Notes

Reaction of Manganese(II) Arsine Oxide Complexes with Sulphur Dioxide: Some Unexpected Products. The *X*-Ray Crystal Structure of $[(Ph_3AsO)_2H]I_3$†

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The reaction of $[Mn(OAsPh_3)_4I_2]$ with sulphur dioxide in toluene yields $[Mn(OAsPh_3)_3(O_2SI)_2)]$. Two unexpected products, $[(Ph_3AsO)_2H]I_3$ and $[AsPh_3I]I_3$, have been isolated from the reaction filtrate. The molecular structure of $[(Ph_3AsO)_2H]I_3$ has been determined by single-crystal *X*-ray diffraction techniques.

We have recently reported[1] the preparation and crystal structure of $[Mn(OPPh_3)_4(O_2SI)_2]$ which reversibly loses one molecule of sulphur dioxide on heating [equation (1)].

$$[Mn(OPPh_3)_4(O_2SI)_2] \underset{SO_2}{\overset{129\,°C}{\rightleftharpoons}} [Mn(OPPh_3)_4(O_2SI)I] + SO_2 \quad (1)$$

Attempted preparation of the corresponding arsine oxide by a similar method yielded the complex $[Mn(OAsPh_3)_3(O_2SI)_2]$, in which the sulphur dioxide appears to be activated. Thus, when $[Mn(OAsPh_3)_3(O_2SI)_2]$ is heated *in vacuo* to *ca.* 100 °C the compound $AsPh_3(I_2)$ is formed, a most interesting observation of reduction of triphenylarsine oxide and the oxidation of iodide.[2]

We have since isolated two more unexpected products from the filtrate of the initial reaction of $[Mn(OAsPh_3)_4I_2]$ with sulphur dioxide in toluene. Small numbers of dark red and orange crystals were observed to form in the filtrate after standing for several days. The dark red crystals have been shown by elemental analysis and visible spectroscopy to be $[AsPh_3I]I_3$ ($\lambda_{max.}$ = 295 and 345 nm). This compound has previously been reported by Zingaro and Meyes[3] to be formed by reaction of $AsPh_3S$ with excess of iodine and, although iodine was found to form an adduct with $AsPh_3O$, these workers did not observe reduction of the oxide. Presumably it is co-ordination to the manganese(II) centre by some or all of these ligands (triphenylarsine oxide, iodide, sulphur dioxide) which promotes the facile formation of $[AsPh_3I]I_3$ from $AsPh_3O$.

The orange crystals proved to be suitable for single-crystal *X*-ray analysis, which shows them to be $[(Ph_3AsO)_2H]I_3$. Selected bond lengths and angles and atomic co-ordinates are given in Tables 1 and 2, respectively. The Figure shows the asymmetric unit which contains two independent $[(Ph_3AsO)_2H]^+$ cations together with two I_3^- anions. Compounds in which two phosphoryl or arsenyl fragments are linked together by hydrogen bonding have been reported previously.[4,5] The As–O···O bond angles of *ca.* 120° are consistent with linear OHO hydrogen bonds and the short O···O distances of 2.40 and 2.42 Å in our complex are similar to those previously observed. Short hydrogen bonds of the OHO type may be symmetric, almost symmetric, or asymmetric, and all three types have been observed in the $[(Ph_3YO)_2H]^+$ cations (Y = P or As). However, it is not known to which category our compound belongs since the bridging protons were not located in the structure determination.

Table 1. Selected bond lengths (Å) and angles (°) in $[(Ph_3AsO)_2H]I_3$

I(1)–I(2)	2.940(2)	I(1)–I(2)–I(3)	179.5(1)
I(2)–I(3)	2.903(2)	I(4)–I(5)–I(6)	178.7(1)
I(4)–I(5)	2.890(2)	As(1)–O(1)···O(2)	121.5
I(5)–I(6)	2.954(1)	As(2)–O(2)···O(1)	125.0
As(1)–O(1)	1.666(7)	As(3)–O(3)···O(4)	118.2
As(2)–O(2)	1.685(7)	As(4)–O(4)···O(3)	117.0
As(3)–O(3)	1.674(10)		
As(4)–O(4)	1.667(8)		
O(1)···O(2)	2.40		
O(3)···O(4)	2.42		

Experimental

Preparation of $[Mn(OAsPh_3)_3(O_2SI)_2]$.—The compound $[Mn(OAsPh_3)_4I_2]$ (0.7 g, 0.4 mmol) was slurried in dry toluene (100 cm^3) in a round-bottomed flask (250 cm^3) fitted with a side arm and vacuum stopcock. The flask was evacuated and filled with sulphur dioxide which produced a colour change from beige to orange. After stirring for 3 d the orange $[Mn(OAsPh_3)_3(O_2SI)_2]$ was isolated by standard Schlenk techniques. The filtrate was stored in a stoppered flask and the $[AsPh_3I]I_3$ and $[(Ph_3AsO)_2H]I_3$ formed after standing for several days were isolated by filtration in a dry, argon-filled glove-box.

