Synthesis and structure of the adduct $Cl_3AsO{\cdot}AsF_5$

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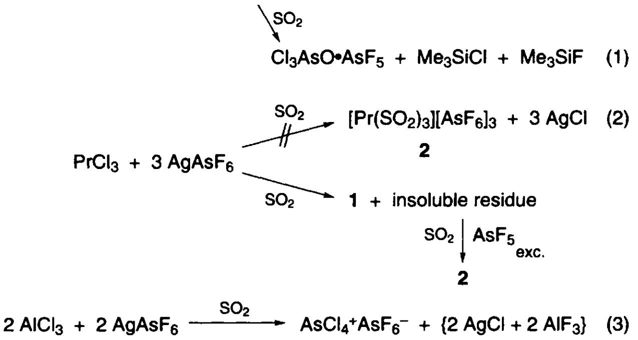
The relatively thermally stable adduct $Cl_3AsO{\cdot}AsF_5$ 1 is prepared in high yield from $AsCl_4^+AsF_6^-$ and $Me_3SiOSiMe_3$ in liquid SO_2 at −40 °C, and originally surprisingly isolated from the reaction of $PrCl_3$ and $AgAsF_6$ in liquid SO_2; the X-ray crystal structure of 1 is compared with that of $Cl_3PO{\cdot}AsF_5$.

Inorganic arsenic(v)–chloro derivatives are rare, the only stable compound reported is $AsCl_4^+AsF_6^-$.[1–3] $AsCl_5$, prepared photochemically from $AsCl_3$ and Cl_2 at −105 °C, decomposes rapidly above −50 °C.[4] The synthesis of $AsOCl_3$ by hydrolysis of the pentachloride is not possible;[5] its formation in a microwave discharge and isolation in an argon matrix[6] and its preparation from $AsCl_3$ and O_3 at −78 °C in $CFCl_3$–CH_2Cl_2 solution on a preparative scale[5,7] has been reported. The compound readily decomposes at 0 °C with formation of $AsCl_3$, Cl_2 and $As_2O_3Cl_4$.[5,7]

The adduct $Cl_3AsO{\cdot}AsF_5$ **1** is formed in 85% yield as a stable, colourless solid, mp 138 °C (decomp.) from the reaction of $AsCl_4^+AsF_6^-$ and $Me_3SiOSiMe_3$ in liquid SO_2 [Scheme 1, eqn. (1)].[†]

The primary step in this reaction will be a nucleophilic attack of the siloxane at the highly electrophilic cationic centre, followed by elimination of Me_3SiCl and Me_3SiF (from AsF_6^-). The exact reaction pathway is not known.



Scheme 1

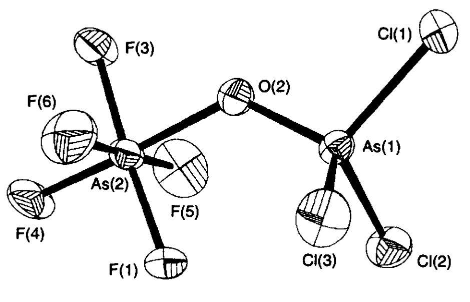


Fig. 1 Structure of **1** with 50% thermal ellipsoids; bond distances (pm) and bond angles (°): As(1)–O(2) 165.8(4), As(2)–O(2) 184.9(4), As(1)–Cl(1) 205.3(2), As(1)–Cl(2) 205.5(2), As(1)–Cl(3) 204.6(2), As(2)–F(1) 170.4(3), As(2)–F(3) 169.5(4), As(2)–F(4) 169.5(4), As(2)–F(5) 168.3(5), As(2)–F(6) 169.8(4), As(1)–O(2)–As(2) 129.1(2), O(2)–As(1)–Cl(1) 105.4(2), O(2)–As(1)–Cl(2) 114.3(2), O(2)–As(1)–Cl(3) 113.2(2), Cl–As(1)–Cl 107.7(1)–108.9(1), O(2)–As(2)–F_{cis} 85.4(2)–90.3(2), O(2)–As(2)–F(4) 177.1(2), F(4)–As–F91.5(3)–92.5(2)

We isolated **1** for the first time unexpectedly from the reaction of $PrCl_3$ and $AgAsF_6$ in liquid SO_2 [Scheme 1, eqn. (2)].[†] In the primary reaction an insoluble residue is also formed, which could not be characterised. When this residue was treated in a second step with excess AsF_5, the praseodymium complex **2** was crystallised from the resulting solution.[8] From the $YbCl_3$–$AgAsF_6$–SO_2 system **1** and $[Yb(SO_2)_3][AsF_6]_3$[8] were characterised by IR spectroscopy. $AlCl_3$ reacts with $AgAsF_6$ in liquid SO_2 in a very slow reaction, $AsCl_4^+AsF_6^-$ [Scheme 1, eqn. (3)] was detected also by IR spectroscopy.

As the first step in these reactions chloride abstraction from MCl_3 by Ag^+ was expected, followed by occupation of the empty coordination site by the solvent SO_2. Due to the high Lewis acidities of $LnCl_3$ and $AlCl_3$ or the expected cationic intermediates, AsF_6^- will interact with the metal centres, followed by F/Cl exchange at the arsenic. The formation of $OAsCl_3$ is explained from solvolysis with SO_2. This solvolysis seems to occur specifically in the coordination sphere of some lanthanide metals.

