bonds of the basal plane are shorter than the correspon-ding $Cu-N(1) = 2\cdot005$ (3) and $Cu-N(3) = 2\cdot007$ (2) Å of the ternary Cu^{II} complex $[Cu(dpa)(sal)]ClO_4$, but similar to the corresponding distances in the $[Cu(dp)(sal)]ClO_4$ complex, $Cu-N(1) = 1\cdot981$ (3) and $Cu-N(2) = 1\cdot983$ (3) Å. The values reported in this work are similar to $Cu-N$ distances for $[Cu(phen)$ or $(dp)_2OXO]Y$ complexes (Simmons, Seff, Clifford & Hathaway, 1983).

The deviations of Cu and of the four donor atoms N(1), N(2), O(1) and O(2) from their mean unweighted plane are $-0\cdot014, 0\cdot058, -0\cdot052, 0\cdot055$ and $-0\cdot047$ Å respectively. The dihedral angle between the planes through Cu, O(1), O(2) and through Cu, N(1), N(2) is $4\cdot7°$. This value is lower than that found for (di-2-pyridylamine)salicylaldehydatocopper(II) perchlorate, $11\cdot8°$ (Garland, Le Marouille & Spodine, 1986). The copper distance to the mean plane of the benzene ring is $-0\cdot536$ Å, comparable to the distances, $-0\cdot700$ and $0\cdot465$ Å, of the other two dimeric ternary complexes of Cu^{II}. The out-of-plane displacements of the Cu atom from the two pyridine rings of the 1,10-phenanthroline molecule are $0\cdot026$ and $0\cdot074$ Å. The corresponding values for the di-2-pyridylamine complex are $0\cdot250$ and $0\cdot379$ Å, and $0\cdot022$ and $-0\cdot086$ Å for the di-2-pyridyl one.

The copper–phenoxo-oxygen–copper angle in the dimeric unit is $95\cdot00$ (8)°. This value is similar to that obtained for the ternary di-2-pyridyl complex $[96\cdot1$ (2)°], but lower than the value found for the di-2-pyridylamine complex $[99\cdot2$ (2)°].

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Structure of 1,1-Diphenylarsenanium Bromide Monohydrate

BY J. A. CAMPBELL* AND R. LARSEN

Chemistry Department, Montana State University, Bozeman, Montana 59715, USA

C. CAMPANA

Nicolet Analytical Instruments, Madison, Wisconsin 53711, USA

AND S. E. CREMER AND A. GAMLIEL

Chemistry Department, Marquette University, Milwaukee, Wisconsin 53233, USA

Abstract. $C_{17}H_{20}As^+.Br^-.H_2O$, $M_r = 397\cdot19$, orthorhombic, $P2_12_12_1$, $a = 8\cdot637$ (2), $b = 12\cdot168$ (4), $c = 16\cdot066$ (7) Å, $V = 1688\cdot44$ Å^3, $Z = 4$, $D_m = 1\cdot56$, $D_x = 1\cdot56$ g cm^{-3}, $Cu K\alpha$, $\lambda = 1\cdot54178$ Å, $\mu = 54\cdot8$ cm^{-1}, $F(000) = 800$, $T = 295$ K, $R = 0\cdot057$, $wR = 0\cdot061$, 1248 observed reflections. The arsenic heterocyclic ring is in the chair form and the torsion angles indicate that it is nearly symmetrical. The As–C bond

* To whom all correspondence should be addressed. Present address: Battelle, Pacific Northwest Laboratories, PO Box 999, Richland, Washington 99352, USA.

distances are 1·911 (11), 1·916 (10), 1·902 (10) and 1·917 (11) Å. The bond angles around As are 103·5 (5), 109·4 (5), 109·9 (4), 109·6 (5), 112·0 (5) and 112·2 (5)°.