X-Ray Structure Determination.—*Crystal data.* $C_{36}H_{31}As_2I_3O_2$, M = 1 026.2, triclinic, a = 11.968(6), b = 12.926(7), c = 25.326(6) Å, α = 102.86(4), β = 102.93(4), γ = 92.30(4)°, U = 3 705.9 Å^3, space group $P\bar{1}$, D_c = 1.84 g cm^{-3}, Z = 4, $F(000)$ = 1 952, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 4.26 cm^{-1}; rectangular crystal: 0.45 × 0.45 × 0.20 mm.

X-Ray diffraction data were collected on a CAD4 diffractometer at ambient temperature using graphite-monochromatised Mo-K_α radiation, in the ω—2θ mode. Least-squares refinement on diffractometer angles for 25 automatically centred reflections, 9 < θ < 14°, gave the unit cell. 12 432 Reflections were measured (1 < θ < 24°) yielding 6 803 unique reflections with $F > 3\sigma(F)$. Iodine atoms were located from Patterson synthesis followed by normal heavy-atom procedures.

† Bis(triphenylarsine oxide)hydrogen(I) tri-iodide.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii–xx.

Table 2. Final fractional atomic co-ordinates for non-hydrogen atoms (× 10^4) of $[(Ph_3AsO)_2H]I_3$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
I(1)	4 087(1)	3 608(1)	2 153(1)	C(34)	6 277(15)	1 444(14)	7 240(6)
I(2)	3 204(1)	4 401(1)	3 147(1)	C(35)	6 640(12)	2 133(12)	6 957(7)
I(3)	2 352(1)	5 190(1)	4 135(1)	C(36)	5 920(10)	2 283(10)	6 467(6)
I(4)	2 810(1)	−1 468(1)	6 983(1)	As(3)	2 542(1)	5 622(1)	8 952(1)
I(5)	2 109(1)	−645(1)	8 006(1)	O(3)	1 815(7)	5 352(6)	9 406(4)
I(6)	1 380(1)	241(1)	9 042(1)	C(37)	3 192(10)	4 365(9)	8 640(6)
As(1)	1 210(1)	94(1)	3 990(1)	C(38)	4 032(11)	4 405(11)	8 359(7)
O(1)	2 282(6)	−104(6)	4 493(3)	C(39)	4 449(14)	3 507(14)	8 129(7)
C(1)	351(9)	1 200(10)	4 260(4)	C(40)	3 988(16)	2 524(14)	8 174(7)
C(2)	−421(10)	1 055(9)	4 555(5)	C(41)	3 166(15)	2 484(12)	8 451(7)
C(3)	−1 046(11)	1 840(12)	4 759(5)	C(42)	2 741(11)	3 406(9)	8 695(6)
C(4)	−872(11)	2 849(12)	4 681(6)	C(43)	1 500(10)	6 054(9)	8 358(6)
C(5)	−75(10)	3 047(11)	4 357(6)	C(44)	1 749(13)	6 009(11)	7 865(6)
C(6)	553(10)	2 237(9)	4 167(5)	C(45)	975(15)	6 316(12)	7 448(7)
C(7)	1 851(11)	518(8)	3 435(6)	C(46)	−13(14)	6 716(12)	7 555(8)
C(8)	2 966(11)	969(9)	3 571(6)	C(47)	−251(12)	6 800(13)	8 049(8)
C(9)	3 368(14)	1 347(11)	3 194(7)	C(48)	514(12)	6 474(12)	8 490(6)
C(10)	2 707(15)	1 221(10)	2 657(7)	C(49)	3 765(10)	6 717(10)	9 309(5)
C(11)	1 582(14)	740(12)	2 507(6)	C(50)	3 603(13)	7 749(11)	9 264(6)
C(12)	1 150(11)	390(11)	2 900(6)	C(51)	4 482(17)	8 549(14)	9 532(8)
C(13)	191(10)	−1 181(9)	3 670(5)	C(52)	5 494(18)	8 297(17)	9 829(9)
C(14)	603(11)	−2 162(10)	3 698(5)	C(53)	5 658(13)	7 315(16)	9 888(7)
C(15)	−116(13)	−3 084(11)	3 463(6)	C(54)	4 784(11)	6 469(12)	9 616(6)
C(16)	−1 210(15)	−3 028(13)	3 169(7)	As(4)	1 762(1)	7 171(1)	10 654(1)
C(17)	−1 636(12)	−2 054(12)	3 122(6)	O(4)	2 527(6)	6 234(6)	10 383(3)
C(18)	−931(10)	−1 119(10)	3 389(5)	C(55)	2 736(9)	8 505(9)	10 896(5)
As(2)	3 754(1)	2 026(1)	5 678(1)	C(56)	2 264(11)	9 442(10)	11 072(5)
O(2)	2 695(6)	1 021(6)	5 420(4)	C(57)	2 995(13)	10 356(11)	11 277(6)
C(19)	4 581(9)	2 219(9)	5 144(5)	C(58)	4 174(13)	10 300(12)	11 322(6)
C(20)	4 400(10)	3 081(10)	4 895(5)	C(59)	4 569(13)	9 361(13)	11 137(7)
C(21)	5 014(12)	3 238(13)	4 523(6)	C(60)	3 869(10)	8 450(10)	10 924(6)
C(22)	5 771(12)	2 494(13)	4 369(6)	C(61)	347(9)	7 277(9)	10 147(5)
C(23)	5 933(12)	1 634(13)	4 602(7)	C(62)	−539(10)	6 552(9)	10 040(5)
C(24)	5 337(10)	1 477(10)	4 993(6)	C(63)	−1 564(12)	6 569(11)	9 665(6)
C(25)	3 099(9)	3 308(10)	5 906(5)	C(64)	−1 652(12)	7 396(13)	9 407(6)
C(26)	3 722(11)	4 146(10)	6 321(6)	C(65)	−733(11)	8 128(11)	9 489(6)
C(27)	3 313(12)	5 112(10)	6 450(6)	C(66)	279(11)	8 097(10	9 853(5)
C(28)	2 201(12)	5 247(11)	6 170(6)	C(67)	1 373(9)	6 781(9)	11 274(5)
C(29)	1 568(11)	4 435(11)	5 768(6)	C(68)	597(10)	7 326(11)	11 546(5)
C(30)	2 004(10)	3 444(10)	5 638(6)	C(69)	310(12)	7 019(12)	11 981(6)
C(31)	4 819(10)	1 761(9)	6 298(5)	C(70)	832(14)	6 183(12)	12 157(6)
C(32)	4 454(11)	1 042(10)	6 586(6)	C(71)	1 608(15)	5 642(12)	11 888(6)
C(33)	5 174(14)	890(12)	7 065(6)	C(72)	1 850(12)	5 958(10)	11 465(6)

