

The Synthesis and Crystal Structure of [*cyclo*-(CH₂)₅As(OH)₂]Cl: A Protonated Arsenic Acid

James W. Pasterczyk,^a Atta M. Arif,^b and Andrew R. Barron*^a

^a Chemical Laboratories, Harvard University, Cambridge, MA 02138, U.S.A.

^b Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, U.S.A.

The first example of a protonated arsenic acid, [*cyclo*-(CH₂)₅As(OH)₂]Cl, has been characterized by X-ray crystallography, ¹H n.m.r. and i.r. spectroscopy.

The hydrolysis of triphenylarsenic dihalides in hot caustic alkaline solution gives a product whose stoichiometry corresponds to the dihydroxide Ph₃As(OH)₂, whereas hydrolysis with cold water produces compounds of formula [Ph₃As(OH)]X.¹ Dipole moment measurements in benzene revealed that the dihydroxide is more accurately formulated as the oxide monohydrate, Ph₃AsO·H₂O.² This formulation was

confirmed by conductance measurements³ and an X-ray crystallographic structure determination⁴ which, together with its i.r. spectrum, revealed hydrogen bonding between the arsine oxygen and the water hydrogens. Similar studies indicated that the hydroxyhalides also have tetrahedrally-coordinated arsenic centres with strong hydrogen bonding to the halide anions.⁵

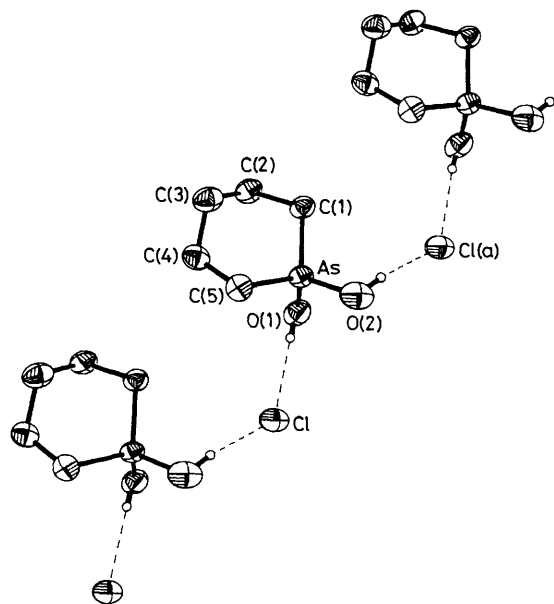


Figure 1. Diagram of $[\text{cyclo}-(\text{CH}_2)_5\text{As}(\text{OH})_2]\text{Cl}$, (1), showing the co-ordination environment about the arsenic atom and the hydrogen-bonded solid-state structure. Pertinent distances (\AA) and angles ($^\circ$): As–O(1), 1.708(4); As–O(2), 1.735(3); As–C, 1.890(4) avg.; C–C, 1.527(6) avg.; O(1)–H(1), 0.699(51); O(2)–H(2), 0.880(56); O(1)–As–O(2), 108.6(2); O(1)–As–C(1), 107.0(2); O(1)–As–C(5) 110.6(2); O(2)–As–C(1), 113.3(2); O(2)–As–C(5), 109.1(2); C(1)–As–C(5), 108.2(2); As–O(1)–H(1), 106.4(4.8); As–O(2)–H(2), 96.2(3.8); H(1) \cdots Cl, 2.299(52); H(2) \cdots Cl(a), 2.165(58); O(1) \cdots Cl, 2.986(2); O(2) \cdots Cl(a), 3.019(2); Cl \cdots H–O, 169.5(3) $^\circ$ avg.; H(1) \cdots Cl \cdots H(2), 128.2(2.1).

In the course of our investigations into the synthesis and reactivity of heterocyclic compounds containing trivalent arsenic,⁶ we have observed that exposure of benzene solutions of $\text{cyclo}-(\text{CH}_2)_5\text{AsCl}$ to air results in the deposition of colourless crystals of $[\text{cyclo}-(\text{CH}_2)_5\text{As}(\text{OH})_2]\text{Cl}$ (1),[†] and not the arsenic acid analogue $\text{cyclo}-(\text{CH}_2)_5\text{As}(\text{O})\text{OH}$ as is found for the atmospheric hydrolysis of $\text{cyclo}-(\text{CH}_2)_5\text{AsH}$ and $[\text{cyclo}-(\text{CH}_2)_5\text{As}]_2\text{O}$.⁷ The structure of (1) has been determined by X-ray crystallography.[‡] A diagram depicting the extended structure found in the solid state is given in Figure 1.

The arsenic atom possesses a four-co-ordinate tetrahedral geometry with the AsC_5 ring in a chair conformation. The chloride ion interacts with two hydroxide ligands, one on each adjacent arsenic centres. As with other arsenic hydroxy-containing compounds,^{4,5,8,9} extensive hydrogen bonding is

[†] Compound (1), $[\text{cyclo}-(\text{CH}_2)_5\text{As}(\text{OH})_2]\text{Cl}$, may also be obtained by the dissolution of $\text{cyclo}-(\text{CH}_2)_5\text{AsCl}$ in wet toluene.

