Preparation of Tertiary Arsine Sulphides. Crystal and Molecular Structures of the Adduct of $AsMePh_2S$ and $P(NMe_2)_3O$

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Several tertiary arsine sulphides have been prepared by the action of sulphur on tertiary arsines in $C_6H_4Cl_2$-*o* at high temperatures. $AsPh_3$ and $AsMePh_2$ react with S_2Cl_2 to produce $AsPh_3Cl_2$ and $AsMePh_2Cl_2$, respectively, and no tertiary arsine sulphide, contrary to an earlier report. The reversible transfer of sulphur from $AsPh_3S$ to $AsMePh_2$ occurs readily in solution. Methyldiphenylarsine sulphide, a liquid at room temperature, forms a 1 : 1 crystalline adduct with $P(NMe_2)_3O$. The structure of the adduct has been determined from 1 913 independent diffractomer data and refined to a final *R* factor of 0.050. The crystals are orthorhombic, space group *Pbca* with *a* = 11.866(3), *b* = 17.134(7), *c* = 22.657(2) Å, and *Z* = 8. There were no interactions between the two components other than normal van der Waals forces. Bond lengths and angles appeared normal with As–S 2.069(3), As–C(methyl) 1.932(10), As–C(phenyl) 1.947(average), P–O 1.461(7), and P–N 1.649 Å(average).

SULPHIDES of tertiary phosphines can be readily prepared from the action of sulphur on the phosphines themselves, although other routes can be advantageous in some cases. In general, more basic trialkylphosphines have a greater affinity for sulphur and react more readily than triarylphosphines.[1,2]

The action of sulphur on tertiary arsines is less reliable as a route to AsR_3S and has often failed,[3] although under some conditions or with more reactive arsines the method has met with success.[4] Tertiary arsine sulphides are undoubtedly more difficult to synthesise than their phosphorus analogues, however, and are usually approached by less direct methods. Reported examples include the action of H_2S on AsR_3X_2,[3a] $AsR_3(OH)_2$,[3a] $AsR_3(OH)X$,[5] or AsR_3O;[3a] the action of S_2Cl_2 or SCl_2 on AsR_3;[6] and treatment of AsR_3O by CS_2[7] (interestingly, the analogous reaction between PR_3O and CS_2 failed to proceed).

RESULTS AND DISCUSSION

We have examined the reactions between $AsRPh_2$ (R = Me, Ph, CH_2AsPh_2, and $C_2H_4AsPh_2$) and sulphur. Triphenylarsine has been reported not to react with sulphur in CS_2.[3a] Likewise, we observed no reaction between $AsMePh_2$ and S_8 after refluxing in benzene for 20 h, or between $Ph_2AsCH_2AsPh_2$ and S_8 after refluxing in toluene for 24 h. The use of more rigorous conditions led to success, however. Triphenylarsine sulphide was produced in 60% yield after treating $AsPh_3$ with sulphur at 150 °C for 8 h, in *o*-dichlorobenzene. Similarly, $AsMePh_2$ was converted (80%) into $AsMePh_2S$ after 24 h in *o*-dichlorobenzene at 140 °C, and $Ph_2AsCH_2AsPh_2$ was converted (70%) to the monosulphide $Ph_2(S)AsCH_2AsPh_2$ after 14 h at 150 °C. Previously, it has been reported that $AsMePh_2$ failed to react with sulphur even when the two materials were fused together.[4a] We have converted $Ph_2AsC_2H_4AsPh_2$ into $Ph_2(S)AsC_2H_4As(S)Ph_2$ by heating the diarsine with sulphur at 150 °C until the molten mixture solidified.