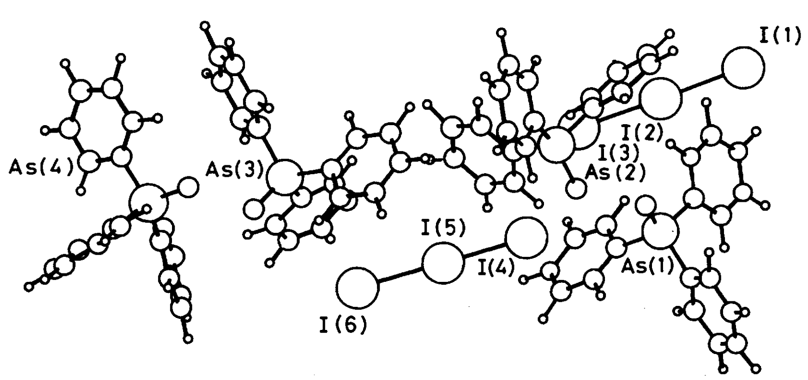

Figure. The asymmetric unit showing the molecular structure of $[(Ph_3AsO)_2H]I_3$

Blocked-matrix least-squares refinement (SHELC 76[6]) with all non-hydrogen atoms anisotropic and H atoms in calculated positions with individual isotropic thermal parameters except for the central protons, which were ignored, gave a final $R = 0.062$ ($R' = 0.068$) $\{w = 1.950_4/[\sigma^2(F_o) + 0.001\ F_o^2]\}$. No chemically significant peaks were observed in the final difference map.

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

Acknowledgements

We are grateful to the S.E.R.C., the Northern Ireland Department of Education, and the British Council for support.

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Received 4*th March* 1987; *Paper* 7/402