Reaction of $[FeL_4X_2][FeX_4]$($L = OPPh_3$ or $OAsPh_3$, X = Cl or Br) with Sulphur Dioxide to yield Some Rare Examples of Iron(III) Complexes of Sulphur Dioxide, $[FeL_4\{OS(O)X\}_2][FeX_4]$. The Oxidation of Sulphur Dioxide by the Iron(III) Complexes and the Isolation of the Sulphuric Acid Derivatives $(PPh_3O)(PPh_3OH)(HSO_4)$ and $(AsPh_3OH)(HSO_4)$. Crystal Structure of the Latter†

Brian Beagley, David G. Kelly, Philomena P. Mac Rory, Charles A. McAuliffe,* and Robin G. Pritchard
Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD

The complexes $[FeL_4X_2][FeX_4]$ ($L = OPPh_3$ or $OAsPh_3$, X = Cl or Br), first prepared by Cotton and Gibson, have been further characterised and their reactions with sulphur dioxide investigated; these reactions have been found to be dependent on the nature of the ligand, the halide, and the reaction medium. In the solid state only the iron(III) complexes containing $OAsPh_3$ ligands react with sulphur dioxide to form $[Fe(OAsPh_3)_4\{OS(O)X\}_2][FeX_4]$ (X = Cl or Br). However, in toluene slurries $[FeL_4\{OS(O)X\}_2][FeX_4]$ ($L = OPPh_3$, X = Br; $L = OAsPh_3$, X = Cl or Br) can be isolated, but $[Fe(OPPh_3)_4Cl_2][FeCl_4]$ is recovered unchanged. Nonetheless, filtrates from all four reactions, when exposed to moist air yield the sulphuric acid derivatives $(PPh_3O)(PPh_3OH)(HSO_4)$ and $(AsPh_3OH)(HSO_4)$; the formation of sulphuric acid can be indefinitely delayed by maintaining dry anaerobic conditions. The compound $(AsPh_3OH)(HSO_4)$ has been characterised by single-crystal *X*-ray analysis which shows hydrogen-bonded chains of HSO_4^- anions running parallel to the *c* axis; each hydrogensulphate ion is then hydrogen bonded to a $[AsPh_3OH]^+$ cation. The As–O bond distance observed, 1.727(5) Å, is substantially longer than that previously reported for Ph_3AsO, 1.645 Å.

Sulphur dioxide is a most noxious atmospheric pollutant and its removal from gas streams is receiving much attention. One of its properties is the ability to bind to transition-metal complexes *via* a number of modes,[1] and the co-ordination chemistry of sulphur dioxide is being extensively investigated academically.

We are currently investigating the binding of SO_2 by a wide range of manganese(II) complexes containing tertiary phosphine oxides and arsine oxides.[2–6] Their reaction with SO_2 is both ligand and halide dependent, and triphenylphosphine oxide complexes of manganese(II) iodide and thiocyanate are proving to be of particular interest.[2–6] Thus, $[Mn(OPPh_3)_4I_2]$ inserts two molecules of SO_2 into the Mn–I bonds to give $[Mn(OPPh_3)_4\{OS(O)I\}_2]$, an adduct complex from which one SO_2 may be subsequently lost by heating to 129 °C; the process is reversible [equation (1)].[6]

$$[Mn(OPPh_3)_4\{OS(O)I\}_2] \underset{SO_2}{\overset{129\,^{\circ}C}{\rightleftharpoons}} [Mn(OPPh_3)_4\{OS(O)I\}I] + SO_2 \qquad (1)$$

From our studies we are able to see some structure–reactivity relationships. Thus, for example, tris and tetrakis complexes $[Mn(OPPh_3)_n(NCS)_2]$ (n = 3 or 4) reversibly bind one SO_2 per manganese, $[Mn(OPPh_3)_n(NCS)_2(SO_2)]$, whereas the mono and bis complexes $[Mn(OPPh_3)_n(NCS)_2]$ (n = 1 or 2) are inactive.[2] As well as binding sulphur dioxide some manganese complexes activate it. Thus, for example, dilute solutions of $[Mn(OPPh_3)_4(NCS)_2(SO_2)]$ in the presence of air cause the oxidation of sulphur dioxide to sulphuric acid, as evidenced by the isolation and *X*-ray crystallographic characterisation of $(PPh_3O)(PPh_3OH)(HSO_4)$.[2]