Interestingly, we failed to obtain the disulphide of bis(diphenylarsino)methane, even after prolonged heating with excess sulphur in *o*-dichlorobenzene, although its isolation from the reaction between $Ph_2AsCH_2AsPh_2$ and S_8 in ethanol has been reported.[4d] The pentavalent arsenic atom of $Ph_2(S)AsCH_2AsPh_2$ probably exerts a deactivating effect on the arsenic(III) centre, slowing the entry of the second sulphur. [Such an effect has been observed with $Ph_2(S)PCH_2PPh_2$, although $Ph_2(S)PCH_2$-$P(S)Ph_2$ has been isolated.[2]] Our failure to obtain the disulphide suggests that a strong solvent influence operates in these reactions (see below).

The compounds $AsPh_3S$, $Ph_2(S)AsCH_2AsPh_2$, and $Ph_2(S)AsC_2H_4As(S)Ph_2$ are solid materials which were readily purified by recrystallisation. $AsMePh_2S$ is a viscous liquid at room temperature and resisted attempts at purification, either by low-temperature crystallisation or vacuum distillation (which led to partial decomposition). When the methyldiphenylarsine sulphide was treated in benzene solution to which $P(NMe_2)_3O$ [tris(dimethylamino)phosphine oxide, tdpo] had been added, a 1 : 1 adduct $AsMePh_2S$·tdpo was produced as colourless crystals. The adduct melted at 90—94 °C, and did not reform on cooling. It could readily be formed by slow crystallisation of $AsMePh_2S$ from a number of solvents to which tdpo was added. Its n.m.r. spectrum suggests that in solution the two components are completely separated, and neither its i.r. spectrum (solid) nor its u.v. spectrum (solution) indicate any strong interactions between the molecules, all of them being essentially the sum of the parameters of the individual components. *X*-Ray crystallographic analysis (see below) showed no interactions other than van der Waals forces between the two components.

Although $AsMePh_2$ failed to react with sulphur in refluxing benzene, a reaction proceeded in 4 : 1 benzene–tdpo after 20 h at room temperature. It thus appears that as well as providing a co-crystallising agent, tdpo can have an activating effect on the reaction itself. Chivers and Drummond[8] have reported such a catalytic effect of tdpo on the reaction between certain tertiary phosphines and sulphur.

The $AsMePh_2S$·tdpo adduct appears to be the first of its type reported. Solid complexes of $POCl_3$ or $POBr_3$ with tdpo have been described,[9] but these are probably ionic in character,[10] $[(Me_2N)_3P^+–O–POCl_2]Cl^-$. Adducts between $P(OR)_3O$ and tdpo, described in the patents literature,[11] are semi-solid and ill defined. Crystalline 1 : 1 adducts of PPh_3S with PPh_3Se, and $AsPh_3S$ with $AsPh_3Se$, prepared by the action of SeS_2 on PPh_3 or $AsPh_3$ respectively, have been reported.[12] We have carefully recrystallised samples of PPh_3S from benzene–trimethyl phosphate, and $AsPh_3S$ from benzene–tdpo, but in neither case was an adduct formed.

Triphenylarsine has been reported to react with S_2Cl_2, to produce triphenylarsine sulphide.[6] We find that the reaction proceeds differently, however, and gives the dichloride $AsPh_3Cl_2$. $AsMePh_2$ reacted similarly to yield $AsMePh_2Cl_2$. In neither case was there any evidence (i.r. or n.m.r.) for the formation of tertiary arsine sulphide. We are unable to account for the difference between our results and those of Glidewell.[6] The S_2Cl_2 was purified by vacuum distillation immediately before use. Treatment of the resulting $AsPh_3Cl_2$ with H_2S led to good yields of $AsPh_3S$.

