–O$ angle of 65.4(4)° and $O_{As}–O$ distances averaging 2.616(11) Å. The dimensions of the triphenylarsine oxide and tetrachlorocatechol are equivalent to those observed in other similar compounds except that the configuration of the phenyl rings with respect to the As–O bond is quite distorted. This distortion results from the alternate packing of approximately parallel phenyl and catechol rings along the a axis.

INTRODUCTION

Recently it has been demonstrated that the product, (I), of the reaction of catechols with triarylphosphine[1-3] and arsine oxides[4] is identical to the product produced by hydrolysis of the compound, (II), formed from the reaction of triarylphosphines and arsines with *ortho*-quinones. Products of type (I) can also be produced by the reaction of catechols with amine oxides and sulfoxides[1].

These catechol adducts of P, As, N, and S oxides exhibit considerable stability. In general, they are quite soluble in common organic solvents such as chloroform and benzene without dissociation, and in many cases they can be recovered intact after sublimation. All of the complexes isolated exist with 1/1 mole ratios of catechol to

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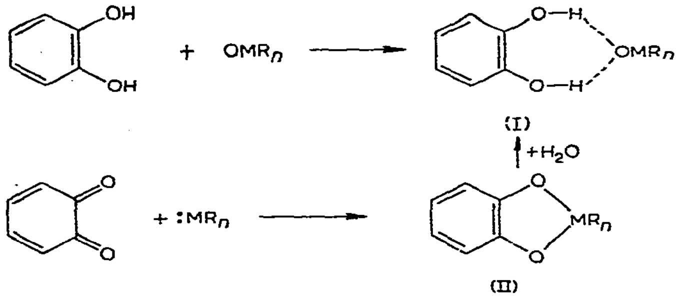

oxide, and in all cases, infrared and nuclear magnetic resonance spectroscopy suggests that the complexes are stabilized by strong hydrogen bonds. These properties, together with the geometry of the catechol group, led to the suggestion[1] that these adducts are stabilized by a chelating hydrogen bond system, and a determination of the crystal structure of the tetrachlorocatechol adduct of triphenylarsine oxide was undertaken to verify this proposal.

UNIT CELL AND DATA COLLECTION

A sample of the adduct of tetrachlorocatechol with triphenylarsine oxide was obtained by the reaction of a 1/1 mole ratio of catechol with arsine oxide in alcohol. Colorless crystals of *mmm* symmetry suitable for diffraction measurements were obtained by slow diffusion of pentane into a concentrated solution of the adduct in chloroform.

From Weissenberg photographs taken with Cu-$K\alpha$ radiation and precession photographs taken with Mo-$K\alpha$ radiation, crystals of the compound were found to exhibit *mmm* diffraction symmetry. From the systematic absences observed on $h0l$, $h1l$, $hk0$ and $hk1$ photographs ($hk0$, $h=2n$; $h0l$, $l=2n$; $0kl$, $k=2n$), the unique orthorhombic space group was found to be *Pbca* (No. 61)[5]. The cell parameters determined from precession photographs calibrated with NaCl reflections were $a=15.07\pm0.02$, $b=18.82\pm0.03$, and $c=16.53\pm0.02$ Å. These parameters were determined at 23°C using 0.7107 Å as the wavelength of Mo-$K\alpha$ radiation, with the errors estimated from several measurements of each photograph. The density of a crystal measured by flotation in aqueous zinc chloride was 1.58 ± 0.02 g/cm^3 while that calculated assuming 8 adducts per unit cell is 1.62 g/cm^3. Since *Pbca* is a space group of order 8, no symmetry restrictions are imposed on the adducts.

Data were collected manually using a Supper diffractometer of equiinclination Weissenberg geometry with Cu-$K\alpha$ radiation filtered through 4 mils of Ni foil. The pulse-height analyzer was set to admit approximately 90% of the Cu-$K\alpha$ intensity detected by a scintillation counter located 7.5 cm from the crystal. With a 2° receiving slit, each reflection was scanned using a 3° ϕ scan centered about the calculated peak maximum with a scan rate of 3.6°/min (a 50 sec scan). Centering of the peak in the scan range was checked by recording each peak on a strip chart recorder. Backgrounds were counted for 10 sec at either end of the scan. Intensity data were collected for a single set of unique reflections within the range $2\theta(\text{Cu-}K\alpha)\leqslant 101°$. The 006 reflection, monitored every 2 h, did not change significantly during the data collection period. Intense reflections whose counting rate exceeded 7000 counts/sec were attenuated using calibrated Ni foils so that the maximum counting rate did not exceed 7000 counts/sec.