We now report an extension of this work to another $3d^5$ metal-ion system, that of iron(III). Iron(III) complexes of triphenylphosphine oxide and triphenylarsine oxide were first investigated by Cotton and Gibson[7] and we have used their FeL_2X_3 (X = Cl or Br) complexes in the present study. Reaction with sulphur dioxide is both halide and ligand dependent, and we also observe the oxidation of SO_2 to sulphuric acid under ambient conditions. We have previously isolated and crystallographically characterised $(PPh_3O)(PPh_3OH)(HSO_4)$,[2] and in this work we report the crystal structure of $(AsPh_3OH)(HSO_4)$. We recognise that these observations are unusual. Although metal co-ordination complexes of sulphur dioxide are now well known[1] they are most commonly found with the heavier transition metals and co-ordination to a first transition-series element in the oxidation state III is surprising; only one previous example of an iron(III) complex of sulphur dioxide, dicarbonyl(η^5-cyclopentadienyl)(sulphur dioxide)-iron(III) hexafluoroarsenate, has been reported.[8]

Results and Discussion

Like Cotton and Gibson,[7] we found that the reaction of FeX_3 (X = Cl or Br) with Ph_3EO (E = P or As) always leads to complexes of stoicheiometry FeL_2X_3, quite independent of the molar ratio of reactants employed in the syntheses. However, whilst Cotton and Gibson reported difficulty in obtaining $[Fe(OAsPh_3)_2Br_3]$ in a pure condition from a preparation in

---

† Hydroxytriphenylarsonium hydrogensulphate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Analytical (%)[a] and some physical data for the iron(III) complexes

Complex	Colour	M.p. (°C)	Analysis C	H	Halogen	P	Fe	ν(OE)[b] (cm^{-1})	ν_3(FeX_4^-)[c] (cm^{-1})	$\mu_{eff.}$ (μ_B)	Λ[d] (ohm^{-1} cm^2 mol^{-1})
$[Fe(OPPh_3)_4Cl_2][FeCl_4]$	Yellow	178—180	60.1 (60.1)	4.2 (4.2)	14.5 (14.8)	8.6 (8.6)	7.5 (7.8)	1 445s	380	5.93	17
$[Fe(OPPh_3)_4Br_2][FeBr_4]$	Orange	174	50.4 (50.7)	3.5 (3.5)	28.3 (28.2)	7.2 (7.3)	6.4 (6.6)	1 140s, 1 118m	290	5.87	17
$[Fe(OAsPh_3)_4Cl_2][FeCl_4]$	Yellow	178	53.3 (53.6)	3.5 (3.7)	13.2 (13.2)		6.6 (6.9)	865s, 890s	380	5.92	24
$[Fe(OAsPh_3)_4Br_2][FeBr_4]$	Orange	170—173	45.7 (46.0)	3.2 (3.2)	26.0 (25.5)		6.0 (6.0)	850s, 820(sh)	285		15

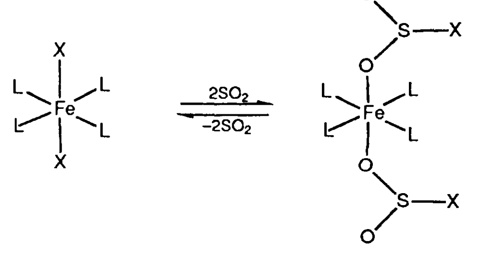
[a] Calculated values are in parentheses. [b] E = P or As; Nujol mulls, KBr plates; ν(OP) of $OPPh_3$ 1 190s; ν(OAs) of $OAsPh_3$ 880s cm^{-1}. [c] Nujol mulls, polyethylene plates. [d] In nitrobenzene.

ethanol, we have found that our method in toluene does lead to a *reproducibly* pure material, Table 1.