The transfer of sulphur from a tertiary phosphine sulphide to a more basic phosphine is a well known reaction of considerable synthetic value.[1] We have treated $AsPh_3S$ with $AsMePh_2$ in the hope of transferring the sulphur to the other arsenic atom, thereby providing an alternative route to $AsMePh_2S$. After mixing the two compounds together in deuteriochloroform solution, n.m.r. investigation showed that the reaction proceeded to the right (see equation) and reached equilibrium at about 85% $AsMePh_2S$ after 19 h at room temperature. After removing the solvent, an attempt

$$AsPh_3S + AsMePh_2 \rightleftharpoons AsPh_3 + As(S)MePh_2$$

was made to remove $AsPh_3$ from the mixture by vacuum sublimation (75 °C/0.06 Torr *) in a cold-finger apparatus. (We have removed $AsPh_3$ from $AsPh_3S$–$AsPh_3$ mixtures by this method.) Unfortunately only $AsMePh_2$, being the most volatile component, distilled out, thereby reversing the reaction. The rate of transfer of sulphur atoms between tertiary arsines appears to be faster than sulphur transfer between tertiary phosphines, but slower than selenium transfer between phosphines, which is fast on the n.m.r. timescale.[2a]

Crystal and Molecular Geometries.—The primary reason for undertaking an *X*-ray analysis was to investigate the solid-state relationship between the two components of the adduct, both of which are liquids at room temperature. However, a close examination of the intermolecular separations and relationships failed to reveal any indication of a strong attractive interaction. In particular, there are few separations involving either S or O of less than 4 Å, and the crystal packing is apparently dominated by van der Waals forces.† A plausible conclusion is that the formation of the crystalline adduct is a fortuitous result of mutual accommodation of steric and space-filling requirements in a manner energetically favourable for crystal formation.

Of the two components of the adduct, the geometry of tdpo is of considerable interest, since this important molecule has hitherto been studied only in its hydrogen-bonded complexes[13] with two molecules of S_7NH or barbital. Two of the N–C bonds reported in the S_7NH adduct appear to be highly abnormal. Our structure is in reasonable agreement with those of the hydrogen-bonded material, but reveals no unusual N–C bonds. We have no explanation for the distortions reported previously.

TABLE 1

Atomic fractional co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x/a*	*y/b*	*z/c*
As(1)	8 128(1)	972(1)	6 081(0)
S(1)	8 846(2)	902(2)	6 912(1)
P(1)	1 929(2)	1 372(1)	1 293(1)
O(1)	2 172(5)	1 717(4)	717(3)
N(1)	683(6)	940(5)	1 317(4)
N(2)	1 970(7)	2 028(4)	1 820(3)
N(3)	2 858(7)	688(5)	1 460(4)
C(1)	8 070(8)	−31(5)	5 687(4)
C(2)	8 130(9)	−695(5)	6 031(4)
C(3)	8 103(10)	−1 424(5)	5 751(5)
C(4)	7 969(9)	−1 481(6)	5 160(6)
C(5)	7 892(9)	−803(7)	4 814(5)
C(6)	7 941(9)	−76(6)	5 091(5)
C(7)	6 583(6)	1 371(4)	6 105(5)
C(8)	6 043(9)	1 414(6)	6 639(4)
C(9)	4 938(9)	1 707(7)	6 645(5)
C(10)	4 417(8)	1 912(6)	6 141(6)
C(11)	4 944(9)	1 849(6)	5 618(5)
C(12)	6 060(8)	1 555(5)	5 585(5)
C(13)	8 914(8)	1 653(6)	5 539(5)
C(14)	−60(11)	990(11)	1 811(7)
C(15)	304(9)	458(7)	841(5)
C(16)	2 338(12)	1 906(7)	2 407(5)
C(17)	1 386(11)	2 773(7)	1 730(5)
C(18)	4 054(9)	837(7)	1 338(6)
C(19)	2 640(12)	30(7)	1 827(6)

The co-ordination at phosphorus is tetrahedral, but slightly distorted from idealised geometry with all three interbond angles involving the P=O bond being systematically larger than those involving P–N bonds. This feature has also been observed in several phosphinamide[14,15] and phosphazene[16] derivatives. The P–N bonds (average length 1.649 Å) are typical of values found in the above examples. The extent to which such bond lengths should be associated with partial double-bond character is the subject of considerable speculation, but we note that in the present case all three NMe_2 groups are planar, whereas in several phosphinamides[14,15] pyramidal geometries have been observed for P-bonded amines, and this feature has been associated with chemical reactivities.