The integrated intensity of each reflection, I, was obtained using the expression $I=[C-(T/t)BG]$ where C was the total count accumulated during the scan; BG, the total background counted in time t; and T, the time of the scan. An estimated standard deviation for each reflection, $\sigma(I)$, was evaluated as $\sigma(I)=[C+(T/t)^2BG]^{\frac{1}{2}}$. Of the 2485 reflections measured, 1219 had $I \geqslant 3\sigma(I)$. These 1219 reflections were used for solution and refinement of the structure. All reflections were corrected for Lorentz and polarization effects $[(\mathrm{LP})^{-1}=\cos^2\bar{\mu}\cdot\sin\gamma/(1+\cos^2 2\theta)]$, and since the linear absorption coefficient for Cu-$K\alpha$ radiation was found to be 65.6 cm^{-1}, an absorption correction* was applied. The crystal was bounded by the face 100, the pinacoids (010) and (001), and the sphenoid (101) with maximum dimensions along a, b, and c of 0.123, 0.217, and 0.267 mm, respectively. Transmission factors ranged from 0.306 to 0.474.

Although the zones $0kl$–$14kl$ were not scaled together since no common data was collected, both refinement of individual scale factors for each level and examination of R for each Weissenberg zone indicated that these levels were on the same scale. Several times during the course of solution and refinement R for each level was checked. These R values did not vary appreciably or in a systematic fashion from level to level. Following location of all atoms, individual scale factors for each level were included in a full matrix refinement with isotropic temperature factors. The various refined scale factors were not significantly different; consequently, only one scale factor for all data was applied during the final anisotropic refinement.

SOLUTION AND REFINEMENT

From a Patterson map**, the 8 As atoms were found to occupy the general positions of *Pbca*. Following least-squares adjustment of a single scale factor, a Fourier map calculated with phases based on the As positions showed the tetrachlorocatechol unit, and two subsequent difference Fourier maps located the remaining carbon and oxygen atoms. Four cycles of full matrix least squares refinement of individual level scale factors, all atomic positions, and isotropic temperature factors reduced $R_1(R_1=\Sigma|F_o-F_c|/\Sigma|F_o|)$ to 0.099 and $R_2(R_7=[\Sigma w|F_o-F_c|^2]^{\frac{1}{2}}/[\Sigma w|F_o|^2]^{\frac{1}{2}})$ to 0.064. During all least squares cycles, anomalous scattering corrections*** for As and Cl were included and a weighting scheme[9] with $\sigma(F^2)=\{[\sigma(F^2)]^2+[0.04F^2]^2\}^{\frac{1}{2}}$ was applied. A difference Fourier then located the positions of the 17 hydrogen atoms.

At this point it was evident from the difference map that anisotropic temperature factors were required for As, Cl, and O atoms. Three cycles of refinement varying these anisotropic temperature factors, isotropic temperature factors for carbon, all atomic positions, and a single scale factor reduced R_1 to 0.070 and R_2 to 0.041. The

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* Using a local modification of Burham's GNABS, see ref. 6.

** Computations were carried out on the Purdue CDC 6500 computer. Programs used included Rossman's FOUR for Fourier synthesis, Wood's MGEOM geometry program, and a local version of Busing and Levy's ORFLS for the full-matrix least squares refinement.

*** Scattering factors used were those of Ibers, see ref. 7; Anomalous dispersion corrections were those of Templeton, see ref. 8.

hydrogen isotropic temperature factors were held constant at 6.0. On the last cycle of refinement shifts in the varied parameters were less than 0.25 times their respective estimated standard deviations.

Final observed and difference Fourier maps were calculated using all atoms for phasing. No areas of electron density greater than 0.3 e/Å^3 appeared on the difference map. The final atomic positions of As, O, and Cl atoms are reported in Table 1, while their anisotropic temperature factors are reported in Table 2. Table 3 lists the atomic positions and isotropic temperature factors for the C and H atoms. Observed and calculated structure factors are listed in Table 4. Those reflections for which $I < 3\sigma(I)$ are indicated with an asterisk. Important bond distances and angles within a single adduct are listed in Tables 5 and 6, respectively.