The complexes had been assigned as the ionic $[FeL_4X_2][FeX_4]$ species and we agree with this formulation. In addition to the information gathered by Cotton and Gibson,[7] Table 1 contains further data which confirms their structural assignment. Moreover, employing the ligand $Ph_2P(O)CH_2CH_2(O)PPh_2$ (dppoe), the complex $Fe(dppoe)Cl_3$ has been shown by *X*-ray crystallography to have the structure $[Fe(dppoe)_2Cl_2][FeCl_4]$.[9] Our attempts to isolate the $[FeL_4X_2]^+$ cations as the BPh_4^- salts were not successful, however.

Reactions with Sulphur Dioxide.—(*i*) *Toluene slurries.* The reactions of the complexes as toluene slurries with sulphur dioxide have been studied under strictly anhydrous conditions. Three of the four complexes $[FeL_4X_2][FeX_4]$ (L = $OPPh_3$, X = Br; $OAsPh_3$, X = Cl or Br) reacted with SO_2 to give a 1:1 adduct (SO_2:Fe), $[FeL_4\{OS(O)X\}_2][FeX_4]$, but $[Fe(OPPh_3)_4Cl_2][FeCl_4]$ was constantly recovered unchanged after repeated exposures to SO_2, Table 2. Since $[Fe(OAsPh_3)_4Cl_2][FeCl_4]$ does form an adduct with SO_2 and $[Fe(OPPh_3)_4Cl_2][FeCl_4]$ does not, it may be concluded that SO_2 binds to the cation and not the anion. Moreover, the adduct complexes exhibit shifts and new peaks for ν(EO) (E = P or As) in the i.r. spectra, whereas $\nu_3(FeX_4^-)$ remains unaltered, Table 2. Neither do we observe any colour change upon co-ordination of SO_2 and, since it is the FeX_4^- chromophore which is responsible for the colour of the $[FeL_4X_2][FeX_4]$ species (halogen–iron charge transfer), this may be taken as further evidence that it is the cation to which the SO_2 binds.

It has not, as yet, been possible to produce crystals suitable for *X*-ray diffraction studies. Despite their appreciable solubility in SO_2-saturated toluene the complexes yield only powders and have not yet yielded crystals of suitable quality for *X*-ray studies. Elevated temperatures have not been applied since the reversibility of SO_2 co-ordination, Table 3, renders such techniques unfeasible. New i.r. peaks due to SO_2 at 1 232—1 265 cm^{-1} do appear for the adducts, Table 2, which indicate the binding mode. Moreover, the reversibility of binding and the energy of the ν(SO) vibration is reminiscent of our $[Mn(OPPh_3)_4I_2]$ complex, another octahedral $3d^5$ system, which allows the insertion of 2 mol of SO_2 into the Mn–I bonds to form $[Mn(OPPh_3)_4\{OS(O)I\}_2]$, ν(SO) 1 232 cm^{-1}.[6] Thus we propose the following reaction scheme in equation (2) (L = $OPPh_3$, X = Br; L = $OAsPh_3$, X = Cl or Br).



(2)

It is known that some SO_2 adduct complexes of transition metals undergo oxidation to sulphate; this is normally a property of σ-pyramidal co-ordinated sulphur dioxide and results in the formation of metal-bound sulphate. A novel oxidation of SO_2 to yield discrete sulphuric acid–ligand adducts has been discovered by us involving manganese(II) complexes with $OPPh_3$ or $OAsPh_3$ ligands.[2] The same products, $(PPh_3O)(PPh_3OH)(HSO_4)$ and $(AsPh_3OH)(HSO_4)$, are produced when the toluene solutions of the iron(III) complexes saturated with SO_2 are exposed to air for *ca.* 7 d, Table 4. It is clear that dioxygen and water are involved, since the formation of sulphuric acid can be indefinitely delayed by maintaining dry anaerobic conditions. The involvement of the iron(III) complexes is demonstrated by our observations that neither the ligand nor the iron(III) salt alone will produce sulphuric acid in this way.