Comparisons with the structures of the closely related derivatives $P[N(C_2H_4)_2O]_3$, $P[N(C_2H_4)_2CH_2]_3$,[17] $P[N(C_2H_4)_2O]_3Se$, $P[N(C_2H_4)_2CH_2]_3Se$, $P(NMe_2)_3Se$,[18] $[Fe(CO)_3\{P(NMe_2)_3\}_2]$,[19] and $P[N(C_2H_4)_2O]Te$[20] reveal the structure of tdpo to be unusual in having all its N atoms planar and in similar environments. In all the other related molecules, at least one N atom is markedly

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* Throughout this paper: 1 Torr = (101 325/760) Pa.

† The shortest distance from sulphur is 3.72 Å to a carbon of a neighbouring dimethylamine group; the shortest distance from O is 3.24 Å to a carbon of a neighbouring phenyl ring. All other contacts are greater than 3.5 Å.

distorted towards pyramidal geometry, and this was believed to be a fundamental structural feature of such molecules.[18] Obviously, the interplay of factors affecting the structures of these materials is subtle, with very minor variations in composition being able to exert a marked structural influence.

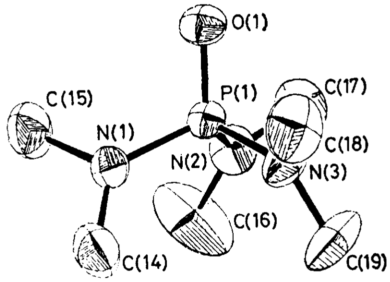

FIGURE 1 A view of tris(dimethylamino)phosphine oxide, defining the atomic numbering

A close examination of the NMe_2 groups and their relationship to the central P atom reveals some further features of interest. Figure 1 in conjunction with the torsion angles presented in Table 2 reveals that the molecule adopts a propeller conformation, and in no case does the P=O bond lie in the plane of an NMe_2 group. Although planar, the NMe_2 groups are consistently distorted from trigonal geometry, with the C–N–C angles contracted (average value 114.8°) and *one* P–N–C angle expanded (average value 124.9°). The average value of the other P–N–C angle is 119.4°.

TABLE 2

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Bonded distances

As(1)–S(1)	2.069(3)	N(3)–C(19)	1.422(15)
As(1)–C(1)	1.937(8)	C(1)–C(2)	1.379(12)
As(1)–C(7)	1.956(7)	C(1)–C(6)	1.361(14)
As(1)–C(13)	1.932(10)	C(2)–C(3)	1.399(13)
P(1)–O(1)	1.461(7)	C(3)–C(4)	1.350(17)
P(1)–N(1)	1.654(8)	C(4)–C(5)	1.403(15)
P(1)–N(2)	1.641(8)	C(5)–C(6)	1.395(15)
P(1)–N(3)	1.652(8)	C(7)–C(8)	1.373(14)
N(1)–C(14)	1.427(17)	C(7)–C(12)	1.368(14)
N(1)–C(15)	1.430(15)	C(8)–C(9)	1.404(15)
N(2)–C(16)	1.415(14)	C(9)–C(10)	1.345(18)
N(2)–C(17)	1.465(14)	C(10)–C(11)	1.344(18)
N(3)–C(18)	1.468(14)	C(11)–C(12)	1.419(14)