TABLE 1

ATOMIC COORDINATES OF THE ARSENIC, CHLORINE AND OXYGEN ATOMS IN FRACTIONS OF UNIT CELL EDGES WITH ESTIMATED STANDARD DEVIATIONS

Atom	x	y	z
As	0.6705(1)	0.4962(1)	0.0966(1)
Cl_3	0.4209(3)	0.2690(2)	0.1137(3)
Cl_4	0.4268(4)	0.2013(3)	0.2855(3)
Cl_5	0.4711(4)	0.2971(3)	0.4325(3)
Cl_6	0.5076(4)	0.4587(3)	0.4062(4)
O_1	0.4889(9)	0.5049(7)	0.2440(7)
O_2	0.4470(8)	0.4189(5)	0.1090(8)
O_3	0.5627(6)	0.5215(5)	0.1013(8)

TABLE 2

ANISOTROPIC TEMPERATURE FACTORS FOR ARSENIC, CHLORINE AND OXYGEN ATOMS, WITH ESTIMATED STANDARD DEVIATIONS

Atom	$B_{1,1}$[a]	$B_{2,2}$	$B_{3,3}$	$B_{1,2}$	$B_{1,3}$	$B_{2,3}$
As	35(1)	18(1)	30(1)	2(1)	0(1)	1(1)
Cl_3	54(3)	33(2)	33(2)	−2(2)	−3(3)	− 5(2)
Cl_4	69(4)	38(2)	61(3)	−7(3)	−8(3)	16(2)
Cl_5	91(4)	75(3)	20(2)	−1(3)	−5(2)	14(2)
Cl_6	59(4)	56(2)	40(3)	1(2)	4(3)	−21(3)
O_1	71(9)	30(5)	50(5)	−5(7)	11(6)	−11(7)
O_2	55(8)	29(5)	26(6)	0(5)	−4(6)	2(5)
O_3	23(6)	19(4)	48(5)	2(4)	3(6)	7(5)

[a] Values are $\times 10^4$. $f = f_o \exp[-(B_{11} \cdot h^2 + B_{22} \cdot k^2 + B_{33} \cdot l^2 + 2B_{12} \cdot h \cdot k + 2B_{13} \cdot h \cdot l + 2B_{23} \cdot k \cdot l)]$

DESCRIPTION OF THE STRUCTURE

The crystal structure consists of triphenylarsine oxide and tetrachlorocatechol moieties hydrogen bonded together to give discrete monomeric adducts. Projections of the unit cell down the *a* and *c* axes are shown in Figs. 1 and 2, respectively. A single

TABLE 3

ATOMIC COORDINATES OF CARBON AND HYDROGEN ATOMS AND ISOTROPIC TEMPERATURE FACTORS[a]

The estimated standard deviation for each value is given in parenthesis. Hydrogen 8–24 are bonded to the corresponding carbon atoms.

Atom	x	y	z	B
C_1	0.4734(13)	0.4368(9)	0.2493(12)	3.22(42)
C_2	0.4578(13)	0.3930(9)	0.1831(11)	2.86(42)
C_3	0.4413(12)	0.3218(9)	0.1965(11)	2.92(42)
C_4	0.4466(13)	0.2922(9)	0.2722(11)	3.55(47)
C_5	0.4652(12)	0.3336(10)	0.3377(10)	3.27(45)
C_6	0.4807(14)	0.4035(11)	0.3239(14)	4.21(56)
C_7	0.7419(12)	0.5806(9)	0.0925(12)	3.24(38)
C_8	0.7131(13)	0.6372(10)	0.0495(11)	3.51(45)
C_9	0.7671(15)	0.6971(11)	0.0410(11)	4.83(55)
C_{10}	0.8490(16)	0.6947(11)	0.0785(12)	5.80(56)
C_{11}	0.8801(14)	0.6408(11)	0.1256(12)	5.22(55)
C_{12}	0.8244(15)	0.5789(9)	0.1300(10)	3.93(45)
C_{13}	0.6994(12)	0.4396(10)	0.1849(11)	2.91(44)
C_{14}	0.6965(14)	0.3659(11)	0.1761(12)	4.83(53)
C_{15}	0.7071(16)	0.3197(11)	0.2409(14)	5.36(62)
C_{16}	0.7161(15)	0.3480(12)	0.3171(14)	4.86(58)
C_{17}	0.7235(14)	0.4211(11)	0.3271(14)	4.57(54)
C_{18}	0.7121(13)	0.4676(9)	0.2628(11)	3.87(45)
C_{19}	0.6985(13)	0.4414(10)	0.0015(11)	3.19(45)
C_{20}	0.6249(13)	0.4143(10)	−0.0424(12)	4.30(51)
C_{21}	0.6460(12)	0.3705(9)	—0.1095(13)	4.79(48)
C_{22}	0.7347(15)	0.3626(11)	−0.1333(11)	4.58(54)
C_{23}	0.8010(13)	0.3913(9)	−0.0859(13)	4.56(49)
C_{24}	0.7829(14)	0.4317(11)	−0.0190(12)	3.90(51)
H_1	0.497(12)	0.520(9)	0.208(9)	6.0[b]
H_2	0.482(11)	0.462(8)	0.104(12)	6.0
H_8	0.659(14)	0.638(8)	0.024(9)	6.0
H_9	0.781(13)	0.749(11)	0.016(8)	6.0
H_{10}	0.868(11)	0.719(8)	0.083(10)	6.0
H_{11}	0.945(13)	0.633(8)	0.159(10)	6.0
H_{12}	0.839(14)	0.549(8)	0.160(10)	6.0
H_{14}	0.693(13)	0.351(8)	0.140(9)	6.0
H_{15}	0.672(14)	0.279(8)	0.223(9)	6.0
H_{16}	0.703(13)	0.330(8)	0.357(9)	6.0
H_{17}	0.705(12)	0.428(8)	0.373(10)	6.0
H_{18}	0.712(13)	0.527(8)	0.263(9)	6.0
H_{20}	0.552(14)	0.424(8)	−0.025(10)	6.0
H_{21}	0.573(12)	0.371(8)	−0.136(9)	6.0
H_{22}	0.726(14)	0.318(8)	−0.180(10)	6.0
H_{23}	0.849(13)	0.393(8)	−0.119(11)	6.0
H_{24}	0.840(14)	0.449(9)	0.013(10)	6.0