(*ii*) *Solid state.* The reaction of sulphur dioxide with the $[FeL_4X_2][FeX_4]$ (L = $OPPh_3$ or $OAsPh_3$, X = Cl or Br) complexes has been examined in the solid state by exposing these complexes to 1 atm (*ca.* 10^5 Pa) and monitoring any change in the mass of the sample. The results, Table 5, show that there is no solid-state absorption for the iron(III) complexes of $OPPh_3$. The change of ligand to $OAsPh_3$ is sufficient to generate the 1:1 Fe:SO_2 adducts also formed in toluene slurries. Elemental analysis confirms the results obtained from the mass changes.

These results from both toluene slurries and the solid state indicate that the $[FeL_4X_2][FeX_4]$ is not a simple 'sink' for sulphur dioxide. The change from $[Fe(OAsPh_3)_4Cl_2][FeCl_4]$ to $[Fe(OPPh_3)_4Cl_2][FeCl_4]$ is sufficient to render the complex inactive to co-ordination of sulphur dioxide in the solid state. Similarly, whilst $[Fe(OPPh_3)_4Br_2][FeBr_4]$ forms an SO_2 adduct when slurried in toluene, no co-ordination is observed for the complex in the solid state. The promotion of the oxidation of sulphur dioxide to sulphuric acid seems, however, to be a more general property, as all complexes promote this, Table 4. To achieve this the SO_2 must at least be transiently bound to the iron(III) complex, since oxidation does not occur in the absence of the complex. It is interesting that Scheidt *et al.*[10] who, whilst finding no evidence for simple direct reaction of SO_2 with either iron(II) or iron(III) porphyrin derivatives, as in all cases only starting materials or products attributable to side reactions were observed, were nonetheless able to isolate three (porphyrinato)sulphatoiron(III) complexes.

Crystallographic Study.—The molecular structure of $(AsPh_3OH)(HSO_4)$, together with the atomic numbering scheme, is shown in the Figure. Atomic co-ordinates and selected bond lengths and angles are given in Tables 6 and 7 respectively. The structure is composed of hydrogen-bonded chains of HSO_4^- anions running parallel to the *c* axis. Each hydrogensulphate ion is then hydrogen bonded to a

Table 2. Reaction of the iron(III) complexes with sulphur dioxide and characterisation data for the products

Reaction[a]	Product	Colour	M.p. (°C)	Analysis (%)[b]			ν(SO)[c] (cm^{-1})		ν(OE)[c,d] (cm^{-1})
				C	H	S	sym	asym	
$[Fe(OPPh_3)_4Cl_2][FeCl_4] + SO_2$	$[Fe(OPPh_3)_4Cl_2][FeCl_4]$	Yellow	178—179	59.8 (60.1)	4.0 (4.2)	0.0 (0.0)	—	—	1 145s
$[Fe(OPPh_3)_4Br_2][FeBr_4] + SO_2$	$[Fe(OPPh_3)_4\{OS(O)Br\}_2][FeBr_4]$	Orange	172	47.4 (47.2)	3.1 (3.3)	3.1 (3.5)	1 265m	1 070(sh)	1 130s, 1 120m
$[Fe(OAsPh_3)_4Cl_2][FeCl_4] + SO_2$	$[Fe(OAsPh_3)_4\{OS(O)Cl\}_2][FeCl_4]$	Yellow	160 (decomp.)	49.2 (49.7)	3.6 (3.4)		1 232w	1 110 w	890s, 875(sh), 815
$[Fe(OAsPh_3)_4Br_2][FeBr_4] + SO_2$	$[Fe(OAsPh_3)_4\{OS(O)Br\}_2][FeBr_4]$	Orange	140 (decomp.)	44.2 (43.0)	3.1 (3.0)	2.4 (3.2)	1 240m	1 105m	905s, 860s, 850s

[a] In toluene slurries. [b] Calculated values in parentheses. [c] Nujol mulls, KBr plates. [d] E = P or As.

Table 3. Thermograms of SO_2 loss for the products of toluene slurries

Complex	Mass of sample/mg	Temp. of SO_2 loss/°C	Mass lost/mg	% Theoretical mass loss	Decomposition temp./°C
$[Fe(OPPh_3)_4Cl_2][FeCl_4]$*	6.40	—	—	—	220
$[Fe(OPPh_3)_4\{OS(O)Br\}_2][FeBr_4]$	3.62	60—150	0.24	95	220
$[Fe(OAsPh_3)_4\{OS(O)Cl\}_2][FeCl_4]$	9.04	40—160	0.67	101	200

* This complex is included to show the behaviour of a non-containing SO_2 complex on heating.

