Structures of Indium Trihalide Complexes with Phosphine Oxides and Dimethyl Sulphoxide, with Comments on the Metal–Oxygen Bonding†

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The crystal structures of several phosphine oxide and dimethyl sulphoxide complexes of indium trihalides have been determined. The compounds $[InCl_3(Me_3PO)_2(MeOH)]$, $[InCl_3(Me_3PO)_2(H_2O)]\cdot H_2O$, $[InCl_3(PhMe_2PO)_3]\cdot H_2O$, $[InCl_3(Me_2SO)_3]$, and $[InBr_3(Me_2SO)_3]$ are all *fac* octahedral, but $[InCl_3(Me_3PO)_3]$ has the *mer* configuration. Triphenylphosphine oxide yields ionic derivatives of the type $[InX_2(Ph_3PO)_4]^+[InX_4]^-$ (X = Cl or Br). Methyldiphenylphosphine oxide gives covalent $[InCl_3(Ph_2MePO)_3]$, but ionic $[InBr_2(Ph_2MePO)_4]^+[InBr_4]^-$. The general development of six-co-ordination is possible through enlargement of the In–O–P bond angles, with individual values (range 135—160°) dependent upon steric interactions. The behaviour is consistent with a predominantly electrostatic metal–oxygen bonding. For the methanol and aqua complexes, determination of the positions of the hydroxylic protons established the ligand orientation with respect to the In–O vector. A quasi-ionic metal–ligand interaction is again in evidence.

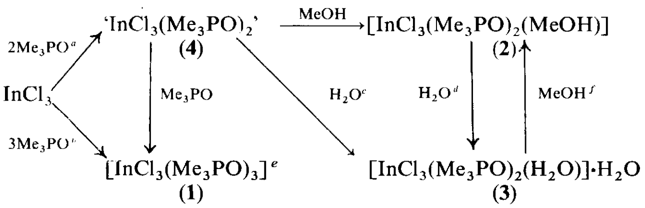
We have recently described the structure of an isomorphous series of thio ligand complexes of indium halides of the type $[InX_3(Me_3MS)_2]$, where X = Cl or Br and M = P or As.[1] The indium is in trigonal bipyramidal co-ordination, although the characteristically low angularity at sulphur (108—113°) leads to intramolecular repulsions which cause marked distortions from ideal geometry. A trigonal bipyramidal hexamethylphosphoramide, $(Me_2N)_3PO$, complex is known,[2] but trimethylphosphine oxide, in its behaviour towards indium trihalides, offers a contrast. Its neutral complexes with indium trichloride contain six-co-ordinated indium as in $[InCl_3(Me_3PO)_3]$ (**1**), $[InCl_3(Me_3PO)_2(MeOH)]$ (**2**), and $[InCl_3(Me_3PO)_2(H_2O)]\cdot H_2O$ (**3**). There is however, also an ionic chloro complex of composition approximating to $InCl_3(Me_3PO)_2$ (**4**), but with analyses indicating a small deficit of ligand, and of as yet unsolved structure. An isomorphous compound (**4a**) is the only product obtainable from indium tribromide and trimethylphosphine oxide. Towards trimethylarsine oxide, the bromide and chloride showed the same behaviour, in forming only the ligand-bridged species $[(InX_3)_2(Me_3AsO)_3]$.[3]

The use of phosphine oxides in which there is progressive introduction of larger phenyl groups does not reduce the indium co-ordination number. The compounds $[InCl_3(PhMe_2PO)_3]\cdot H_2O$ (**5**), and $[InCl_3(Ph_2MePO)_3]$ (**6**) remain covalent octahedral, but triphenylphosphine oxide differs in giving an ionic product $[InCl_2(Ph_3PO)_4]^+[InCl_4]^-$ (**7**). Dimethyl sulphoxide (Me_2SO), a ligand of lower steric requirement than trimethylphosphine oxide gave only the known derivatives $[InCl_3(Me_2SO)_3]$ (**8**) and $[InBr_3(Me_2SO)_3]$ (**9**).[4]

Together with *X*-ray determinations on most of these compounds (Table 1), we now discuss the structural implications, including some broader aspects of the bonding of oxo-ligands at a metal centre.

Experimental

Preparation of Compounds.—Preparations were made through direct combination of anhydrous indium halide and ligand, commonly in a solvent containing 20% (v/v) triethoxymethane (tem) to reduce solubility and maintain anhydrous conditions. Conditions leading to alternative formation of (**1**)—(**4**) are as shown in the Scheme. Microscopic examination assisted identification of crystalline phases. Using phenyl-substituted ligands the compounds (**5**)—(**7**) were



Scheme. [a] In acetone or ethanol. [b] In tetrahydrofuran. [c] Controlled exposure of ethanol solution to atmospheric moisture. [d] Exposure of crystals to atmosphere. [e] The possibility of converting compound (**2**) or (**3**) into (**1**) was not tested. [f] In methanol solution.