[a] In fractions of unit cell edge. [b] *B* not refined for hydrogen atoms.

monomeric adduct is illustrated in Fig. 3. These monomeric adducts pack into a molecular crystal with the closest inter-adduct distances being equal to or greater than the sum of the Van der Waal's radii of the atoms involved. Thus the closest inter-adduct C–C distance (between approximately parallel C_6 rings) is 3.53 Å while the closest inter-adduct O–O distance is 3.64 Å.

(*continued on p.* 382)

TABLE 4

OBSERVED AND CALCULATED STRUCTURE FACTORS

For each range of h, the entries are k, l, F_o, F_c. Those structure factors marked with an asterisk were not included in the refinement.

[illegible]

TABLE 5

INTERATOMIC DISTANCES IN THE TRIPHENYLARSINE OXIDE–TETRACHLOROCATECHOL COMPLEX, WITH ESTIMATED STANDARD DEVIATIONS

Subscripts refer to the atoms in Fig. 3.

Atom		Distance (Å)	Atom		Distance (Å)
a	b		a	b	
As	O_3	1.694(9)	C_7	C_8	1.351(26)
As	C_7	1.919(17)	C_8	C_9	1.398(29)
As	C_{13}	1.859(18)	C_9	C_{10}	1.382(31)
As	C_{19}	1.928(19)	C_{10}	C_{11}	1.362(29)
C_1	O_1	1.307(21)	C_{11}	C_{12}	1.437(28)
C_2	O_2	1.327(22)	C_{12}	C_7	1.390(28)
O_1	O_3	2.627(17)	C_{13}	C_{14}	1.396(27)
O_2	O_3	2.605(13)	C_{14}	C_{15}	1.388(30)
C_3	Cl_3	1.719(18)	C_{15}	C_{16}	1.375(32)
C_4	Cl_4	1.750(19)	C_{16}	C_{17}	1.390(31)
C_5	Cl_5	1.714(18)	C_{17}	C_{18}	1.387(27)
C_6	Cl_6	1.759(23)	C_{18}	C_{13}	1.405(25)
C_1	C_2	1.391(26)	C_{19}	C_{20}	1.421(28)
C_2	C_3	1.381(25)	C_{20}	C_{21}	1.417(28)
C_3	C_4	1.372(25)	C_{21}	C_{22}	1.402(29)
C_4	C_5	1.364(25)	C_{22}	C_{23}	1.380(29)
C_5	C_6	1.354(27)	C_{23}	C_{24}	1.370(29)
C_6	C_1	1.388(30)	C_{24}	C_{19}	1.329(29)

The adduct itself is stabilized by hydrogen bonds with the arsine oxide oxygen, O_{As}, hydrogen bonded symmetrically to the ortho OH groups of the catechol. The experimentally equivalent O_{As}–O distances of 2.627(17)Å and 2.605(13)Å, As–O_{As}–O angles of 115.9(9) and 114.5(9), and O_{As}–O–C angles of 104.6(11)° and 103.6(10)°