Table 4. Filtrate crystals produced by exposing toluene solutions of SO_2 adducts to air

Filtrate	Product[a]	M.p. (°C)	Analysis (%)[b]		
			C	H	S
$[Fe(OPPh_3)_4Cl_2][FeCl_4] + SO_2$	$(Ph_3PO)_2H_2SO_4$	182	66.4 (66.1)	4.9 (4.9)	—
$[Fe(OPPh_3)_4Br_2][FeBr_4] + SO_2$	$(Ph_3PO)_2H_2SO_4$	181	65.9 (66.1)	4.8 (4.9)	5.3 (4.9)
$[Fe(OAsPh_3)_4Cl_2][FeCl_4] + SO_2$	$(Ph_3AsO)H_2SO_4$	135	51.1 (51.4)	3.9 (4.0)	7.8 (7.6)
$[Fe(OAsPh_3)_4Br_2][FeBr_4] + SO_2$	$(Ph_3AsO)H_2SO_4$	139	51.3 (51.4)	4.1 (4.0)	7.8 (7.6)

[a] Empirical formula. [b] Calculated values in parentheses.

Table 5. Uptake of SO_2 by the iron(III) complexes in the solid state

Complex	Mass of complex/g	10^4 Amount (mol)	Increase in mass/g	Ar/SO_2 correction/g	Mass of SO_2 absorbed/g	10^4 Amount of SO_2 (mol)	Molar ratio SO_2/Fe
$[Fe(OPPh_3)_4Cl_2][FeCl_4]$	0.4720	6.57	0.0207	0.0199	0.0008	0.13	<0.1
$[Fe(OPPh_3)_4Br_2][FeBr_4]$	0.6781	7.96	0.0081	0.0079	0.0002	0.03	<0.1
$[Fe(OAsPh_3)_4Cl_2][FeCl_4]$	0.3630	4.50	0.0326	0.0047	0.0279	4.36	0.97
$[Fe(OAsPh_3)_4Br_2][FeBr_4]$	0.0788	0.84	0.0108	0.0047	0.0061	0.95	1.14

$[AsPh_3OH]^+$ cation. The analysis did not reveal the positions of the acidic protons. However, the bonding scheme was deduced from the non-bonded O ··· O distances of 2.67(1) Å within the chain and 2.51 Å to the arsine oxide. Additionally, the As–O bond of 1.727(5) Å is substantially longer than that previously reported in triphenylarsine oxide (1.645 Å),[11] suggesting that the proton is placed on this group rather than remaining on the sulphate.

Experimental

Preparation of $Fe(OEPh_3)_2X_3$ *Complexes.*—These air-stable complexes were synthesised by published techniques under anaerobic conditions, employing a toluene solvent,[2] and in air using ethanol.[7] The products from each method are the same.

Reaction with Sulphur Dioxide.—(*i*) *Solid state.* A dry Rotaflo tube of known volume was evacuated, filled with argon, and weighed. Approximately 0.1—0.5 g of complex was placed in the tube which was evacuated and refilled with argon. Reweighing then gave the precise mass of complex. The vacuum was again applied and removed with 1 atm of sulphur dioxide. More sulphur dioxide was added daily, to a pressure of 1 atm, until a constant mass was reached. The mass of sulphur dioxide absorbed by the complex was determined as the total increase minus an argon/sulphur dioxide correction. This was calculated as the difference in densities of argon and sulphur dioxide at ambient temperature and pressure, multiplied by the volume of the Rotaflo tube used.

(*ii*) *Toluene slurries.* The same techniques and equipment used for the anaerobic syntheses of the complexes were utilised in the preparation of sulphur dioxide-saturated slurries. Approximately 0.5 g of complex was placed in a dry side-arm flask against a flow of argon. The flask was then charged with dry oxygen-free freshly distilled toluene (100 cm^3), repeatedly flushed with argon, and re-evacuated to minimise dioxygen contamination. Finally, the vacuum was removed with sulphur dioxide until the solvent was fully saturated. It was then sealed and stirred for 7 d. Products were isolated by standard Schlenk techniques and dried by a flow of argon.

