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Crystal and Molecular Structure of Trimercury Chloroaluminate, $Hg_3(AlCl_4)_2$[1a]

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The structure of $Hg_3(AlCl_4)_2$ was determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes with the symmetry of space group $P2_1/c$ and cell parameters at 23° of $a = 7.1321$ (2), $b = 15.0468$ (3), $c = 14.1771$ (4) Å, $\beta = 99.050$ (3)°, and $Z = 4$. The structure was solved from the Patterson function and refined by the method of least squares to a discrepancy index R_F of 0.082. The crystal contains discrete molecules having a nearly linear -Cl-Hg-Hg-Hg-Cl- central skeleton, of which the chlorine atoms are shared with two nearly tetrahedral terminal $AlCl_4$ groups. The average Hg-Hg bond length is 2.56 Å, and the average Hg-Cl bond length is 2.54 Å.

The preparation and characterization of the compound $Hg_3(AlCl_4)_2$ has been reported by Torsi, Fung, Begun, and Mamantov.[2] Their observation of two strong lines in the Raman spectrum of the polycrystalline solid, ascribed to symmetric and antisymmetric vibrations of an Hg_3 group, appeared to preclude a linear symmetric configuration of the mercury atoms. The present X-ray study was undertaken to establish the configuration of the Hg_3 grouping and to provide structural-chemical details for the compound.

Yellow needle-shaped crystals were grown from the melt. Because the crystals are highly hygroscopic, all manipulations were carried out in a dry glove box (<2 ppm H_2O). The density was determined to be 3.95 g cm^{-3} from the volume of a known weight of polycrystalline material solidified in a calibrated bulb. All X-ray diffraction measurements were obtained from a specimen about 0.05 × 0.10 × 0.40 mm sealed in a thin-wall glass capillary.

The crystals are monoclinic (space group $P2_1/c$, systematic absences: $h0l$, l odd; $0k0$, k odd); there are four molecules in the unit cell with parameters (at 23° ± 1.5°) $a = 7.1321$ (2), $b = 15.0468$ (3), $c = 14.1771$ (4) Å, $\beta = 99.050$ (3)°, based on the wavelength of 1.54051 Å for Cu $K\alpha_1$ radiation. The calculated density is 4.16 g cm^{-3}, in satisfactory agreement with the observed value.

Measurements of 5580 Bragg reflections, corresponding to a set of 4391 symmetry-nonequivalent reflections, were made on the Oak Ridge computer-controlled X-ray diffractometer[3] with Nb-filtered Mo $K\alpha$ radiation. Observations were made by θ-2θ scans in the range $20 \leqslant 2\theta \leqslant 60°$ and by the ω-scan technique in the range $1 \leqslant 2\theta \leqslant 35°$. Reduction of the intensities to $|F|^2$ values utilized a least-squares refinement (to be reported elsewhere[4]) of the size, shape, and orientation parameters of the specimen to permit calculation of absorption corrections. The linear absorption coefficient is 327 cm^{-1}; the range of transmission factors is 0.15-0.52. Standard errors in the net count $N \equiv T - kB$ were estimated according to the formula $\sigma^2(N) = T + k^2B + (0.04N)^2$, where T is the total count, B the background count, and k is the ratio of times spent measuring T and B; the larger than normal factor 0.04 reflects uncertainties in the absorption correction and was estimated from the concordance of the $F_o{}^2$ values for equivalent reflections.

The structure was solved by inspection of the map of a Patterson function.[5] One scale factor, one parameter for isotropic extinction,[6] the positional coordinates, and the anisotropic temperature factors for the 13 atoms in the asymmetric unit were refined by the method of least squares to a final standard error of fit of 1.055 (4265 degrees of freedom) and a conventional discrepancy index R_F of 0.082 for reflections with $|F|^2 \geqslant \sigma(F^2)$. Calculated structure factors utilized atomic scattering amplitudes and corrections for anomalous dispersion from the sources given in Table I.[7-10]

TABLE I

				References for	
Atoms	Ionization	$\Delta f'$	$\Delta f''$	Amplitude	Correction
Al	+3	0.07	0.07	7	8
Cl	−1	0.15	0.19		
Hg(1)	+2	−3.084	9.223	9	10
Hg(2, 3)	0				

The final value of the extinction parameter (g' of Coppens and Hamilton[6]) corresponds to a mosaic spread parameter of 22″ or to a spherical domain radius of 0.19 μ. The most severe correction factors, those for reflections (022) and (102), are 0.82. Observed structure factors, scaled according to the least-squares scale factor and corrected for extinction, are listed[11] in Table II, together with estimated standard errors and the final calculated values.