(*b*) Interbond angles

C(1)–As(1)–S(1)	112.5(3)	C(7)–As(1)–S(1)	112.4(3)
C(13)–As(1)–S(1)	114.5(3)	C(7)–As(1)–C(1)	106.8(4)
C(13)–As(1)–C(1)	105.0(4)	C(2)–C(1)–As(1)	118.0(7)
C(6)–C(1)–As(1)	120.8(7)	C(13)–As(1)–C(7)	105.0(4)
C(8)–C(7)–As(1)	118.7(7)	C(12)–C(7)–As(1)	118.9(7)
N(1)–P(1)–O(1)	112.7(4)	N(2)–P(1)–O(1)	111.6(4)
N(3)–P(1)–O(1)	111.1(4)	N(2)–P(1)–N(1)	107.9(4)
N(3)–P(1)–N(1)	105.8(4)	C(14)–N(1)–P(1)	123.5(9)
C(15)–N(1)–P(1)	120.9(7)	N(3)–P(1)–N(2)	107.3(4)
C(16)–N(2)–P(1)	126.4(7)	C(17)–N(2)–P(1)	118.7(7)
C(18)–N(3)–P(1)	118.6(7)	C(19)–N(3)–P(1)	125.0(8)
C(15)–N(1)–C(14)	115.6(10)	C(17)–N(2)–C(16)	113.9(9)
C(19)–N(3)–C(18)	115.0(9)	C(6)–C(1)–C(2)	121.3(8)
C(3)–C(2)–C(1)	118.5(9)	C(5)–C(6)–C(1)	120.1(9)
C(4)–C(3)–C(2)	121.1(9)	C(5)–C(4)–C(3)	120.1(10)
C(6)–C(5)–C(4)	118.9(10)	C(12)–C(7)–C(8)	122.4(8)
C(9)–C(8)–C(7)	117.6(9)	C(11)–C(12)–C(7)	117.4(9)
C(10)–C(9)–C(8)	121.0(11)	C(11)–C(10)–C(9)	120.9(10)
C(12)–C(11)–C(10)	120.6(10)		

(*c*) Selected torsion angles

S(1)–As(1)–C(1)–C(2)	21.1(8)
S(1)–As(1)–C(1)–C(6)	–160.8(7)
S(1)–As(1)–C(7)–C(8)	–12.9(8)
S(1)–As(1)–C(7)–C(12)	170.7(6)
O(1)–P(1)–N(1)–C(14)	–139.5(10)
O(1)–P(1)–N(1)–C(15)	43.2(9)
O(1)–P(1)–N(2)–C(16)	–145.8(9)
O(1)–P(1)–N(2)–C(17)	46.7(9)
O(1)–P(1)–N(3)–C(18)	42.8(9)
O(1)–P(1)–N(3)–C(19)	–151.3(9)

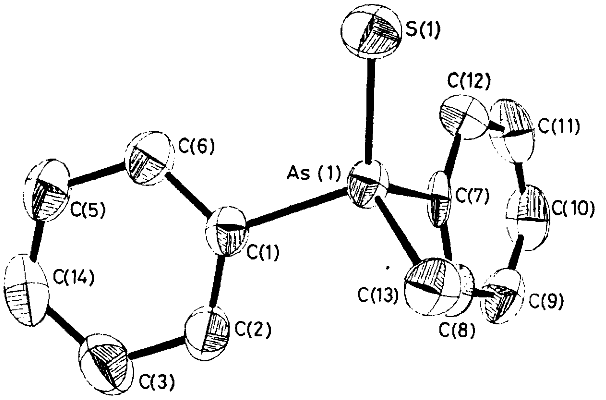

FIGURE 2 A view of methyldiphenylarsine sulphide, defining the atomic numbering

The methyldiphenylarsine sulphide group is also characterised by tetrahedral geometry, again slightly distorted such that the interbond angles involving As–S are systematically larger than those involving only As–C. The As–S bond length is 2.069(3) Å. The overall geometry and bond lengths compare closely with those of $AsPh_3S$.[21]

EXPERIMENTAL

Reactions were performed under an atmosphere of pure dry nitrogen. Proton n.m.r. spectra were recorded on a Varian T60 or JEOL C-60HL spectrometer, and i.r. spectra were recorded on a Perkin-Elmer 225 instrument.