Table 1. Oxo ligand complexes

	Compound	Structure	Evidence
(**1**)	$[InCl_3(Me_3PO)_3]$	*mer* Octahedral	*X*-Ray analysis
(**2**)	$[InCl_3(Me_3PO)_2(MeOH)]$	*fac* Octahedral	*X*-Ray analysis
(**3**)	$[InCl_3(Me_3PO)_2(H_2O)]\cdot H_2O$	*fac* Octahedral	*X*-Ray analysis
(**4**) (**4a**)	'$InX_3(Me_3PO)_2$'[a]	Ionic, $[InX_4]^-$	Vibrational spectra
(**5**)	$[InCl_3(PhMe_2PO)_3]\cdot H_2O$[b]	*fac* Octahedral	*X*-Ray analysis
(**6**)	$[InCl_3(Ph_2MePO)_3]$	Octahedral	I.r. spectrum[c]
(**7**)	$[InCl_2(Ph_3PO)_4]^+[InCl_4]^-$	Ionic	I.r. spectrum
(**7a**)	Anisole solvate of (**7**)[d]	Ionic	*X*-Ray analysis
(**8**)	$[InCl_3(Me_2SO)_3]$	*fac* Octahedral	*X*-Ray analysis
(**9**)	$[InBr_3(Me_2SO)_3]$	*fac* Octahedral	*X*-Ray analysis
(**10**)	$[(InBr_3)_2(Me_3AsO)_3]$	Ligand bridged	*X*-Ray analysis

[a] The chloride (**4**) and bromide (**4a**) are isomorphous. [b] There are also solvates with ethanol (**5a**) and acetone (**5b**), but with corresponding ν(In–Cl) bands. [c] Isomer not identifiable from spectrum. [d] A chlorobenzene solvate (**7b**) has corresponding ν(In–Cl) bands.

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

Non-S.I. unit employed: D ≈ 3.336×10^{-30} Cm.

obtained irrespective of the reactant proportions. The reaction becomes slower with increasing phenyl substitution.

$[InCl_3(Me_3PO)_3]$ (**1**). Acicular crystals of this product formed slowly from tetrahydrofuran containing 20% (v/v) tem (Found: C, 21.8; H, 5.7. Calc. for $C_9H_{27}Cl_3InO_3P_3$: C, 21.7; H, 5.4%).

$[InCl_3(Me_3PO)_2(MeOH)]$ (**2**). Solutions of $InCl_3$ (0.22 g) and ligand (0.18 g) in hot methanol (3 cm^3) deposited crystals slowly on cooling (Found: C, 18.3; H, 5.15. Calc. for $C_7H_{22}Cl_3InO_3P_2$: C, 19.2; H, 5.0%).

$[InCl_3(Me_3PO)_2(H_2O)]\cdot H_2O$ (**3**). Ethanol solutions containing halide and ligand in 1:2 molar proportions, and exposed to air for 30—60 min, gave crystals suitable for *X*-ray analysis. I.r. spectra showed that (**2**) was converted slowly into (**3**) upon exposure to air.

'$InCl_3(Me_3PO)_2$' (**4**) and '$InBr_3(Me_3PO)_2$' (**4a**). For (**4**), the components were dissolved in the minimum quantity of acetone–tem. Light petroleum (b.p. 50—70 °C was added until the appearance of a second liquid layer. Small platy crystals separated in low yield. Well developed crystals of (**4a**) were obtained when the crude product separating from anisole after addition of diethyl ether was recrystallised from methanol–tem (70:30 v/v). Compound (**4a**) differs from (**4**) in showing no reaction with excess of ligand, with methanol, or with atmospheric moisture [Found (hand-sorted samples from different preparations): (*i*) C, 12.45; H, 3.60, (*ii*) 12.05; 3.10, (*iii*) 12.50; 3.15, (*iv*) 12.20; 3.35. Calc. for $C_6H_{18}Br_3InO_3P_3$: C, 13.4; H, 3.35%].

Solvates of $[InCl_3(PhMe_2PO)_3]$. These were obtained with water (**5**), ethanol (**5a**), or acetone (**5b**). Using $InCl_3$ (0.22 g) and $PhMe_2PO$ (0.46 g) in anhydrous ethanol, but without protection from atmospheric moisture, crystals of $[InCl_3(PhMe_2PO)_3]\cdot H_2O$ (**5**) formed on cooling. Under anhydrous conditions with tem, the crystals were of composition $[InCl_3(PhMe_2PO)_3]\cdot EtOH$ (**5a**) (Found: C, 42.9; H, 5.7. Calc. for $C_{26}H_{39}Cl_3InO_4P_3$: C, 42.8; H, 5.35%). The acetone solvate $[InCl_3(PhMe_2PO)_3]\cdot Me_2CO$ (**5b**) was obtained from that solvent (Found: C, 43.8; H, 5.8. Calc. for $C_{27}H_{39}Cl_3InO_4P_3$: C, 43.7; H, 5.3%). The i.r. spectra of the three solvates are identical apart from the distinguishing bands from the solvate molecules. Microscope examination of crystals of (**5a**) and (**5b**) showed trigonal symmetry, as for (**5**) on which the *X*-ray analysis was made.