[‡] Crystal data for $\text{C}_5\text{H}_{12}\text{AsClO}_2$ at 20 $^\circ\text{C}$: $a = 6.236(1)$, $b = 10.618(2)$, $c = 12.566(2)$ \AA ; $\beta = 91.02(2)^\circ$, monoclinic space group $P2_1/n$. Of the 1725 reflections collected [$(\text{Mo-K}\alpha)$, $3^\circ \leq 2\theta \leq 46^\circ$], 1484 were unique and the 1194 having $I > 3\sigma(I)$ were used in the full-matrix least-squares refinement. Non-hydrogen atoms were refined using anisotropic thermal parameters. All H atoms were located, but only those on oxygen were positionally refined. The final residuals are $R(F) = 0.0269$, $R_w(F) = 0.0293$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

present in the solid state. The As–O distances of (1), while not statistically equivalent, are considerably larger than those found for As=OH bonds (1.64–1.67 \AA),^{4,8,9} but are in the range of distances reported for As–OH bonds (1.70–1.75 \AA).^{5a,8,9} All hydrogen atoms in the crystal structure were located and refined isotropically. While both H \cdots Cl distances are much smaller than the sum of van der Waals radii (3.0 \AA),¹⁰ the O–H distances are well within the range for covalent bonding. The O \cdots Cl distances are somewhat larger than those found in $\text{Ph}_3\text{As}(\text{OH})\text{Cl}$ [2.836(14) \AA].^{5a} The i.r. spectrum of (1)§ also reveals the presence of hydrogen bonding in the solid state. The O–H stretching band, 2000–3300 cm^{-1} , is broad, intense, and shifted to a lower energy than found for non-hydrogen bonded systems.¹¹ An envelope of bands centred around 770 cm^{-1} corresponds to As–O single bond stretching frequencies found previously.^{3,5b}

It should be noted that there is an apparent asymmetry in the two hydrogen bonds. The smaller H \cdots Cl distance is associated with the longer As–O and O–H bonds and the smaller As–O–H angle, but this could be attributed to the uncertainty in the hydrogen atom locations or to crystal packing forces. These distortions, however, are consistent with π -bonding between the arsenic atom and O(1).

We conclude, nevertheless, that the compound can be considered as an arsenic(v) cationic diol, or the protonated form of a dialkyl-arsenic acid rather than as an arsenic acid with an HCl molecule of crystallization. Although the oxo lone pair of phosphonic and arsenic acids commonly acts as a Lewis base, this is, we believe, the first example of a Group 5 acid acting as a Brønsted base.

A. R. Barron is a DuPont Young Faculty Fellow 1987–1988. Financial support of this work is provided by the National Science Foundation.

Received, 13th December 1988; Com. 8/049001

References

- 1 A. E. Goddard, 'A Textbook of Inorganic Chemistry,' ed. J. N. Friend, Griffin and Co. Ltd., London, 1930, vol. XI, part 2, pp. 123, 130.
- 2 K. A. Jensen, *Z. Anorg. Allg. Chem.*, 1943, **250**, 268.
- 3 G. S. Harris and F. Inglis, *J. Chem. Soc. (A)*, 1967, 497.
- 4 G. Ferguson and E. W. Macaulay, *J. Chem. Soc. (A)*, 1969, 1.
- 5 (a) G. Ferguson and E. W. Macaulay, *J. Chem. Soc., Chem. Commun.*, 1968, 1288; (b) M. H. O'Brien, G. O. Doak, and G. G. Long, *Inorg. Chim. Acta*, 1967, **1**, 34.
- 6 For a comprehensive review of this subject, see: R. E. Atkinson, in 'Comprehensive Heterocyclic Chemistry,' vol. 1, eds. A. R. Katritzky and C. W. Rees, Pergamon, Oxford, 1984.
- 7 (a) E. Wiberg and K. Mödritzer, *Z. Naturforsch., Teil B.*, 1957, **12**, 135; (b) I. Gorski, W. Schpanski, and L. Muljar, *Chem. Ber.*, 1934, **67**, 730.
- 8 A. Chatterjee and S. P. Sen Gupta, *Acta Crystallogr., Sect. B*, 1977, **33**, 3593.
- 9 A. Chatterjee and S. P. Sen Gupta, *Acta Crystallogr., Sect. B.*, 1977, **33**, 164.
- 10 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., 1960, Ithaca, Cornell University Press, p. 260.
- 11 W. C. Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids,' 1968, New York, W. A. Benjamin, p. 85.

§ ¹H N.m.r. data (250 MHz, D₂O, 20 $^\circ\text{C}$): $\delta = 1.51$ (m, 2H), 1.69 (m, 4H), 2.32 (t, 4H). M.p. 129–133 $^\circ\text{C}$ (decomp.). I.r. data (Nujol mull, CsI plates, cm^{-1}): 3300–2000 vs br, 2300 s sh, 1410 m sh, 1400 m sh, 1350 s, 1340 m sh, 1263 m, 1180 vs, 1120 m, 1100 w sh, 1085 w sh, 1032 s, 942 s, 893 m, 810 s, 798 s, 775 vs sh, 770 vs, 760 vs sh, 695 s, 673 m, 645 m, 495 m, 320 s.