Introduction. The mechanism and stereochemical outcome involving the attack of nucleophiles at a phosphorus center (specifically phosphonium salts) have been actively pursued (Gallagher & Jenkins, 1968; Holmes, 1980). In contrast, very little has been reported regarding nucleophilic attack at an arsenic center. The primary reason for this is the short half-life of racemization of arsine oxides (Horner & Winkler, 1964; Horner & Hofer, 1965; Gatilov, Ionov & Molodtsov, 1972) which would result from hydroxide ion attack on arsenium salts with appropriate leaving groups. On the other hand, arsine sulfides are more stable to racemization and have occasionally served as substrates for stereochemical evaluation (Stackhouse, Cook & Mislow, 1973; Horner & Fuchs, 1963).

As part of a general program to probe the stereochemistry of nucleophilic attack at arsenic, we have incorporated the heteroatom into a ring system, since analogous substrates have been so useful in the evaluation of phosphorus stereochemistry (Gallucci & Holmes, 1980). The present investigation is concerned with a structural study of 1,1-diphenylarsenanium bromide monohydrate (I).

(I)
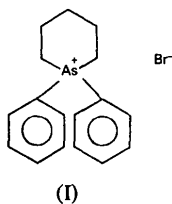
Experimental. The synthesis is based on analogous reactions of α,ω-dihaloalkanes with diphenyltrimethyl-silylphosphine (Haque, Horne, Cremer, Kremer & Mast, 1980) and is illustrated in the following scheme
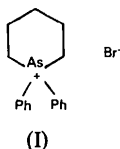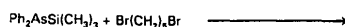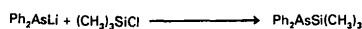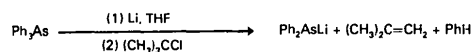
Colorless crystals of the title compound suitable for X-ray analysis obtained by recrystallization from acetonitrile, D_m by flotation in ethanol and methyl iodide, crystal size 0·3 × 0·4 × 0·4 mm, Nicolet $R3m$ diffractometer, graphite monochromator, precise unit-cell parameters (Campana, 1981) from least-squares refinement of 25 reflections (θ range 10–20°), Cu $K\alpha$ radiation ($\lambda = 1·54178$ Å); three standard reflections (057, 434, 623) measured every 120 minutes, average intensity variation < 3%. Range of hkl: $0 \le h \le 10$, $0 \le k \le 14$, $0 \le l \le 18$, data collected by θ–2θ scan, 1800 unique data measured, $3 \le 2\theta \le 55°$, 1248 observed reflections, $I \ge 2\sigma(I)$, Lorentz, polarization, and absorption corrections. Absorption corrections by numerical Gaussian integration method from crystal dimensions and indexed faces. Maximum and minimum transmission coefficients 0·66 and 0·59, respectively. Br⁻ position from Patterson map, full-matrix least squares, $\sum w(|F_o| - |F_c|)^2$ minimized where $w = 1/[\sigma^2(F) + G(F)^2]$ and $G = 0·001$; non-hydrogen atoms anisotropic, H atoms located in ΔF map, idealized coordinates calculated and not refined, isotropic thermal parameters for H's assigned as 0·06 Å², $R = 0·057$ and $wR = 0·061$, scattering factors for As, C, Br, O and H from *International Tables for X-ray Crystallography* (1962), $S = 1·28$. In the final cycle, largest shift in any parameter was 0·06σ. Final difference map showed no peaks larger than 0·50 e Å⁻³ (at 0·90 Å from Br). Calculations carried out with *SHELXTL* package on Nicolet $R3m$ crystallographic system (Sheldrick, 1980).

Discussion. The final atomic parameters are given in Table 1, and the structure and numbering scheme are shown in Fig. 1.* Table 2 is a list of selected interatomic distances and angles with their e.s.d.'s in parentheses. A projection of the structure along c is shown in Fig. 2.

The bond angles around the As atom vary from 103·5 to 112·2° and the average is 109·4°, which is not significantly different from the tetrahedral angle of 109·5°. The As—C bond lengths vary from 1·902 to 1·917 Å with an average bond length of 1·911 (10) Å, which is similar to other published values, *e.g.* 1·915 (8) Å in tetraphenylarsonium trichloride (Bogaard, Peterson & Rae, 1981) and 1·923 (13) and 1·941 (36) Å in tetramethylarsonium dichloro-dimethylgallate and tetramethylarsonium trichloro-monomethylgallate, respectively (Hausen, Guder & Schwarz, 1977).