$[InCl_3(Ph_2MePO)_3]$ (**6**) and '$InBr_3(Ph_2MePO)_2$' (**6a**). Indium trichloride (0.22 g) and Ph_2MePO (0.65 g) were heated under reflux in ethanol (4 cm^3) for 30—40 min. A felted mass of silky needles separated on cooling (Found: C, 54.2; H, 5.0. Calc. for $C_{39}H_{39}Cl_3InO_3P_3$: C, 53.9; H, 4.5%). The bromo derivative was obtained similarly, but required recrystallisation from methanol (Found: C, 39.0; H, 3.5. Calc. for $C_{26}H_{26}Br_3InO_2P_2$: C, 39.6; H, 3.3%).

$[InCl_2(Ph_3PO)_4]^+[InCl_4]^-$ (**7**) *and solvates.* After heating the reactants to reflux in ethanol for 2 h[4] crystals of compound (**7**) separated overnight, typically as truncated pyramids. However, they bore striated faces, perhaps through multiple twinning, and proved unsuitable for diffractometry. Recrystallisation from anisole or chlorobenzene gave well formed crystals of $[InCl_2(Ph_3PO)_4][InCl_4]\cdot PhOMe$ (**7a**) or $[InCl_2(Ph_3PO)_4][InCl_4]\cdot PhCl$ (**7b**) [Found (**7a**): C, 56.8; H, 4.3; Cl, 13.0. Calc. for $C_{31}H_{28}Cl_6In_2O_5P_5$: C, 57.0; H, 4.1; Cl, 12.8. Found (**7b**): C, 56.3; H, 4.4; Cl, 14.9. Calc. for $C_{30}H_{25}Cl_7In_2O_4P_4$: C, 56.2; H, 3.9; Cl, 14.9%]. Excepting the solvate bands, the i.r. spectra of compounds (**7**), (**7a**), and (**7b**) were identical. (**7a**) was used for *X*-ray analysis. Of related compounds, analytically pure samples of $[InBr_2(Ph_3PO)_4]^+[InBr_4]^-$ (again as striated crystals) and $[InCl_2(Ph_3AsO)_4]^+[InCl_4]^-$ were also obtained. Their vibrational spectra pointed to these same ionic formulations. Both $[InCl_2(Ph_3PO)_4]^+[InCl_4]^-$ (**7**) and $[InBr_2(Ph_3PO)_4]^+[InBr_4]^-$ gave molar conductivities in nitrobenzene corresponding to 1:1 electrolytes (Λ = 22.0 and 20.0 ohm^{-1} cm^2 mol^{-1}).

$[InCl_3(Me_2SO)_3]$ (**8**) and $[InBr_3(Me_2SO)_3]$ (**9**). Using ethanol solutions of the halides (0.2—0.4 g in 10 cm^3), with Me_2SO in 10% excess,[4] crystals formed overnight, but those of the bromide were always of high mosaicity.

$[(InBr_3)_2(Me_3AsO)_3]$ (**10**). Like its chloride analogue (**10a**),[3] (**10**) is immediately precipitated from ethanol or acetone, irrespective of reactant ratios. Small truncated tetrahedral crystals were obtained through slow extraction into boiling acetone (Found: C, 9.5; H, 2.5; Br, 43.2. Calc. for $C_9H_{27}As_3Br_6InO_3$: C, 9.7; H, 2.4; Br, 43.6%). Neither (**10**) nor (**10a**) forms methanolates.

Spectra.—I.r. spectra were run between 4000 and 200 cm^{-1} as previously.[1] Raman spectra were obtained at the University of Auckland, using a Jasco R300 spectrometer with argon-ion laser excitation. Solutions in $CDCl_3$ for n.m.r. were made up and handled under dry air and calibrated against plasma emission lines.

X-Ray Structure Determinations.—Data were obtained using a Nicolet R3M four-circle diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.701 69 Å) and with the crystals at low temperature. The general procedure was as follows: space group deduced from systematic absences; cell parameters obtained using 25 automatically centred reflections; crystal and instrument stability monitored using three standards every 97 reflections (no significant variations); Lorentz and polarisation corrections included, absorption corrections, based on ψ scans, applied.

The In atoms were usually located from Patterson maps and other atoms (excepting hydrogen) from difference Fourier syntheses. For compound (**3**) the origin was determined by fixing the appropriate indium co-ordinates and there was some consequent difficulty initially in resolving the rest of the structure, similar to that experienced by Whitlow and Gabe[5] for a related structure. Least-squares refinement with anisotropic thermal parameters, excepting isotropic refinement of C atoms of compound (**7a**); function minimised, $\Sigma w(|F_o| - |F_c|)^2$, with reflection weights $w = [\sigma^2|F_o| + g|F_o|^2]^{-1}$; H atoms introduced at idealised positions with fixed thermal parameters. With (**2**) and (**3**), where refinement of positions of hydroxylic protons was included, rotation of methyl groups was allowed. Other details for individual compounds are given in Table 2. Final atomic co-ordinates are listed in Table 3, bond lengths and angles around In in Table 4. Results for compound (**10**) are abbreviated to a comparison with $[(InCl_3)_2(Me_3AsO)_3]$[3] (**10a**), in Table 5.