1 was characterised by elemental analysis and IR spectroscopy [899s ($\nu_{As=O}$), 772vs, 699s, 647m ($\nu_{As-F,\,As-O}$), 508(sh), 489m cm^{-1} (ν_{AsCl})]. The structure of the adduct is shown in Fig. 1.[‡]

For comparison, the structure of the related adduct $Cl_3PO{\cdot}AsF_5$[§] was also determined [average bond distances (pm) and selected bond angles (°): P–Cl 193.5(3)–194.2(3), P–O 150.0(6), As–O 189.0(6); O–P–Cl 108.2(3)–112.7(3), O–As–F_{cis} 85.5(3)–88.8(3), O–As–F_{trans} 177.9(3)]. Since the O–AsF_5 distance in **1** [184.9(4) pm] is shorter than that in the phosphorus analogue it might be assumed that Cl_3AsO is a better donor than Cl_3PO.[9] The As–Cl bond lengths (average 205.1 pm) in **1** are similar to those in $AsCl_4^+AsF_6^-$ (205.5 pm)[10] and suggest a zwitterion type charge distribution Cl_3As^+–O–As^-F_5, which helps to explain the unexpected thermal stability of **1**.

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Footnotes

[†] *Preparation of* **1**: *method A*; in a glass vessel equipped with Teflon valves a slight excess of $Me_3SiOSiMe_3$ (1.05 g, 6.5 mmol) was condensed onto $AsCl_4^+AsF_6^-$ (2.36 g, 5.8 mmol) in SO_2 (15 ml) under vacuum at −196 °C. The reaction mixture was warmed to −70 °C, and the temperature then slowly raised to −40 °C. Reaction began at −50 °C, when formation of a yellow gas (Cl_2) was observed. After stirring for an additional hour at −30 °C, all volatiles were removed *in vacuo* at room temp. The solid residue was recrystallised from SO_2 to give **1** (1.8 g, 4.9 mmol, 85% yield).

Method B; in a Schlenk vessel, equipped with Teflon valves and a sintered glass frit, stoichiometric amounts of $PrCl_3$ (0.84 g, 3.4 mmol) and $AgAsF_6$ (2.74 g, 10.2 mmol) were stirred in SO_2 (15 ml) for three days at room temp. in the dark. The insoluble residue was removed by filtration and washed several times as described.[11] After removal of the volatiles, **1** was isolated (0.25 g, 0.7 mmol, 20% yield). Suitable single crystals for the X-ray structure determination were obtained by recrystallisation from SO_2.

[‡] *Crystal data*: for $F_5AsOAsCl_3$: monoclinic, space group $P2_1/c$, a = 599.1(2), b = 1858.9(4), c = 774.7(2) pm, β = 107.69(2)°, U = 0.8220(4) nm^3, Z = 4, D_c = 2.967 g cm^{-3}, μ = 9.131 mm^{-1},

F(000) = 680, crystal dimensions 0.6 × 0.5 × 0.2 mm. 7500 reflections collected with $2.97 < \theta < 27.5°$, 1882 unique ($R_{int} = 0.0849$) used in the structural analysis. The data set was collected on a Siemens P4 diffractometer using Mo-Kα radiation ($\lambda = 71.073$ pm) at 173 K. The structure was solved by direct methods. All non-H atoms were refined anisotropically.[12] An absorption correction was applied using the program DIFABS.[13] The refinement (100 parameters) converged with $wR2 = 0.0739$ ($R1 = 0.0378$) and final difference electron density maximum, minimum of 769, −1164 e nm^{-3}.

For $F_5AsOPCl_3$: monoclinic, space group $P2_1/n$, $a = 598.70(10)$, $b = 1837.3(4)$, $c = 763.7(2)$ pm, $\beta = 107.16(3)°$, $U = 0.8027(3)$ nm^3, $Z = 4$, $D_c = 2.675$ g cm^{-3}, $\mu = 5.459$ mm^{-1}, *F*(000) = 608, crystal dimensions 0.7 × 0.4 × 0.4 mm. 2551 reflections collected with $3.00 < \theta < 27.49°$, 1821 unique ($R_{int} = 0.0970$) used in the structural analysis. The data set was collected on a Siemens P4 diffractometer using Mo-Kα radiation ($\lambda = 71.073$ pm) at 173 K. The structure was solved by direct methods. All non-H atoms were refined anisotropically.[12] An absorption correction was applied using DIFABS.[13] The refinement (101 parameters) converged with $wR2 = 0.1771$ ($R1 = 0.0775$) and final difference electron density maximum, minimum 2793, −1316 e nm^{-3}. The high remaining electron density is located near F(2) and F(3) indicating a possible disordering of these fluorine atoms. Further treatment of these peaks was not satisfactory. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/162.

§ $Cl_3PO{\cdot}AsF_5$ was obtained in quantitative yield from the reaction of Cl_3PO and AsF_5 in liquid SO_2. The colourless solid, [mp 153 °C (decomp.)] is readily sublimed *in vacuo*. IR (Nujol): 1307w, 1144vs (ν_{PO}), 733vs, 707vs (ν_{AsF}), 656vs ($\nu_{asymPCl_3}$), 587w, 547vw, 456w cm^{-1}.

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