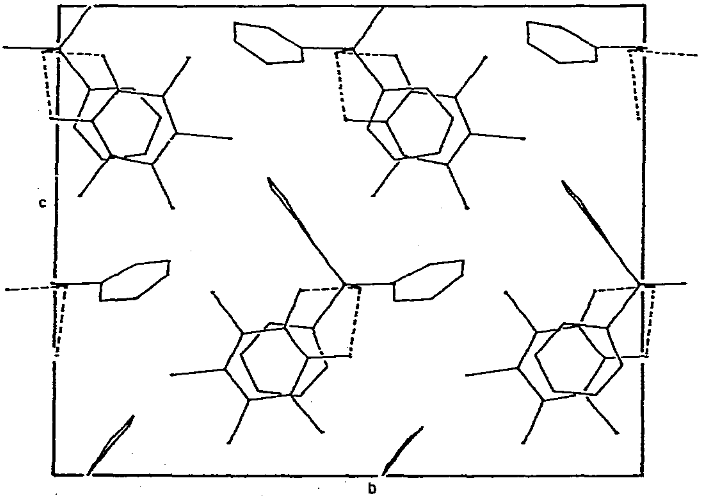


Fig. 1. View down the *a* axis of the front half of the unit cell. The front and rear halves of the unit cell are related by a center at 1/2, 1/2, 1/2.

TABLE 6

INTERATOMIC ANGLES IN THE TRIPHENYLARSINE OXIDE–TETRACHLOROCATECHOL COMPLEX, WITH ESTIMATED STANDARD DEVIATIONS

Atom			Angle (°)	Atom			Angle (°)
a	b	c		a	b	c	
O_3	As	C_7	107.9(7)	C_{16}	C_{17}	C_{18}	121.6(19)
O_3	As	C_{13}	110.5(6)	C_{17}	C_{18}	C_{13}	118.8(18)
O_3	As	C_{19}	113.4(6)	C_{18}	C_{13}	C_{14}	118.2(17)
C_7	As	C_{13}	111.8(8)	C_{19}	C_{20}	C_{21}	115.7(17)
C_7	As	C_{19}	107.0(8)	C_{20}	C_{21}	C_{22}	119.7(17)
C_{13}	As	C_{19}	106.4(8)	C_{21}	C_{22}	C_{23}	119.3(18)
C_1	O_1	O_3	104.6(11)	C_{22}	C_{23}	C_{24}	122.1(18)
C_2	O_2	O_3	103.6(10)	C_{23}	C_{24}	C_{19}	118.2(18)
As	O_3	O_1	114.5(9)	C_{24}	C_{19}	C_{20}	124.6(18)
As	O_3	O_2	115.9(9)	Cl_3	C_3	C_2	117.7(14)
O_1	O_3	O_2	65.4(4)	Cl_3	C_3	C_4	120.1(14)
C_1	C_2	C_3	118.6(17)	Cl_4	C_4	C_3	120.1(15)
C_2	C_3	C_4	122.0(17)	Cl_4	C_4	C_5	119.6(15)
C_3	C_4	C_5	120.3(17)	Cl_5	C_5	C_4	120.5(14)
C_4	C_5	C_6	117.1(18)	Cl_5	C_5	C_6	122.3(15)
C_5	C_6	C_1	125.0(19)	Cl_6	C_6	C_1	116.0(16)
C_6	C_1	C_2	116.5(18)	Cl_6	C_6	C_5	118.9(16)
C_7	C_8	C_9	120.1(18)	O_1	C_1	C_2	123.9(17)
C_8	C_9	C_{10}	116.6(18)	O_1	C_1	C_6	119.3(18)
C_9	C_{10}	C_{11}	126.1(19)	O_2	C_2	C_1	121.9(17)
C_{10}	C_{11}	C_{12}	115.5(20)	O_2	C_2	C_3	118.9(16)
C_{11}	C_{12}	C_7	118.8(16)	As	C_7	C_8	119.4(14)
C_{12}	C_7	C_8	122.7(16)	As	C_7	C_{12}	117.8(14)
C_{13}	C_{14}	C_{15}	122.6(20)	As	C_{13}	C_{14}	118.8(14)
C_{14}	C_{15}	C_{16}	118.4(21)	As	C_{13}	C_{18}	122.5(14)
C_{15}	C_{16}	C_{17}	120.0(21)	As	C_{19}	C_{20}	116.0(14)
				As	C_{19}	C_{24}	119.4(15)