The SHELXTL (version 5.1) package[6] used included atomic scattering factors and the programs needed for data reduction and structure solution.

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

Results and Discussion

Comments on Structures of Individual Compounds.—As indicated in Table 1 most of the compounds are neutral six co-ordinate complexes, but (**7a**) is ionic with an octahedral cation and an $InCl_4^-$ anion.

$[InCl_3(Me_3PO)_3]$ (**1**). The atoms In, O(1), P(1), Cl(1), Cl(2), and Cl(3) lie on a mirror plane (Figure 1). Orientation of the $Me_3P(2)$ groups places C(21) almost equidistant from Cl(2) and Cl(3), at 3.700 and 3.716 Å. There is significant enlargement of angles subtended by Cl(3), with Cl(2)–In–Cl(1) 175.4° and O(2)–In–O(2′) 172.3°.

Table 2. Crystal data, experimental conditions, and refinement

Compound	$[InCl_3(Me_3PO)_3]$	$[InCl_3(Me_3PO)_2(MeOH)]$	$[InCl_3(Me_3PO)_2(H_2O)]\cdot H_2O$	$[InCl_3(PhMe_2PO)_3]\cdot H_2O$	$[InCl_2(Ph_3PO)_4][InCl_4]\cdot PhOMe$	$[InCl_3(Me_2SO)_3]$	$[InBr_3(Me_2SO)_3]$	$[(InBr_3)_2(Me_3AsO)_3]$
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Trigonal	Monoclinic	Triclinic	Triclinic	Orthorhombic
Space group	*Pnma*	$Pna2_1$	$P2_1$	*R*3*c*	*Cc*	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$
a/Å	16.220(3)	27.159(6)	6.331(3)	16.688(3)	32.234(9)	7.813(1)	7.997(11)	13.321(4)
b/Å	13.213(2)	6.289(1)	9.958(4)	16.688(3)	14.928(4)	8.830(1)	9.068(13)	14.343(4)
c/Å	9.460(1)	9.597(1)	13.132(4)	20.367(4)	17.857(5)	13.474(2)	13.686(24)	14.457(4)
α/°	90	90	90	90	90	81.09(1)	90.06(13)	90
β/°	90	90	93.47(3)	90	117.50(2)	78.88(1)	77.74(13)	90
γ/°	90	90	90	120	90	64.19(1)	65.59(10)	90
U/Å^3	2 027.4(5)	1 639.2(5)	826.4(5)	4 912.1(1.6)	7 621.7(3.7)	818.4(2)	878.7(2.4)	2 762.2(1.4)
Z	4	4	2	6	4	2	2	4
F(000)	1 000	872	440	2 136	3 368	452	560	2 048
M	497.1	437.2	441.2	701	1 662	455.35	588.3	1 116.9
$D_c(D_m)^a$/g cm^{-3}	1.63(1.61)	1.77(1.73)	1.77(1.75)	1.42	1.45	1.85	2.22(2.17)	2.69(2.65)
Crystal size (mm)	0.09 × 0.46 × 0.1	0.16 × 0.25 × 0.54	0.1 × 0.12 × 0.4	0.36 × 0.12 × 0.26	0.32 × 0.1 × 0.5	0.26 × 0.22 × 0.24	0.20 × 0.20 × 0.44	0.16 × 0.16 × 0.16
μ/cm^{-1}	17.88	21.06	20.9	11.27	9.36	22.84	84.26	138.23
Scan mode	ω	ω	ω	ω	ω	ω	ω	ω
Range, 2θ/°	4—45	4—52	4—52	4—52	4—45	4—45	4—52	4—50
Range, *h*	0—18	0—34	−7 to 7	0—21	0—35	0—9	0—10	0—15
Range, *k*	0—15	0—8	0—12	0—21	0—17	−10 to 10	−12 to 12	0—16
Range, *l*	0—11	0—12	0—16	−25 to 25	−20 to 20	−15 to 15	−17 to 17	0—16
Temperature/°C	−100	−135	−80	−90	−120	−110	−120	−110
Total reflections	1 622	1 778	1 866	2 543	4 963	2 216	3 482	2 792
Unique reflections	1 404	1 709	1 717	2 085	4 544	2 057	3 446	2 681
Obs. reflections [$I > 3\sigma(I)$]	855	1 635	1 573	1 469	3 127	1 900	1 622	1 390
Transmission range	0.820—0.851	0.409—0.448	0.671—0.869	0.862—0.906	0.748—0.844	0.642—0.725	0.419—0.742	
Method of solving	Patterson	Patterson	Patterson	Patterson	Direct	Patterson	Direct	Direct
Weighting, *g*	0.0006	0.000 54	0.000 66	0.0022	0.002 (not refined)	0.000 22	0.002 17	0.001 19
Parameters refined	97	170	170	103	464	145	145	178
Treatment of protons	Idealised positions	H–O refined	H–O(3) refined	Idealised positions	Idealised positions	Idealised positions	Idealised positions	Not included
Residual density, e Å^{-3}	1.03, −0.76	0.753, −1.076	0.671, −0.869	1.87, −1.25	0.58, −1.59	0.273, −0.508	2.38, −1.70	1.70, −1.34
$R(R')^b$	0.0500 (0.0602)	0.0211 (0.0274)	0.0335 (0.0391)	0.0544 (0.0720)	0.0565 (0.0689)	0.0189 (0.0264)	0.0645 (0.0780)^c	0.0619 (0.0693)^c

[a] D_m at room temperature. [b] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [c] Refinement prejudiced by inherent high mosaicity of crystals.