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(1) (a) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp. and Contract AT(40-1)-3518. (b) Oak Ridge National Laboratory. (c) University of Tennessee.

(2) G. Torsi, K. W. Fung, G. M. Begun, and G. Mamantov, *Inorg. Chem.*, **10**, 2285 (1971).

(3) W. R. Busing, R. D. Ellison, H. A. Levy, S. P. King, and R. T. Roseberry, "The Oak Ridge Computer Controlled X-ray Diffractometer," Report ORNL-4143, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1967.

(4) H. A. Levy and R. D. Ellison, to be submitted for publication in *J. Appl. Crystallogr.*; Report No. ORNL-4706, Oak Ridge National Laboratory, 1971, p 204.

(5) The Patterson function was computed using A. Zalkin's program FORDAPER as modified by G. Brunton of this laboratory. Computer programs used in this study include data library and sorting programs written by the authors; XFLS, a recent version of the Busing-Levy program ORFLS; C. K. Johnson's program ORTEP, as well as the program to be described in ref 4.

(6) The extinction correction is that derived by W. H. Zachariasen, *Acta Crystallogr.*, **23**, 558 (1967), and incorporated into the least-squares refinement as described by P. Coppens and W. H. Hamilton, *ibid., Sect. A*, **26**, 71 (1970).

(7) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, pp 202, 203.

(8) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(9) D. T. Cromer, A. C. Larson, and J. T. Waber, Report No. LA-2987, Los Alamos Scientific Laboratory, Los Alamos, N. M., 1963.

(10) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(11) Table II will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE III

STRUCTURAL PARAMETERS[a] FOR $Hg_3(AlCl_4)_2$

	Hg(1)	Hg(2)	Hg(3)	Al(4)	Cl(5)	Cl(6)	Cl(7)	Cl(8)	Al(9)	Cl(10)	Cl(11)	Cl(12)	Cl(13)
x	−18,404 (9)	−717 (9)	−36,836 (10)	39,421 (59)	31,815 (57)	40,606 (60)	17,632 (49)	64,602 (50)	−80,499 (57)	−84,623 (61)	−51,528 (49)	−99,464 (55)	−82,452 (58)
y $\times 10^5$	13,704 (4)	25,968 (4)	2510 (5)	31,796 (29)	32,796 (30)	18,420 (26)	38,322 (22)	39,109 (25)	−10,232 (29)	−23,794 (25)	−8778 (27)	−6305 (29)	−2137 (25)
z	10,988 (5)	3601 (4)	19604 (5)	−9490 (29)	−24,468 (25)	−4485 (31)	−2709 (26)	−4707 (30)	22,323 (28)	18,960 (26)	29,828 (25)	31,540 (26)	9877 (23)
β_{11}	1850 (13)	2033 (14)	1978 (15)	1510 (87)	2235 (93)	2411 (100)	1582 (72)	1320 (69)	1249 (80)	2703 (101)	1392 (68)	2000 (86)	2622 (99)
β_{22}	346 (3)	370 (3)	435 (3)	317 (18)	602 (23)	337 (16)	307 (15)	388 (16)	332 (18)	341 (15)	496 (19)	550 (21)	378 (17)
β_{33} $\times 10^5$	489 (3)	425 (3)	681 (4)	348 (20)	327 (16)	680 (25)	553 (21)	658 (23)	339 (20)	431 (18)	417 (18)	424 (18)	304 (16)
β_{12}	−76 (5)	−217 (5)	−102 (6)	−22 (33)	−180 (39)	40 (33)	−127 (26)	−98 (27)	−41 (33)	−171 (34)	−165 (31)	163 (35)	108 (33)
β_{13}	281 (5)	230 (5)	436 (7)	131 (34)	−10 (32)	208 (41)	340 (33)	51 (33)	57 (33)	179 (34)	−31 (28)	277 (34)	8 (32)
β_{23}	101 (2)	66 (3)	178 (3)	38 (17)	68 (17)	143 (19)	14 (15)	−83 (17)	9 (17)	−30 (15)	159 (16)	−56 (18)	82 (14)
ν_1	58	57	61	395	344	378	316	347	392	361	327	346	319
ν_2 $\times 10^5$	65	63	72	421	399	418	337	383	399	370	345	394	375
ν_3	69	69	80	437	464	445	374	421	435	438	425	445	411
μ $\times 10^{-2}$	3623	4375	3694	94	123	118	156	119	100	120	133	123	137
λ	−958	−1165	−1012	−38	−50	−47	−60	−46	−40	−48	−53	−49	−53
$R \times 10^2$	10	17	11	12	12	13	8	13	11	13	12	10	8

