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Crystallographic report

Hydroxytrimethylarsonium iodide, [Me_3AsOH]I

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Hydroxytrimethylarsonium iodide, [Me_3AsOH]I, was obtained from the reaction of Me_2AsI and MeI in strong basic aqueous solution. The arsenic atom, lying on a mirror plane, is surrounded by one OH and three Me groups, forming a tetrahedral centre. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: crystal structure; trimethylhydroxyarsonium iodide; trimethylarsine oxide; Mayer reaction; arsenic

COMMENT

The reaction of Me_2AsI with MeI, affords the adduct of Me_3AsO and HI, which is a convenient precursor of Me_3AsO. The conventional route to Me_3AsO involves oxidation of Me_3As with H_2O_2.[1] In our hands this procedure is unsafe and can result in the formation of highly unstable explosive products that are possibly peroxides of arsenic. Adducts of trialkylarsine oxide (R_3AsO) with acids (HX) have been reported,[2–5] and the IR spectra of some are interpreted in terms of a hydrogen-bonded complex cation ($R_3AsO\cdots H^+\cdots OAsMe_3$).[3] The X-ray crystal structure of the [Me_3AsOH]I adduct (Fig. 1) shows a simple anion and cation in the solid state. The geometry of the arsenic atom (which lies on a mirror plane) is a slightly distorted tetrahedron. The As–C bond lengths, 1.89 Å, are slightly shorter than in $[M(Me_3AsO)_5]^{2-}$ (M = Ni, Mg; 1.94 Å),[6] but the As–O distance (1.73 Å) is longer than in these complexes[6] and $[Sc(Me_3AsO)_6]X_3$[7] (1.65–1.69 Å), perhaps indicating some π-bonding with the metal. The closest interaction between the ions is O–H···I of 2.65 Å (O···I is 3.3909(18) Å).

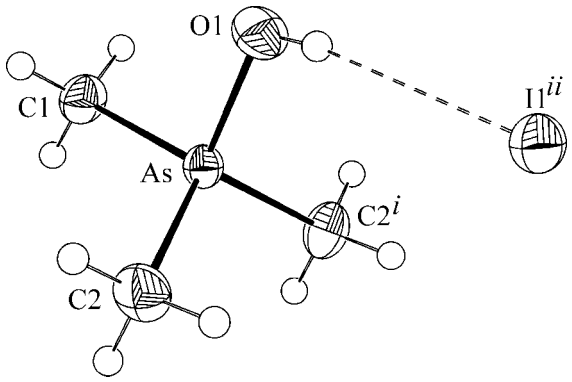

Figure 1. Selected geometric parameters for [Me_3AsOH]I: As–O1 1.7309(16), As–C1 1.889(2), As–C2 1.8930(17) Å; O1–As–C1 101.13(10), O1–As–C2 108.98(7), C1–As–C2 113.66(7), C2–As–C2^i 109.93(12)°. Symmetry operations *i*: x, $1/2-y$, z and *ii*: $1/2+x$, $1/2-y$, $3/2-z$.

EXPERIMENTAL

Me_2AsI (2.2 g, 9.5 mmol), MeI (2.7 g, 19 mmol), and NaOH (1.9 g, 47.5 mmol) in water (10 ml) was sealed in a tube under inert atmosphere and heated in an oven (60 °C) overnight. The resulting clear solution was acidified with 9 M H_2SO_4 and evaporated, leaving a white solid. The solid was dissolved in methanol to give an orange solution from which colourless needle crystals were isolated (1.5 g, 60% based on Me_2AsI). M.p. 140 °C (dec.). Anal. Found: C, 13.70; H, 3.88. Calc. for $C_3H_{10}AsIO$: C, 13.65; H, 3.83%. ^1H NMR δ 2.10. m/z: 137 $[M-I]^+$, 122 $[M-I-Me]^+$. The intensity data were collected at −100.0(1) °C for a crystal 0.05 × 0.05 × 0.10 mm^3 on a Bruker X8 APEX diffractometer (Mo Kα radiation). Crystal data: $C_3H_{10}AsIO$, $M = 263.93$, orthorhombic, *Pnma*, $a = 15.6130(3)$, $b = 8.2369(2)$, $c = 6.1938(1)$ Å, $V = 769.54(3)$ Å^3, $Z = 2$, 1016 unique data ($2\theta_{max} = 55.8°$), 970 data with $I > 2\sigma(I)$, $R = 0.012$, $wR = 0.026$ (all data). All hydrogen atoms were refined isotropically. Programs used: SAINT, SADABS, SIR92 and SHELXTL. CCDC deposition number: 236542.

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