The As—C distances are 1·911 (11), 1·916 (10), 1·902 (10) and 1·917 (11) Å. The C—C distances of

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43807 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the heterocyclic ring are 1·557 (17), 1·521 (18), 1·517 (17) and 1·528 (17) Å. In comparison, the P—C distances in the isomorphous analog, 1,1-diphenyl-phosphorinanium bromide (Campbell, Larsen, Ekeland & Cremer, 1986), are 1·794 (9), 1·806 (10), 1·796 (9), and 1·783 (10) Å and C—C distances are 1·544 (13), 1·524 (14), 1·516 (15) and 1·542 (15) Å for the phosphorus analog. The bond angles around the As atom are 103·5 (5), 109·4 (5), 109·6 (5), 112·0 (5), 112·2 (5) and 109·9 (4)°. The bond angles around the P atom in the phosphorus analog are similar: 103·7 (5), 111·7 (4), 110·5 (4), 109·8 (4), 111·0 (4) and 109·9 (4)°.

Table 1. *Atom coordinates* (× 10⁴) *and equivalent isotropic thermal parameters* (Å² × 10³)

	x	*y*	*z*	U_{eq}*
Br	5131 (2)	8376 (1)	5845 (1)	63 (1)
As	9053 (1)	8928 (1)	7519 (1)	36 (1)
C(1)	9415 (13)	8322 (11)	6439 (6)	47 (4)
C(2)	10010 (14)	9264 (10)	5866 (7)	55 (4)
C(3)	8933 (17)	10249 (10)	5800 (7)	59 (4)
C(4)	8679 (17)	10862 (10)	6611 (8)	56 (5)
C(5)	7849 (16)	10217 (6)	7294 (7)	45 (4)
C(6)	10974 (12)	9339 (9)	8006 (6)	35 (3)
C(7)	11017 (14)	10156 (10)	8628 (7)	44 (4)
C(8)	12417 (16)	10447 (12)	8970 (7)	58 (4)
C(9)	13742 (16)	9934 (12)	8700 (8)	57 (5)
C(10)	13727 (14)	9113 (10)	8113 (8)	50 (4)
C(11)	12322 (14)	8818 (12)	7762 (7)	56 (4)
C(12)	7989 (13)	7916 (9)	8233 (6)	41 (3)
C(13)	7016 (14)	7144 (11)	7900 (7)	52 (4)
C(14)	6310 (15)	6397 (9)	8392 (8)	53 (4)
C(15)	6588 (16)	6407 (10)	9255 (9)	62 (5)
C(16)	7529 (20)	7193 (12)	9584 (8)	73 (6)
C(17)	8246 (16)	7942 (11)	9082 (7)	61 (4)
O	7369 (12)	8488 (9)	4118 (7)	76 (4)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.
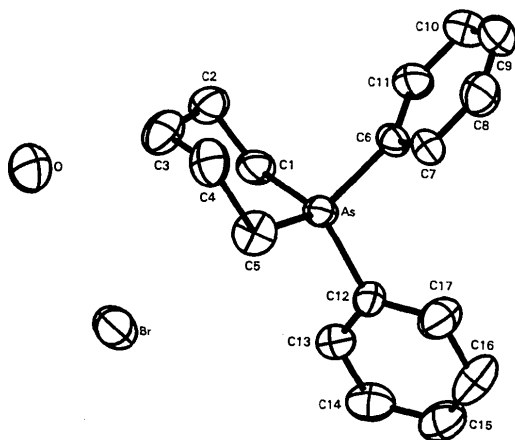
The heterocyclic ring is in the chair form and only slightly distorted from that observed for cyclohexane. The angle between the normal to the least-squares plane through C(1), C(2), C(4) and C(5) and the normal to the plane defined by C(5), As, and C(1) is 46·9°. The angle for this same normal to the least-squares plane of C(1), C(2), C(4), C(5) with the normal to the plane C(2), C(3) and C(4) is 55·4°. For the cyclohexane structure determined by electron diffraction (Davis & Hassel, 1963), the above dihedral angles are 49·2°. Thus, the arsenic portion of the ring is slightly flattened. The Br—O distance is 3·385 (5) Å which indicates hydrogen bonding between the anion and the water molecule.