$[InCl_3(Me_3PO)_2(MeOH)]$ (**2**). As is noticeable from Figure 2 there is some approach towards a mirror-image relationship between the right and left-hand halves of the molecule. The O(1) • • • C(21) and O(1) • • • C(13) distances are 3.505 and 3.301 Å respectively. With the high polarity of the O(3)–H(1) bond, its length refined to the low value 0.57(8) Å. The shortest intermolecular approach to H(1) is 2.71 Å by a Cl(1) atom, with O(3) • • • Cl(1) 3.21 Å at the upper limit of the hydrogen bonding range.

$[InCl_3(Me_3PO)_2(H_2O)]\cdot H_2O$ (**3**). With respect to the disposition of the Me_3P groups, this molecule (Figure 3) is less symmetrical than (**2**). The torsion angles Cl(3)–In–O(1)–P(1) and Cl(3)–In–O(2)–P(2) have values +99.2 and −122.6° respectively. Atom H(1) of the co-ordinated water molecule lies 2.79 Å from O(1) and 2.70 Å from O(2); H(2) forms a strong hydrogen bond with O(w) of the unco-ordinated water molecule, with O(w) • • • H(2) 2.02 Å and O(w) • • • O(3) 2.674 Å. Atom O(w) could be considered a component of a water dimer,[7] but the role of this second molecule is essentially space-filling.

$[InCl_3(PhMe_2PO)_3]\cdot H_2O$ (**5**). The molecule, as viewed along its C_3 axis, is shown in Figure 4. The molecules lie in columns parallel with the *c* axis of the trigonal cell which contains three such columns. Along the columns alternate molecules have right- and left-handed dispositions of the phenyl 'propeller blades,' giving a racemic crystal. The water molecule is enclosed between the 'downwards projecting' PMe_2Ph groups of one molecule and the 'upwards projecting' Cl atoms of its neighbour. It is disordered, and for refinement its statistical position was taken as one-third occupancy of each of three sites (which in terms of this analysis were found to be 0.74 Å from the C_3 molecular axis).

$[InCl_2(Ph_3PO)_4]^+[InCl_4]^-\cdot PhOMe$ (**7a**). Figure 5 shows the cation structure as viewed almost along Cl(5)In(2)Cl(6). Atom Cl(6) lies within the phenyl rings A, E, J, L, Q, and T, and Cl(5) within D, G, M, R, X, and Z. With the influence of