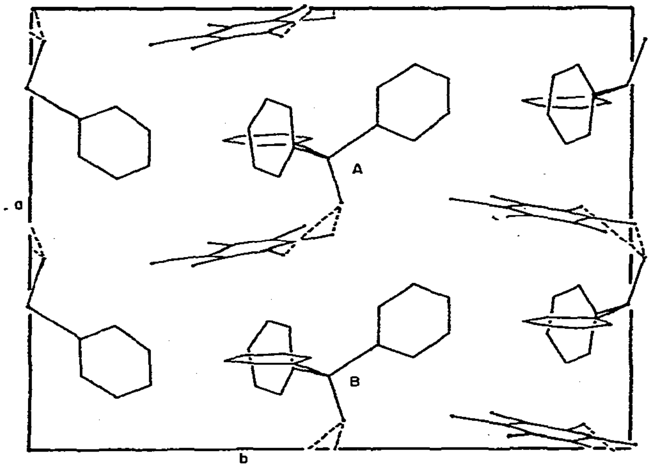


Fig. 2. View down the c axis of the front half of the unit cell. The front and rear halves are related by a center at 1/2, 1/2, 1/2.

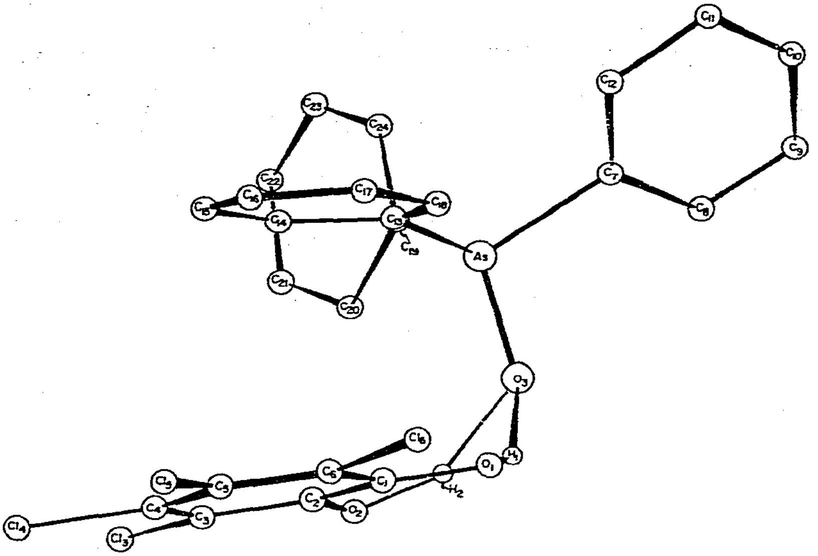


Fig. 3. View of the triphenylarsine oxide–tetrachlorocatechol complex down the *c* axis. Hydrogens 8–24 have been omitted for clarity. The As–C_{19} bond is obscured.

suggest that the two O_{As}–H bonds do not differ significantly. The O–O_{As}–O angle is particularly acute with a value of 65.4(4)°. The hydrogen bond system thus forms as a seven membered ring, $O_{As}H_2(O_C)_2C_2$, with O_{As} chelated by the two H atoms.

The dimensions of the triphenylarsine oxide group (Table 5) are similar to those found in $HgCl_2 \cdot 2[(C_6H_5)_3AsO]$[10]; $HgCl_2 \cdot (C_6H_5)_3AsO$[11]; $SbCl_3 \cdot 2[(C_6H_5)_3AsO]$[12]; $UO_2(NO_3)_2 \cdot 2[(C_6H_5)_3AsO]$[13]; and $\{[(C_6H_5)_3AsO]_2H\}_2Hg_2Br_6$[14]; although the configuration of the phenyl rings with respect to the As=O bond is quite different from that found in the compounds noted above. There is also a significant shortening of one of the As–C bonds. The geometry about the As is essentially tetrahedral with C–As–C angles of 111.8(8)°, 107.0(8)° and 106.4(8)° and O–As–C angles of 107.9(7)°, 110.4(6)°, and 113.4(6)°. The As=O distance is 1.694(9)Å, while the As–C distances are 1.919(17)Å, 1.859(18)Å and 1.928(19)Å for As–C_7, As–C_{13}, and As–C_{19}, respectively. The phenyl rings are hexagonal within experimental error with C–C bond lengths averaging 1.384(24)Å.