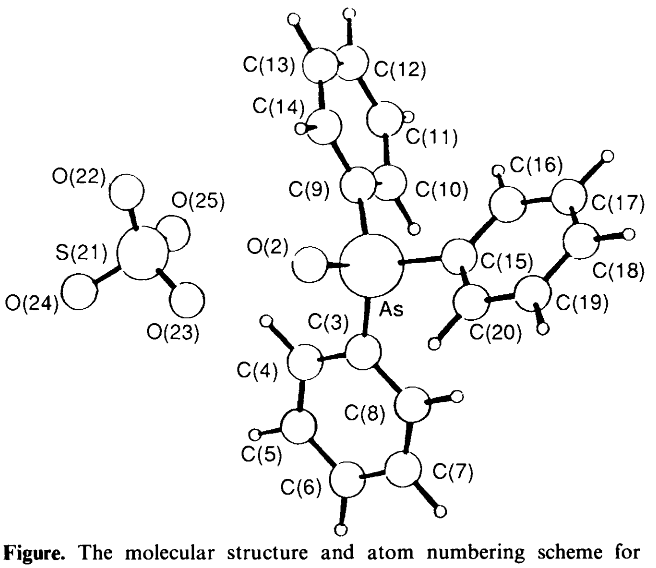


Figure. The molecular structure and atom numbering scheme for ($AsPh_3OH$)(HSO_4)

Table 6. Atomic co-ordinates for ($AsPh_3OH$)(HSO_4)

Atom	*x*	*y*	*z*
As	0.756 12(8)	0.432 95(4)	0.409 56(9)
O(2)	0.911 6(5)	0.410 8(3)	0.342 0(6)
C(3)	0.780 6(7)	0.448 3(4)	0.615 3(9)
C(4)	0.801 2(9)	0.396 9(5)	0.711 5(10)
C(5)	0.826 4(10)	0.409 5(6)	0.860 6(12)
C(6)	0.832 9(10)	0.471 5(7)	0.912 7(12)
C(7)	0.815 6(10)	0.521 4(6)	0.818 7(12)
C(8)	0.786 9(9)	0.510 1(5)	0.668 1(10)
C(9)	0.623 1(8)	0.368 7(4)	0.362 8(9)
C(10)	0.501 7(9)	0.367 2(4)	0.436 8(11)
C(11)	0.397 6(11)	0.324 0(6)	0.387 4(15)
C(12)	0.418 9(14)	0.283 8(6)	0.273 0(17)
C(13)	0.539 1(14)	0.285 2(5)	0.203 6(14)
C(14)	0.644 3(11)	0.328 1(5)	0.246 4(11)
C(15)	0.708 5(9)	0.508 0(4)	0.299 1(8)
C(16)	0.581 6(9)	0.513 3(4)	0.224 0(9)
C(17)	0.555 6(9)	0.566 9(5)	0.136 5(10)
C(18)	0.653 9(11)	0.613 7(5)	0.127 2(10)
C(19)	0.780 1(11)	0.608 0(5)	0.205 8(11)
C(20)	0.808 8(9)	0.555 6(4)	0.292 5(10)
S(21)	1.003 8(3)	0.260 5(1)	0.481 4(2)
O(22)	1.008 2(13)	0.232 4(4)	0.347 1(8)
O(23)	1.041 2(7)	0.326 4(3)	0.490 4(7)
O(24)	1.091 1(12)	0.224 3(4)	0.590 2(11)
O(25)	0.865 2(11)	0.252 3(5)	0.526 6(14)

Elemental analyses were performed by the UMIST Microanalytical Service. Infrared spectra were obtained for Nujol mulls on KBr plates over the 4 000—200 cm^{-1} range on a Perkin-Elmer 598 spectrophotometer. Thermogravimetric analyses were carried out on a Stanton Redcroft TG750 thermobalance. Magnetic susceptibilities were recorded on a Johnson Matthey balance.