Table 3. Atomic co-ordinates (10^4) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(1) $[InCl_3(Me_3PO)_3]$							
In	6 829(1)	7 500(0)	1 708(1)	P(2)	6 788(2)	4 982(2)	792(3)
Cl(1)	8 110(3)	7 500(0)	3 098(4)	C(11)	5 441(11)	7 500(0)	6 263(19)
Cl(2)	5 476(3)	7 500(0)	491(5)	C(12)	9 806(8)	6 404(9)	1 099(15)
Cl(3)	7 618(3)	7 500(0)	−555(5)	C(21)	6 291(8)	5 217(10)	−844(12)
O(1)	6 216(7)	7 500(0)	3 740(11)	C(22)	7 797(8)	4 630(12)	375(16)
O(2)	6 760(5)	5 861(5)	1 807(7)	C(23)	6 297(10)	3 934(10)	1 561(15)
P(1)	5 373(3)	7 500(0)	4 377(5)				
(2) $[InCl_3(Me_3PO)_2(MeOH)]$							
In	1 232(1)	11 269(1)	2 501(1)	P(2)	150(1)	9 239(2)	1 269(1)
Cl(1)	1 210(1)	12 342(2)	26(1)	C(11)	2 161(2)	7 711(8)	4 666(5)
Cl(2)	2 089(1)	12 482(2)	2 809(1)	C(12)	1 887(2)	11 095(8)	6 566(6)
Cl(3)	846(1)	14 519(2)	3 395(1)	C(13)	1 404(2)	7 054(9)	6 680(6)
O(1)	1 260(1)	9 776(5)	4 521(4)	C(21)	399(2)	7 751(8)	−135(5)
O(2)	526(1)	9 728(5)	2 389(4)	C(22)	−334(2)	7 659(8)	1 947(5)
O(3)	1 488(1)	8 066(5)	1 813(4)	C(23)	−116(2)	11 616(7)	589(5)
P(1)	1 657(1)	8 996(2)	5 509(1)	C(1)	1 810(2)	7 501(8)	702(5)
(3) $[InCl_3(Me_3PO)_2(H_2O)]\cdot H_2O$							
In	1 567(1)	0	7 541(1)	P(2)	−432(4)	2 986(2)	8 367(2)
Cl(1)	3 293(4)	284(2)	9 277(1)	C(11)	1 445(15)	−2 014(10)	4 821(7)
Cl(2)	2 364(4)	−2 448(2)	7 566(2)	C(12)	−2 309(14)	−2 580(10)	5 873(7)
Cl(3)	4 678(3)	755(2)	6 675(2)	C(13)	−2 441(15)	−608(10)	4 298(6)
O(1)	−178(8)	−182(6)	6 085(4)	C(21)	−1 531(16)	2 236(10)	9 443(7)
O(2)	270(9)	1 993(6)	7 582(4)	C(22)	−2 448(21)	4 044(11)	7 803(8)
O(3)	−1 494(11)	−498(8)	8 158(5)	C(23)	1 684(18)	4 053(11)	8 827(8)
P(1)	−800(4)	−1 280(2)	5 338(1)	O(w)	−3 211(11)	−2 807(7)	8 740(5)
(5) $[InCl_3(PhMe_2PO)_3]\cdot H_2O$							
In	6 667	3 333	5 000	C(4)	4 875(10)	−744(12)	6 616(7)
Cl	6 164(2)	4 281(2)	4 372(2)	C(5)	5 687(10)	−727(9)	6 508(7)
O	7 092(5)	2 627(5)	5 710(4)	C(6)	6 451(9)	48(10)	6 271(6)
P	7 325(2)	1 866(2)	5 767(2)	C(7)	8 306(9)	2 219(9)	6 282(7)
C(1)	6 369(8)	827(7)	6 126(5)	C(8)	7 600(8)	1 522(9)	5 002(6)
C(2)	5 559(10)	816(10)	6 213(8)	O(w)	2 979(30)	−3 833(24)	5 809(19)
C(3)	4 792(9)	4(10)	6 462(8)				
(7a) $[InCl_2(Ph_3PO)_4]^+[InCl_4]^-\cdot PhOMe$*							
In(1)	1 183(1)	−1 936(1)	630(1)	O(1)	4 504(4)	2 988(8)	4 635(8)
Cl(1)	1 009(3)	−772(5)	−344(4)	P(1)	4 854(2)	3 692(3)	4 720(3)
Cl(2)	1 980(2)	−1 909(5)	1 534(4)	O(2)	3 263(4)	1 378(7)	3 443(7)
Cl(3)	787(4)	−1 747(11)	1 414(8)	P(2)	2 878(2)	757(3)	2 888(3)
Cl(4)	1 034(4)	−3 280(6)	−33(10)	O(3)	3 464(4)	3 315(7)	3 847(7)
In(2)	3 892	2 166(1)	4 018	P(3)	3 130(2)	3 963(3)	3 959(3)
Cl(5)	3 944(2)	1 910(3)	5 401(3)	O(4)	4 294(4)	978(7)	4 132(7)
Cl(6)	3 855(2)	2 477(3)	2 654(3)	P(4)	4 624(2)	207(3)	4 531(3)

Table 3 (*continued*) Atomic co-ordinates (10^4) with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z	Atom	x	y	z
(8) $[InCl_3(Me_2SO)_3]$							
In	2 426(1)	1 917(1)	2 591(1)	S(2)	1 665(1)	814(1)	5 048(1)
Cl(1)	−691(1)	3 933(1)	3 395(1)	S(3)	3 182(1)	5 302(1)	2 704(1)
Cl(2)	2 273(1)	3 391(1)	892(1)	C(11)	8 445(5)	−2 301(5)	1 414(3)
Cl(3)	1 346(1)	−161(1)	2 237(1)	C(12)	7 325(6)	816(6)	488(3)
O(1)	5 441(3)	173(3)	2 213(2)	C(21)	1 945(6)	2 291(5)	5 686(3)
O(2)	3 110(4)	565(3)	4 068(2)	C(22)	2 827(5)	−1 034(5)	5 823(3)
O(3)	3 788(3)	3 414(3)	2 999(2)	C(31)	3 767(6)	5 978(5)	3 720(3)
S(1)	6 291(1)	−528(1)	1 172(1)	C(32)	5 034(6)	5 416(5)	1 732(3)
(9) $[InBr_3(Me_2SO)_3]$							
In	5 465(2)	2 013(2)	2 405(1)	S(2)	7 520(7)	672(6)	49(4)
Br(1)	6 568(3)	4 125(2)	1 509(2)	S(3)	1 515(8)	5 192(6)	2 352(4)
Br(2)	4 273(4)	3 535(3)	4 183(2)	C(11)	6 206(36)	2 184(26)	6 471(19)
Br(3)	8 750(3)	−58(3)	2 662(2)	C(12)	1 811(36)	757(29)	4 559(18)
O(1)	4 200(21)	292(15)	2 811(10)	C(21)	6 312(29)	1 835(25)	−834(16)
O(2)	6 014(20)	708(15)	935(11)	C(22)	8 285(30)	−1 297(24)	−577(17)
O(3)	2 636(18)	3 359(14)	2 125(11)	C(31)	552(38)	5 766(27)	1 286(18)
S(1)	4 139(9)	−427(7)	3 820(4)	C(32)	−509(34)	5 422(31)	3 281(18)
(10) $[(InBr_3)_2(Me_3AsO)_3]$*							
In(1)	3 864(2)	6 018(2)	−816(2)	Br(6)	7 372(3)	5 168(3)	333(3)
In(2)	5 494(2)	4 761(2)	348(2)	As(1)	2 997(3)	3 815(3)	9(3)
Br(1)	2 818(3)	5 264(4)	−2 115(3)	As(2)	6 103(3)	5 295(3)	−2 026(3)
Br(2)	2 435(3)	6 759(3)	125(3)	As(3)	4 923(3)	7 071(3)	1 204(3)
Br(3)	4 480(4)	7 427(3)	−1 739(3)	O(1)	3 866(18)	4 714(15)	45(15)
Br(4)	5 692(4)	3 017(3)	−52(3)	O(2)	5 285(16)	5 197(16)	−1 120(16)
Br(5)	5 317(4)	4 556(3)	2 108(3)	O(3)	4 921(15)	6 230(15)	393(14)