Triphenylarsine Sulphide.—$AsPh_3$ (1 g, 3.27 mmol) was heated with sulphur (0.2 g, 6.25 mmol) in *o*-dichlorobenzene (10 cm^3) at 50 °C for 8 h. The solution volume was reduced on a rotary evaporator. A white crystalline sample of $AsPh_3S$ (0.65 g, 59%) was produced, filtered off, and washed with n-pentane, m.p. 165—166 °C (lit.[3a] 163.5 °C) (Found: C, 64.1; H, 4.35. Calc. for $C_{18}H_{15}AsS$: C, 63.9; H, 4.4%).

Diphenylarsino(diphenylarsinothioyl)methane, $Ph_2(S)AsCH_2AsPh_2$.—The compound $Ph_2AsCH_2AsPh_2$ (3 g, 6.36 mmol) and sulphur (0.43 g, 14 mmol) were heated in $C_6H_4Cl_2$-*o* at 150 °C for 14 h. A white solid was deposited, which was recrystallised from benzene (15 cm^3) to produce $Ph_2(S)AsCH_2AsPh_2$ (2.2 g, 70%), m.p. 136—140 °C (lit.[5] 138—139 °C), ν(As–S) 489, 478 cm^{-1} (Found: C, 59.7; H, 4.4; S, 6.8. $C_{25}H_{22}As_2S$ requires C, 59.5; H, 4.4; S, 6.4%). A similar reaction in toluene failed to proceed.

1,2-*Bis(diphenylarsinothioyl)ethane*, $Ph_2(S)AsC_2H_4As(S)Ph_2$.—The compound $Ph_2AsC_2H_4AsPh_2$ (4 g, 8.23 mmol) and sulphur (0.55 g, 17.2 mmol) were heated together at 150 °C. The diarsine melted and a suspension of sulphur in the diarsine resulted. The mixture resolidified suddenly after 30 min.

The resultant solid was extracted into boiling toluene. Removal of the solvent and recrystallisation from ethanol produced pure $Ph_2(S)AsC_2H_4As(S)Ph_2$ (1.8 g, 40%), m.p. 200—203 °C (lit.[4b] 200 °C), ν(As–S) 499 cm^{-1} (Found: C, 56.9; H, 4.45. $C_{26}H_{24}As_2S_2$ requires C, 56.7; H, 4.4%).

Methyldiphenylarsine Sulphide.—(*a*) Methyldiphenylarsine (0.5 cm^3, 2.6 mmol) was added by syringe to a suspension of sulphur (83.5 mg, 2.61 mmol) in a mixture of benzene (20 cm^3) and tdpo (5 cm^3). The resulting clear, colourless solution was stirred at room temperature for 20 h, at which time n.m.r. examination of an aliquot indicated substantial (but not complete) conversion to an arsenic(v) compound. Benzene–water extraction, followed by drying of the benzene layer by $Mg[SO_4]$ (anhydrous), reduction of the volume by evaporation then the addition of some n-pentane produced clear colourless crystals of $AsMePh_2S{\cdot}P(NMe_2)_3O$, which was recrystallised from cyclohexane (0.4 g, 30%), ν(As–S) 491, 480 cm^{-1}, ν(P–O) 1 208 cm^{-1} (Found: C, 50.2; H, 6.9; N, 9.1. $C_{19}H_{31}AsN_3OPS$ requires C, 50.1; H, 6.9; N, 9.2%).

A similar experiment without the presence of tdpo in the benzene failed to proceed, even after refluxing for 20 h.