[a] x, y, and z are fractional atomic coordinates. β_{ij} are the elements of the thermal tensor β. The remaining symbols are defined in the text. Least-squares-estimated standard errors in the least significant digits are given in parentheses.

In Table III are presented the parameters from least-squares refinement with their estimated standard errors. In addition to the usual atomic parameters, we list five additional quantities—ν_1, ν_2, ν_3, λ, μ—which according to a new formulism developed by Johnson[12] are sufficient to specify in good approximation all the significant components of the covariance matrices for intraatomic parameters. The quantities ν_j are the three principal rms errors of the cartesian positional parameters of an atom. If the associated second-rank tensor is referred to the principal-axis system of the thermal tensor β for that atom and appropriately transformed to crystal coordinates, its elements c^{ij} form a good approximation to $\mathrm{cov}(x^i, x^j)$. A good approximation to $\mathrm{cov}(\beta^{ij}, \beta^{kl})$ is then furnished by the quantities $[\mu(c^{ik}c^{jl} + c^{il}c^{jk}) + \lambda c^{ij}c^{kl}]4\pi^4$. Elements of the type $\mathrm{cov}(x^i, \beta^{jk})$ are small and may be neglected. The final entries R in Table III provide measures of misfit as defined by Johnson[12] between the approximate and actual covariances.

Bond distances and angles for the structure are listed in Table IV. The molecule, illustrated in Figure 1, contains Hg–Hg bonds averaging 2.56 Å in length and Hg–Cl bonds averaging 2.54 Å; it is well isolated from neighboring molecules, for which the closest approach is a contact Hg···Cl of 3.21 Å. The central skeleton is nearly linear with angles Cl(7)–Hg(2)–Hg(1) = 176.6 (1)°, Cl(11)–Hg(3)–Hg(1) = 172.8 (1)°, and Hg(2)–Hg(1)–Hg(3) = 174.42 (4)°. The coordination of Cl atoms around both Al atoms is nearly that of a regular tetrahedron, the angles ranging from 104.5 to 113.3°. The bonds from Al to the bridging Cl atoms average 2.18 Å, longer by 0.06 Å than the average of those to terminal Cl atoms. There is an approximation to twofold rotational symmetry about an axis through the central Hg atom.

TABLE IV

BOND DISTANCES AND BOND ANGLES IN $Hg_3(AlCl_4)_2$

Distance, Å			
Hg(1)–Hg(2)	2.551 (1)	Hg(1)–Hg(3)	2.562 (1)
Hg(2)–Cl(7)	2.517 (3)	Hg(3)–Cl(11)	2.562 (4)
Al(4)–Cl(5)	2.113 (6)	Al(9)–Cl(10)	2.106 (6)
Al(4)–Cl(6)	2.131 (6)	Al(9)–Cl(11)	2.181 (5)
Al(4)–Cl(7)	2.185 (5)	Al(9)–Cl(12)	2.108 (5)
Al(4)–Cl(8)	2.124 (6)	Al(9)–Cl(13)	2.131 (5)

Angle, deg			
Hg(2)–Hg(1)–Hg(3)	174.42 (4)		
Hg(1)–Hg(2)–Cl(7)	176.6 (1)	Hg(1)–Hg(3)–Cl(11)	172.8 (1)
Hg(2)–Cl(7)–Al(4)	105.7 (2)	Hg(3)–Cl(11)–Al(9)	103.4 (2)
Cl(5)–Al(4)–Cl(6)	113.1 (3)	Cl(10)–Al(9)–Cl(11)	107.2 (2)
Cl(5)–Al(4)–Cl(7)	108.8 (2)	Cl(10)–Al(9)–Cl(12)	109.4 (2)
Cl(5)–Al(4)–Cl(8)	110.8 (2)	Cl(10)–Al(9)–Cl(13)	112.2 (2)
Cl(6)–Al(4)–Cl(7)	105.8 (2)	Cl(11)–Al(9)–Cl(12)	108.7 (2)
Cl(6)–Al(4)–Cl(8)	113.3 (2)	Cl(11)–Al(9)–Cl(13)	106.3 (2)
Cl(7)–Al(4)–Cl(8)	104.5 (2)	Cl(12)–Al(9)–Cl(13)	112.9 (2)