Table 7. Selected bond lengths (Å) and angles (°) for ($AsPh_3OH$)(HSO_4)

As–O(2)	1.727(5)	S(21)–O(23)	1.428(7)
S(21)–O(22)	1.354(7)	S(21)–O(25)	1.44(1)
S(21)–O(24)	1.466(8)		
C(3)–As–O(2)	109.9(3)	O(25)–S(21)–O(24)	104.7(7)
C(9)–As–O(2)	109.1(3)	O(23)–S(21)–O(22)	116.6(5)
C(15)–As–O(2)	102.8(3)	O(24)–S(21)–O(23)	109.2(5)
O(24)–S(21)–O(22)	109.2(6)	O(25)–S(21)–O(23)	109.7(5)
O(25)–S(21)–O(22)	106.8(7)		

X-Ray Structure Determination.—Crystallographic measurements were made at ambient temperature on an Enraf-Nonius CAD-4 diffractometer, operating in the ω—2θ scan mode with graphite-monochromatised Mo-K_α radiation (λ = 0.710 69 Å). Structure calculation was performed using the SHELX 76 program.[12]

Crystal data for ($AsPh_3OH$)(HSO_4). $C_{18}H_{15}AsO_5S$, M = 420.31, crystal dimensions 0.2 × 0.2 × 0.3 mm, monoclinic, space group $P2_1/c$, a = 9.691(3), b = 20.941(7), c = 9.060(3) Å, β = 93.82(2)°, U = 1 834.5 Å^3, Z = 4, D_c = 1.52 Mg m^{-3}, $F(000)$ = 856.0, μ(Mo-$K\alpha$) = 1.947 mm^{-1}, R = 0.064 and R' = 0.062 for 2 421 unique reflections [$F \geqslant 3\sigma(F)$], w = $1.9687/[\sigma^2(F) + 0.0005 F^2]$.

Standard heavy-atom techniques were used to solve the structure followed by full-matrix least-squares refinement. Hydrogen atoms were constrained to chemically reasonable positions with individual isotropic thermal parameters; those attached to oxygen atoms were ignored. All non-hydrogen atoms were treated anisotropically.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

References

1 R. R. Ryan, G. J. Kubas, and P. G. Eller, *Struct. Bonding (Berlin)*, 1981, **46**, 48.
2 K. Al-Farhan, B. Beagley, O. El-Sayrafi, G. A. Gott, C. A. McAuliffe, P. P. Mac Rory, and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1990, 1243.
3 C. A. McAuliffe, B. Beagley, G. A. Gott, A. G. Mackie, P. P. Mac Rory, and R. G. Pritchard, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 264.
4 B. Beagley, C. B. Colburn, O. El-Sayrafi, G. A. Gott, D. G. Kelly, A. G. Mackie, P. P. Mac Rory, and R. G. Pritchard, *Acta Crystallogr., Sect. C*, 1988, **44**, 38.
5 B. Beagley, O. El-Sayrafi, G. A. Gott, D. G. Kelly, C. A. McAuliffe, A. G. Mackie, P. P. Mac Rory, and R. G. Pritchard, *J. Chem. Soc., Dalton Trans.*, 1988, 1095.
6 G. A. Gott, J. Fawcett, C. A. McAuliffe, and D. R. Russell, *J. Chem. Soc., Chem. Commun.*, 1984, 1283.
7 S. A. Cotton and J. F. Gibson, *J. Chem. Soc. A*, 1971, 859; 1970, 2105.
8 G. Hartman, R. Frobose, R. Mews, and G. M. Sheldrick, *Z. Naturforsch., Teil B*, 1982, **37**, 1234.
9 T. S. Lobana, personal communication.
10 W. R. Scheidt, Y. J. Lee, and M. G. Finnegan, *Inorg. Chem.*, 1988, **27**, 4275.
11 M. Shao, X. Jin, Y. Tang, Q. Muang, and Y. Huang, *Tetrahedron Lett.*, 1982, **23**, 5343.
12 G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.

Received 23*rd October* 1989; *Paper* 9/04552J