(*b*) Methyldiphenylarsine (1 cm^3, 5.2 mmol) and sulphur (0.2 g, 6.25 mmol) were heated in $C_6H_4Cl_2$-*o* (20 cm^3) at 140 °C for 24 h. Hydrogen-1 n.m.r. examination of an aliquot indicated 80% conversion to $AsMePh_2S$. Removal of the solvent left a brown oil. Attempts to crystallise the oil from a variety of solvents were unsuccessful. When tdpo was added to a benzene solution, the 1 : 1 adduct $AsMePh_2S{\cdot}P(NMe_2)_3O$ crystallised readily (71%), m.p. 90—94 °C.

Reaction between $AsPh_3$ *and* S_2Cl_2.—(*a*) Disulphur dichloride (0.5 cm^3, 6.25 mmol) was condensed under vacuum onto a solution of $AsPh_3$ (1.59 g, 5.2 mmol) in dry ether (20 cm^3) at −196 °C. On warming to melt the ether, immediate reaction occurred to produce $AsPh_3Cl_2$ (1.82 g, 93%), ν 472, 365, 310 cm^{-1},[13] and sulphur, which was removed by chloroform extraction.

(*b*) In a similar experiment, S_2Cl_2 was added dropwise to the ether solution of $AsPh_3$ at room temperature. This also resulted in $AsPh_3Cl_2$ being formed. No evidence (n.m.r. or i.r.) for the formation of $AsPh_3S$ at any stage could be found.

Reaction of $AsMePh_2$ *with* S_2Cl_2.—In a reaction similar to (*a*) above, S_2Cl_2 was condensed onto a solution of $AsMePh_2$ in ether. Immediate reaction took place, depositing sulphur. The ether was removed and the product extracted into chloroform, leaving behind sulphur of plastic consistency. Removal of the chloroform produced $AsMePh_2Cl_2$ (1.6 g, 96%), ν(As–Cl) 310 cm^{-1}.[22]

The $AsMePh_2Cl_2$ was dissolved in ethanol, and H_2S gas was bubbled through the solution for 1 h. After filtration and removal of the solvent, a green-tinted oil of $AsMePh_2S$ remained. As before, attempts to crystallise this compound in the absence of tdpo failed. Vacuum distillation (120 °C, 0.06 Torr) caused extensive decomposition.

Crystal Data.—$As(CH_3)(C_6H_5)_2S{\cdot}P[N(CH_3)_2]_3O$ (1/1), $M = 485$, Orthorhombic, $a = 11.866(3)$, $b = 17.134(7)$, $c = 22.657(2)$ Å, $U = 4\,601.04$ Å^3, $D_m = 1.39$ g cm^{-3} (by flotation), $Z = 8$, $D_c = 1.40$ g cm^{-3}, $F(000) = 1\,824$, space group *Pbca*, (Mo-K_α) radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 1.96 cm^{-1}.

Crystallographic Measurements and Structure Determination.—A small crystal was exposed to graphite-monochromated radiation on an Enraf Nonius CAD 4 diffractometer, and the intensities of 1 913 independent reflections $[I > 2.5\,\sigma(I)]$ were measured using the θ,ω-scan technique in the range 2θ 0—60°. The intensities were corrected for Lorentz and polarisation factors, but not for absorption.

The structure was partially resolved by direct methods using the MULTAN set of programs to derive phases for 204 reflections with $|E| > 2.09$. The complete structure was revealed by a subsequent structure-factor and electron-density calculation. Refinement of the atomic positional and anisotropic parameters by full-matrix least-squares calculations using the SHELX set of programs converged when *R* was 0.050. Unit weights were applied through the refinement. Positions were calculated for hydrogen atoms and these were included as fixed contributors in the least-squares calculations.

Views of the two molecules comprising the adduct are shown in Figures 1 and 2, and define the atomic numbering. Atomic co-ordinates are presented in Table 1, while Table 2 contains interatomic distances and angles. Further details of the molecular geometry, together with observed and calculated structure factors and anisotropic thermal parameters, are in Supplementary Publication No. SUP 23043 (19 pp.).*

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.