The Hg_3 group has been found also in a study[13] of the compound $Hg_3(AsF_6)_2$, which came to our attention after completion of the present work; in this case the group is required by site symmetry to be linear and

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(12) C. K. Johnson, Program and Abstracts, American Crystallographic Association Summer Meeting, Ames, Iowa, 1971, Paper No. B3; Chemistry Division Annual Progress Report ORNL-4706, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1971, p 205.

(13) C. G. Davies, P. A. W. Dean, R. J. Gillespie, and P. K. Ummat, *Chem. Commun.*, 782 (1971).

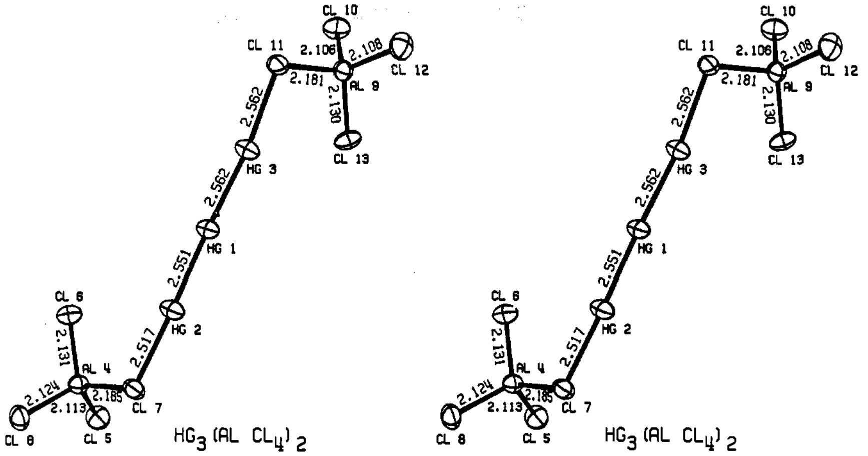

Figure 1.—Stereoscopic illustration of the molecular structure of $Hg_3(AlCl_4)_2$. Atoms are represented by 50% probability thermal ellipsoids. Interatomic distances in ångström units are shown; their standard errors are as follows: Hg–Hg, 0.001 Å; Hg–Cl, 0.004 Å; Al–Cl, 0.006 Å. The view was chosen to illustrate the approximate twofold rotational symmetry. Note that since both Al atoms lie behind the central skeleton the departure from inversion symmetry is considerable.

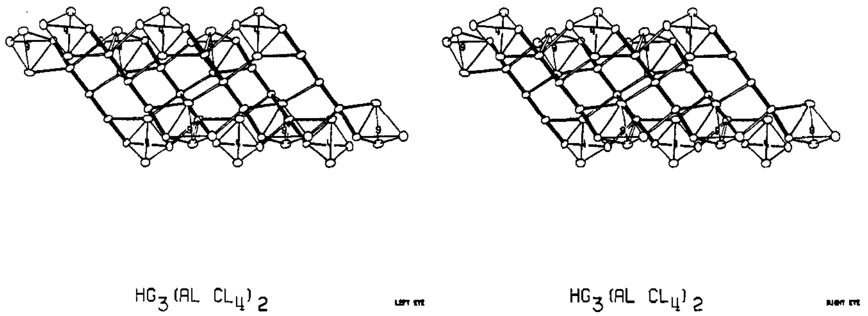

Figure 2.—Stereoscopic illustration of the packing of $Hg_3(AlCl_4)_2$ molecules into chains. Three repeating units are shown. The $AlCl_4^-$ tetrahedra are outlined with single, light lines, and nonbonded Hg · · · Cl contacts are indicated by double lines. The *a* axis of the crystal is horizontal.