The 15 H atoms of the $(C_6H_5)_3AsO$ group were located from difference maps and refined rather than positioned from geometrical and bond length considerations. This technique was utilized in order to determine the reliability of hydrogen positions determined in this fashion so that an estimate of the deviations associated with the hydrogen atoms of the catechol ring would be available. The C–H distances in the triphenylarsine oxide group were found to range from 0.54 Å to 1.19 Å with an average of 0.95 Å and a deviation of 0.20 Å. In view of the large variations in these hydrogen positions, the best that can be said for the average O–H and O_{As}–H distances of 0.82(19)Å and 1.84(19)Å, respectively, is that they are not inconsistent with the proposed hydrogen bonded system.

The best planes for the atoms of each phenyl group were calculated using the least squares technique of Schomaker *et al.*[15] The results of this calculation (Table 7) show that all atoms of a given ring and the As atom are coplanar within experimental error. The angles between the planes of the phenyl rings (Table 8) range from 91° 1′ to 122° 16′. The angles between the phenyl rings and the plane defined by O_{As}, As, and the substituted carbon of the phenyl ring range from 15° 17′ to 80° 8′, with the phenyl ring which is approximately parallel to the catechol ring forming the 80° 8′ angle.

TABLE 7

EQUATIONS OF PLANES REFERRED TO THE CRYSTALLOGRAPHIC AXES[a]

Atoms in Plane	M_1	M_2	M_3	D
C_1–C_6, Cl_3–Cl_6, O_1, O_2	14.70	−3.283	−2.255	4.992
C_7–C_{12}	−6.237	7.343	13.60	0.8939
C_{13}–C_{18}	14.92	−0.3525	−2.349	9.847
C_{19}–C_{24}	−1.392	18.72	0.8453	7.179
As, O_3, C_7	0.7585	0.1618	16.51	2.184
As, O_3, C_{13}	3.961	15.33	8.545	11.09
As, O_3, C_{19}	3.351	15.84	−8.142	9.318
C'_1–C'_6, Cl'_3–C'_6, O'_1, O'_2	14.70	−3.283	2.255	13.47

[a] The equation for a plane is $M_1(X)+M_2(Y)+M_3(Z)=D$, where D is the origin to plane distance. Unprimed atoms are in molecule A, Fig. 2; primed atoms are in molecule B.

TABLE 8

ANGLES BETWEEN PLANES[a]

Plane 1	Plane 2	Angle
C_1–C_6, Cl_3–Cl_6, O_1, O_2	C_{13}–C_{18}	8° 58′
C'_1–C'_6, Cl'_3–Cl'_6, O'_1, O'_2	C_{13}–C_{18}	18° 23′
C_7–C_{12}	C_{13}–C_{18}	122° 16′
C_7–C_{12}	C_{19}–C_{24}	97° 39′
C_{13}–C_{18}	C_{19}–C_{24}	88° 59′
C_7–C_{12}	As, O, C_7	36° 32′
C_{13}–C_{18}	As, O, C_{13}	80° 8′
C_{19}–C_{24}	As, O, C_{19}	15° 7′
As, O, C_7	As, O, C_{13}	118° 16′
As, O, C_7	As, O, C_{19}	122° 27′
As, O, C_{13}	As, O, C_{19}	119° 18′

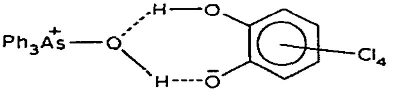
[a] Unprimed atoms are in molecule A, Fig. 2; primed atoms are in molecule B.

The dimensions of the tetrachlorocatechol group are similar to those observed in tetrachlorohydroquinone[16]. The C_6 ring is hexagonal with C–C distances averaging 1.375(14)Å. All C, Cl, and O atoms are coplanar within experimental error. The C–O distances are equivalent with values of 1.307(20)Å, and 1.327(22)Å while the C–Cl distances average 1.736(22)Å.