The torsion angles for the heterocyclic ring are listed in Table 3 and indicate the heterocyclic ring has near-mirror-plane symmetry. The torsion angles are quite similar to those of the phosphorus analog which are also listed in Table 3.

Table 2. *Bond lengths* (Å) *and angles* (°)

As—C(1)	1·911 (11)	As—C(5)	1·916 (10)
As—C(6)	1·902 (10)	As—C(12)	1·917 (11)
C(1)—C(2)	1·557 (17)	C(2)—C(3)	1·521 (18)
C(3)—C(4)	1·517 (17)	C(4)—C(5)	1·528 (17)
C(6)—C(7)	1·410 (16)	C(6)—C(11)	1·382 (16)
C(7)—C(8)	1·374 (18)	C(8)—C(9)	1·373 (19)
C(9)—C(10)	1·375 (18)	C(10)—C(11)	1·386 (17)
C(12)—C(13)	1·369 (17)	C(12)—C(17)	1·382 (15)
C(13)—C(14)	1·350 (17)	C(14)—C(15)	1·408 (19)
C(15)—C(16)	1·362 (20)	C(16)—C(17)	1·365 (19)

| C(1)—As—C(5)	103·5 (5)	C(1)—As—C(6)	109·4 (5)
C(5)—As—C(6)	109·6 (5)	C(1)—As—C(12)	112·0 (5)
C(5)—As—C(12)	112·2 (5)	C(6)—As—C(12)	109·9 (4)
As—C(1)—C(2)	107·9 (8)	C(1)—C(2)—C(3)	114·8 (10)
C(2)—C(3)—C(4)	114·6 (10)	C(3)—C(4)—C(5)	115·6 (10)
As—C(5)—C(4)	107·6 (9)	As—C(6)—C(7)	120·0 (8)
As—C(6)—C(11)	119·8 (8)	C(7)—C(6)—C(11)	120·1 (10)
C(6)—C(7)—C(8)	119·2 (11)	C(7)—C(8)—C(9)	119·3 (12)
C(8)—C(9)—C(10)	122·7 (12)	C(9)—C(10)—C(11)	118·4 (12)
C(6)—C(11)—C(10)	120·2 (12)	As—C(12)—C(13)	120·0 (8)
As—C(12)—C(17)	119·9 (9)	C(13)—C(12)—C(17)	120·0 (11)
C(12)—C(13)—C(14)	120·7 (11)	C(13)—C(14)—C(15)	119·6 (12)
C(14)—C(15)—C(16)	119·3 (12)	C(15)—C(16)—C(17)	120·7 (12)
C(12)—C(17)—C(16)	119·6 (12)		

Fig. 1. The structure and numbering scheme for 1,1-diphenylarsenanium bromide monohydrate. Non-hydrogen atoms are represented as thermal ellipsoids scaled to enclose 50% probability. The hydrogen atoms are omitted for clarity.
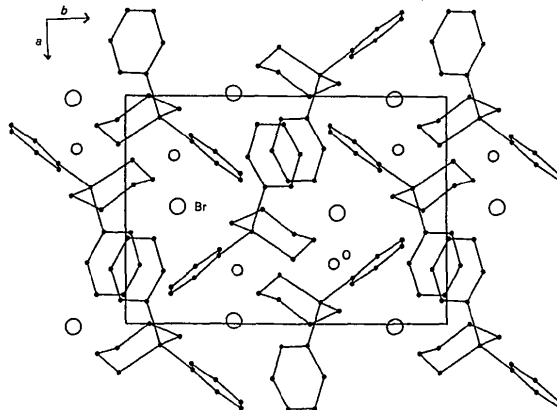

Fig. 2. Crystal structure viewed along the *c* axis.