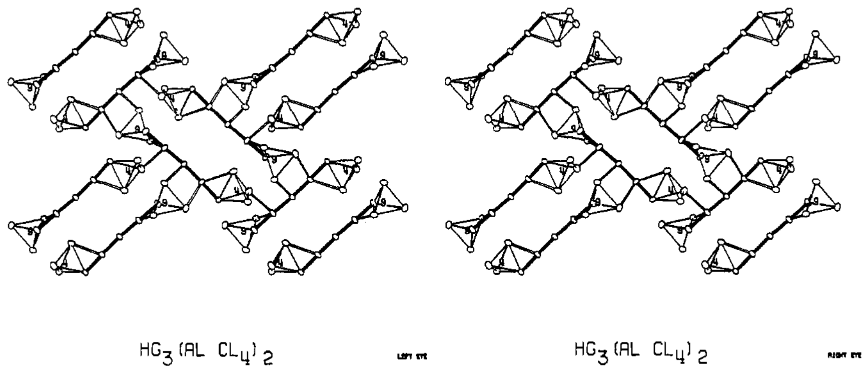

Figure 3.—Stereoscopic illustration of the net of $Hg_3(AlCl_4)_2$ molecules parallel to (102) planes of the crystal. The view direction is along the normal to (102); the *b* axis is vertical and the [20$\bar{1}$] zone axis is horizontal.

symmetric, and the Hg–Hg bond length of 2.55 Å is in good agreement with the value 2.56 Å found in $Hg_3(AlCl_4)_2$. These values are somewhat larger than those in the range 2.49–2.54 Å reported for the Hg–Hg bond lengths in several halide[14] and other salts[15–20] of the mercurous ion Hg_2^{2+}. The increase is in accord with expectation for the lower average oxidation state of mercury in Hg_3^{2+}.

The average Hg–Cl bond length of 2.54 Å in $Hg_3(AlCl_4)_2$, in which the Cl atom is a bridge between Hg and Al, is significantly greater than the recently reported[14] values of 2.43 Å in Hg_2Cl_2, in which no bridging occurs. The Al–Cl distances, 2.106–2.185 Å, are similar to those reported[21] for $Co(AlCl_4)_2$, 2.105 Å for the terminal Cl atoms and 2.151–2.188 Å for the bridging Cl atoms. The distances[22] in $NaAlCl_4$, all to nonbridging Cl atoms, are also similar, 2.11–2.16 Å. (The variation of 0.05 Å is within the expected experimental error of this relatively early study; it should not be attributed to the effects of packing.)

[14] E. Dorm, *Chem. Commun.*, 466 (1971).
[15] D. Grdenić, *J. Chem. Soc.*, 1312 (1956).
[16] G. Johansson, *Acta Chem. Scand.*, **20**, 553 (1966).
[17] E. Dorm, *ibid.*, **21**, 2834 (1967).
[18] B. Lindh, *ibid.*, **21**, 2743 (1967).
[19] R. C. Elder, J. Halpern, and J. S. Pond, *J. Amer. Chem. Soc.*, **89**, 6877 (1967).
[20] E. Dorm, *Acta Chem. Scand.*, **23**, 1607 (1969).
[21] J. A. Ibers, *Acta Crystallogr.*, **15**, 967 (1962).
[22] N. C. Baenziger, *ibid.*, **4**, 216 (1951).

The structural evidence shows that $Hg_3(AlCl_4)_2$ is appropriately formulated as a molecular compound. The Hg–Cl bond distance of 2.54 Å is not much longer than 2.47 Å, the sum of the covalent radii according to Pauling;[23] in any case, it is much shorter than the distance of at least 3 Å to be expected on the basis of an ionic formulation of the compound, *i.e.*, $(Hg_3)^{2+}(AlCl_4^-)_2$. Since the distances from the Al atoms to the bridging Cl atoms are both significantly longer than those to nonbridging Cl atoms, it is clear that Hg competes effectively with Al for the valence electrons of Cl.

Two strong Raman lines have been reasonably assigned[2] to stretching vibrations involving the central Hg_3 group. The small departure of this group from linearity, while sufficient to permit the appearance of the two lines, may not completely explain their comparable intensity. It seems likely that the Hg_3 group interacts with the noncentrosymmetrically disposed terminal $AlCl_4$ groups to enhance the intensity of the line involving the pseudoantisymmetric vibration.