DISCUSSION

Chelating hydrogen bonds of the type observed in the adduct of tetrachlorocatechol with triphenylarsine oxide are not uncommon, but they are observed only in special circumstances. The spatial requirements for chelating hydrogen bonds are similar to those required for the formation of intramolecular hydrogen bonds[17]. Thus, not only are α,α; α,β; or *ortho*-hydrogen bonding radicals required, but also the molecular geometry must be such that crystal packing with formation of extended hydrogen bonding networks is not possible. For example, crystals of tartaric acid[18], sucrose[19], oxalic acid dihydrate[20], and glycylglycine[21], do not contain chelated hydrogen bond systems although these molecules have the necessary α,α- or α,β-hydrogen bonding radicals. On the other hand, compounds such as tris(ethylenediammine)nickel(II) sulfate[22]; urea[23]; tris(cyclohexane-1,2-diamine)cobalt(III) trichloride pentahydrate[24]; bis(benzoylhydrazine)copper(II) pentachlorotricuprate-(I)[25]; ethylenebis(biguanidine)nickel(II) chloride hydrate[26]; bis[2,2′-iminobis-(acetamidoxime)]nickel(II) chloride dihydrate[27]; *trans*-bis(dimethylamine)diammineplatinum(II) chloride[28]; dicyandiamide[29]; and the triphenylarsine oxide–tetrachlorocatechol adduct; in which the O–H or N–H hydrogen bonding radicals are constrained to a chelating configuration by the molecular geometry or are prevented from forming extended hydrogen bonding networks by the bulk of the remainder of the molecule, do form chelating hydrogen bonded systems. The 65.4° angle between the two hydrogen bonded pairs of oxygens, $O-O_{As}-O$, in the arsine oxide–catechol adduct is quite small, but similar angles of this size have been observed[24,25,27].

A description of the adduct as a zwitterion, is not consistent with the equivalent



O_C–H distances nor, more significantly, with the As–O distance. The As–O distance of 1.694(9)Å may reflect some reduction from the As–O multiple bond order in free triphenylarsine oxide, but it is appreciably less than the As–O single bond distance of 1.87 Å calculated from covalent radii and the observed[30,31] As–OH distances of 1.747(8)Å in two salts of $AsO_3(OH)^{2-}$.

In addition to the catechol–arsine oxide hydrogen bonding, it appeared at first sight that the adduct was stabilized by a π–π interaction between the catechol ring and one of the phenyl rings of the triphenylarsine oxide. It may be seen (Figs. 2 and 3) that one of the phenyl rings is approximately parallel to the catechol ring of the same molecule. This, in combination with the staggered configuration of the two rings, suggested that π-bonding interactions might exist between the two rings. The angle between these rings is 8° 58′ (Table 8). These rings, however, are separated by a minimum distance of 3.53 Å, (Table 9), a distance considered[32] too great for effective overlap. The absence of a π-interaction is consistent with near infrared, visible and ultraviolet spectroscopic studies which showed no features attributable to a π donor–acceptor complex. In viewing the entire unit cell (Figs. 1 and 2), it may be seen that this staggered, parallel

TABLE 9

PERPENDICULAR DISTANCE BETWEEN CATECHOL AND PHENYL RINGS[a]

Plane 1	Point (atom) in plane 2	Distance (Å)
C_1–C_6, Cl_3–Cl_6, O_1, O_2	C_{15}	3.81
C_1–C_6, Cl_3–Cl_6, O_1, O_2	C_{16}	3.67
C_{13}–C_{18}	C_1	3.53
C_{13}–C_{18}	C_2	3.59
C_{13}–C_{18}	C_6	3.58
C_1–C_6	C'_{14}	4.04
C_1–C_6	C'_{15}	3.58
C'_1–C'_6	C_{14}	4.03
C'_1–C'_6	C_{15}	3.58
C'_{13}–C'_{18}	C_1	3.93
C'_{13}–C'_{18}	C_2	3.56
C'_{13}–C'_{18}	C_6	4.23

[a] These are the perpendicular distances between a catechol (or phenyl) plane and a point (atom) in an adjacent phenyl (or catechol) ring. Unprimed atoms are in molecule A, Fig. 2; primed atoms are in molecule B.

arrangement of phenyl and catechol rings is not limited to those rings within a molecule, but exists throughout the structure. The crystal contains alternating phenyl and catechol rings, each approximately parallel and in a staggered arrangement to the rings adjacent to it. Again, the angles between these rings appear to indicate π interactions, but the interplanar distances (Table 9) and near infrared, visible, and ultraviolet spectra are consistent only with van der Waal's interactions.

The crystal packing of alternate, approximately parallel phenyl and catechol rings results in a gross distortion of the commonly observed geometry of triphenylarsine oxide. Although somewhat sensitive to packing effects, coordinated triphenylarsine oxide groups approximate, albeit rather roughly in some cases, C_3 symmetry with respect to the As=O axis. Observed angles[10–14] between the phenyl rings and the planes defined by the O,As, and substituted C of the phenyl groups range from 10° to 33°. In the catechol adduct these angles are 15° 17′, 36° 32′, and 80° 8′, with the phenyl ring which is approximately parallel to the catechol forming the 80° 8′ angle.

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