*Co-ordinates for C atoms given in Supplementary Data.

Table 4. Bond lengths (Å) and angles (°)

	(1)	**(2)**	**(3)**	**(5)**[a]		**(8)**	**(9)**		**(7a)**
In–Cl(1)	2.459(4)	2.470(3)	2.484(3)	2.484(4)	In–X(1)	2.465(1)	2.625(4)	In(2)–Cl(5)	2.428(6)
In–Cl(2)	2.478(5)	2.466(3)	2.490(3)		In–X(2)	2.449(1)	2.579(4)	In(2)–Cl(6)	2.428(6)
In–Cl(3)	2.495(5)	2.452(3)	2.452(3)		In–X(3)	2.466(1)	2.620(4)	In(2)–O(1)	2.146(12)
In–O(1)	2.164(11)	2.155(4)	2.157(5)	2.196(7)	In–O(1)	2.191(2)	2.199(17)	In(2)–O(2)	2.151(11)
In–O(2)	2.171(7)	2.151(3)	2.149(6)		In–O(2)	2.190(2)	2.198(15)	In(2)–O(3)	2.133(12)
In–O(3)		2.231(4)	2.202(7)		In–O(3)	2.204(3)	2.200(14)	In(2)–O(4)	2.150(12)
O(1)–P(1)	1.493(12)	1.518(3)	1.505(6)	1.507(10)	O(1)–S(1)	1.531(3)	1.528(15)	O(1)–P(1)	1.498(14)
O(2)–P(2)	1.507(7)	1.514(4)	1.515(6)		O(2)–S(2)	1.538(2)	1.506(15)	O(2)–P(2)	1.499(11)
O(3)–C(1)		1.423(6)			O(3)–S(3)	1.530(3)	1.520(12)	O(3)–P(3)	1.528(14)
								O(4)–P(4)	1.505(11)
Cl(1)–In–Cl(2)	175.4(2)	93.1(1)	91.3(1)	95.9(1)	X(1)–In–X(2)	96.7(1)	96.2(1)	Cl(5)–In(2)–Cl(6)	177.8(2)
Cl(1)–In–Cl(3)	91.4(2)	95.7(1)	94.0(1)		X(1)–In–X(3)	97.8(1)	97.8(1)	Cl(5)–In(2)–O(1)	87.3(4)
Cl(2)–In–Cl(3)	93.2(2)	96.1(1)	98.0(1)		X(2)–In–X(3)	96.1(1)	96.1(1)	Cl(5)–In(2)–O(2)	90.4(4)
O(1)–In–O(2)	86.5(2)	83.1(1)	85.6(2)	81.4(3)	O(1)–In–O(2)	78.3(1)	78.3(5)	Cl(5)–In(2)–O(3)	90.5(4)
O(1)–In–O(3)		82.1(1)	83.8(2)		O(1)–In–O(3)	81.2(1)	78.9(5)	Cl(5)–In(2)–O(4)	91.1(4)
O(2)–In–O(3)	172.3(4)[b]	81.7(1)	81.5(3)		O(2)–In–O(3)	82.7(1)	83.0(5)	In(2)–O(1)–P(1)	157.6(8)
In–O(1)–P(1)	141.1(7)	136.7(2)	137.6(4)	142.3(5)	In–O(1)–S(1)	123.1(1)	123.1(10)	In(2)–O(2)–P(2)	164.7(10)
In–O(2)–P(2)	137.7(4)	136.8(2)	138.4(3)		In–O(2)–S(2)	124.9(1)	122.6(10)	In(2)–O(3)–P(3)	159.8(8)
In–O(3)–C(1)		129.7(3)			In–O(3)–S(3)	124.4(2)	123.7(10)	In(2)–O(4)–P(4)	159.9(8)

[a] For Cl(1), Cl(2), O(1), O(2), P(1) read Cl, Cl′, O, O′, P (as in Figure 4). [b] For O(3) read O(2′) (as in Figure 1).