Table 3. *Comparison of the torsion angles* (°) *in the* As *heterocyclic ring and corresponding phosphorus analog*

	$X = \text{As}$	$X = \text{P}$
X–C(1)–C(2)–C(3)	$-57\cdot1$ (11)	$-58\cdot0$ (9)
C(2)–C(3)–C(4)–C(5)	$-64\cdot9$ (16)	$-64\cdot0$ (12)
C(1)–C(2)–C(3)–C(4)	$63\cdot4$ (14)	$63\cdot0$ (11)
C(5)–X–C(1)–C(2)	$49\cdot1$ (8)	$52\cdot2$ (7)
C(4)–C(5)–X–C(1)	$-49\cdot5$ (9)	$-52\cdot9$ (8)
C(3)–C(4)–C(5)–X	$58\cdot5$ (13)	$. 59\cdot6$ (10)

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Tetraphenylarsonium Tetra(selenocyanato)aurate(III)

BY PETER G. JONES AND CARSTEN THÖNE

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, 3400 Göttingen, Federal Republic of Germany

Abstract. $[\text{As}(\text{C}_6\text{H}_5)_4][\text{Au}(\text{SeCN})_4]$, $M_r = 1000\cdot2$, monoclinic, $C2/c$, $a = 21\cdot226$ (4), $b = 6\cdot460$ (1), $c = 22\cdot307$ (4) Å, $\beta = 99\cdot42$ (2)°, $V = 3017$ Å³, $Z = 4$, $D_x = 2\cdot20$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 10\cdot7$ mm⁻¹, $F(000) = 1856$, $T = 293$ K. The structure was refined to $R = 0\cdot046$ for 2431 absorption-corrected observed reflections. The anion is planar, with Au–Se $2\cdot457, 2\cdot467$ (1) Å. The gold and arsenic atoms occupy special positions with crystallographic symmetry $\bar{1}$ and 2 respectively.

Introduction. Little is known about complexes of gold with selenium donor ligands. Crystal structure determinations have been performed only for chloro(triphenylphosphine selenide)gold(I) (Hussain, 1986), $(\text{Ph}_3\text{PAu})_3\text{Se}^+\text{PF}_6^-$ (Lensch, Jones & Sheldrick, 1982) and the gold(II) ylide complex $[\{\text{Au}(\text{CH}_2)_2\text{PPh}_2\}_2(\text{Cl})(\text{PhSe})]$ (Porter & Fackler, 1987). We have begun a study of gold–selenium complexes and report here the structure of $\text{Ph}_4\text{As}^+\text{Au}(\text{SeCN})_4^-$. Details of the preparation will be published elsewhere.

Experimental. Wine-red plates were obtained by diffusion of petrol ether into a solution in dichloromethane. The crystals are air stable.

A crystal $0\cdot4 \times 0\cdot35 \times 0\cdot05$ mm [plate face $(10\bar{1})$] was used to collect 3112 profile-fitted intensities (Clegg, 1981) on a Stoe–Siemens four-circle diffractometer (monochromated Mo $K\alpha$ radiation, $2\theta_{max} = 53°$, quadrant $\pm h +k +l$). Three check reflections indicated crystal decay of *ca* 5% and the intensities were corrected accordingly. Absorption corrections based on ψ scans were also applied; transmission factors were $0\cdot22–1\cdot00$. Merging equivalents gave 3030 unique reflections ($R_{int} = 0\cdot023$), of which 2431 with $F > 4\sigma(F)$ were used for all calculations (program *SHELX*76; Sheldrick, 1976). Index ranges: $|h| \le 26$, $k \le 7$, $l \le 28$. Cell constants were refined from 2θ values of 62 reflections in the range $20–23°$.

The structure was solved by the heavy-atom method and refined on F to $R = 0\cdot046$, $wR = 0\cdot051$ |non-H atoms anisotropic, H atoms included using a riding model; full matrix, 175 parameters; weighting scheme