Significant contacts between molecules of $Hg_3(AlCl_4)_2$ are all between Hg and Cl atoms; each Hg is surrounded by five Cl atoms at distances of less than 4 Å. Hg(1), the central atom of the molecular skeleton, has five intermolecular contacts with Cl atoms ranging in length from 3.39 to 3.88 Å. Hg(2) and Hg(3) each have four intermolecular Cl contacts at distances of 3.21–3.84 Å; Hg(2) has in addition one intramolecular Cl contact at 3.52 Å, and Hg(3) has one at 3.40 Å. There are four intermolecular contacts between Cl atoms ranging in length from 3.51 to 3.60 Å; all other intermolecular Cl–Cl contacts are at distances greater than 3.7 Å. The arrangement of the molecules may be visualized as consisting of double chains along the crystal *a* axis, as illustrated in Figure 2. The chains are linked to neighboring chains by Hg···Cl contacts that form a net of molecules in the (102) planes of the crystal, as shown in Figure 3.

Acknowledgments.—The authors are indebted to Professor G. Mamantov[1c] for suggesting this crystal structure determination and for valuable discussions in connection with it.

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[23] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 246.

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The Crystal and Molecular Structure of Diphenyldiarsenic Trisulfide. A Five-Membered Arsenic–Sulfur Ring Compound[1]

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The crystal and molecular structure of diphenyldiarsenic trisulfide, $As_2S_3(C_6H_5)_2$, was determined from three-dimensional X-ray data collected with a manual diffractometer using Mo Kα (λ 0.71069 Å) radiation. The compound crystallizes in the monoclinic space group $C2/c$, with a = 15.966 (3) Å, b = 7.515 (2) Å, c = 12.465 (2) Å, β = 109.55 (1)°, Z = 4, d_{measd} = 1.88 (2) g cm^{-3}, and d_{calcd} = 1.87 g cm^{-3}, at 23°. The structure was determined by Patterson and Fourier methods and refined with 532 observed reflections by full-matrix least squares to an R of 0.061. The molecule consists of a five-membered, nonplanar arsenic–sulfur ring with the sequence –As–S–As–S–S–. One phenyl ring is bonded to each arsenic atom. A crystallographic twofold rotation axis passes through the molecule. The As–S bond distances are 2.252 (5) and 2.253 (4) Å, the As–C bond length is 1.95 (1) Å, and the S–S bond length is 2.036 (6) Å. The bond angles around the arsenic are 98.4 (1), 99.7 (5), and 101.3 (4)°, the As–S–As bond angle is 107.47 (7)°, and the As–S–S bond angle is 101.1 (1)°. These parameters are interpreted to denote little or no π bonding in the As–S ring.

Introduction

The large variety of unique ring structures found in the nitrogen–sulfur system[3] has led us to undertake structural studies of what appears to be an equally varied system of arsenic–sulfur cyclic molecules. Crystal structures of five-, six-, and eight-membered arsenic–sulfur ring systems are being examined. The subject of this report, diphenyldiarsenic trisulfide ($As_2S_3(C_6H_5)_2$), contains a five-membered As–S ring. The compound was first reported almost 100 years ago[4] but it appears it was not considered a ring molecule prior to our structural study.

Data Collection and Reduction

$As_2S_3(C_6H_5)_2$ was prepared by the method of Schulte,[4] which involves successive treatment of a solution of phenylarsenic acid with aqueous ammonia, hydrogen sulfide gas, and concentrated hydrochloric acid. The clear, needlelike crystals were obtained by slow evaporation of a chloroform–octane mixed solvent; mp 130°. A mass spectrum confirmed the molecular formula. The measured density obtained by suspension in a mixture of tetrachloroethylene and 1,3-dibromopropane was 1.88 (2) g cm^{-3}, in agreement with the density of 1.87 g cm^{-3} calculated for four molecules per unit cell. Four molecules per unit cell in space group $C2/c$ implies the molecular centers must lie on a crystallographic center of symmetry or a twofold rotation axis.

The approximately parallelpiped crystal used for the diffractometer data collection measured 0.24 × 0.36 × 0.66 mm (all ±0.01 mm) in the [$\bar{3}$01], [101], and [010] directions. The crystal was mounted with b^* approximately parallel to the ϕ axis. The unit cell parameters at 23° are a = 15.966 (3), b = 7.515 (2), c = 12.465 (2) Å, and β = 109.55 (1)° as determined by a least-squares refinement[5] of the setting angles of

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[3] O. Glemser, *Angew. Chem., Int. Ed. Engl.*, **2**, 530 (1963).

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