the cation charge,[8] d(In–Cl) has fallen to 2.428 Å and d(In–O) to 2.145 Å (average values) [*cf.* averaged values of 2.475 and 2.167 Å for (**1**)—(**3**), and (**5**)]. Within the cell, cation–anion approaches are irregular; around each anion there are six cations giving Cl ··· C distances < 3.75 Å, and Cl ··· H < 3.0 Å. The anisole environment includes five cations giving C ··· C < 3.75 Å. Large thermal parameters for Cl of the anion and for atoms of the anisole molecule showed these units to be only poorly located. Refinement through modelling was not pursued. The compound represents a structural type originally suggested by Nyholm and Ulm[9] for the *o*-phenylenebis(dimethylarsine) (pdma) complex of composition $InX_3(pdma)_2$.

$[InCl_3(Me_2SO)_3]$ (**8**) *and* $[InBr_3(Me_2SO)_3]$ (**9**). The evidence that these compounds are *fac* octahedral removes previous uncertainty[10–12] as to their structure (see Figure 6). As with phosphine oxide derivatives, the O–In–O angles (av. 80.7°) are smaller than the X–In–X (av. 96.8°) between the larger, but more strongly bonded halogen atoms. Torsion angles differ somewhat for molecules (**8**) and (**9**) in their structures.

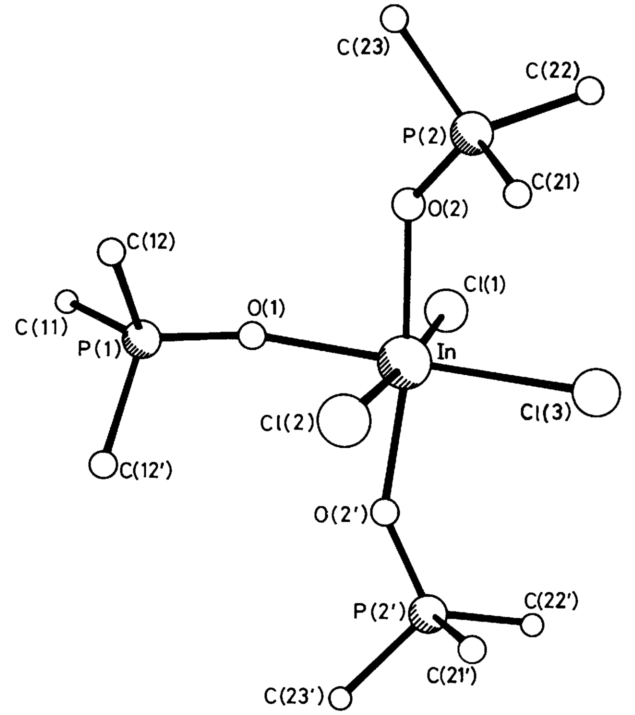

Figure 1. The $[InCl_3(Me_3PO)_3]$ (**1**) molecule, with mirror plane apparent

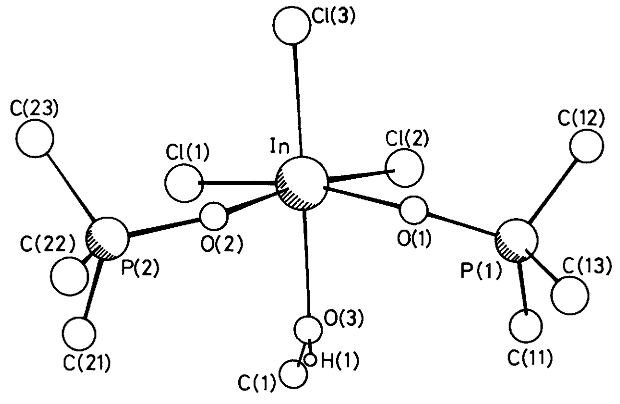

Figure 2. The complex $[InCl_3(Me_3PO)_2(MeOH)]$ (**2**) showing the disposition of the co-ordinated methanol molecule. The closest approach to H(1) is by Cl(1) (*x*, *y*—1, *z*)

Table 5. Bond lengths (Å) and angles (°) for $[(InX_3)_2(Me_3AsO)_3]$

	$[(InCl_3)_2(Me_3AsO)_3]$	$[(InBr_3)_2(Me_3AsO)_3]$[a]
In–X	2.429(4),[b] 2.419(4)[b]	2.568(5),[b] 2.574(5)[b]
In–O	2.241(6), 2.234(6)	2.260(22), 2.228(23)
As–O	1.710(6)	1.709(23)
In • • • In	3.286(4)	3.285(4)
X–In–X	97.2(1), 99.7(1)	99.0(2), 97.0(2)
X–In–O	92.9(2), 93.9(2)	93.2(6), 94.0(6)
O–In–O	71.9(2), 72.1(2)	71.7(8), 72.9(8)
In–O–In	94.5(2)	94.1(8)
In–O–As	131.7(3), 128.4(3)	128.7(12), 133.0(12)

[a] Averaged values for bromide. [b] Sequence In(1), In(2) throughout.

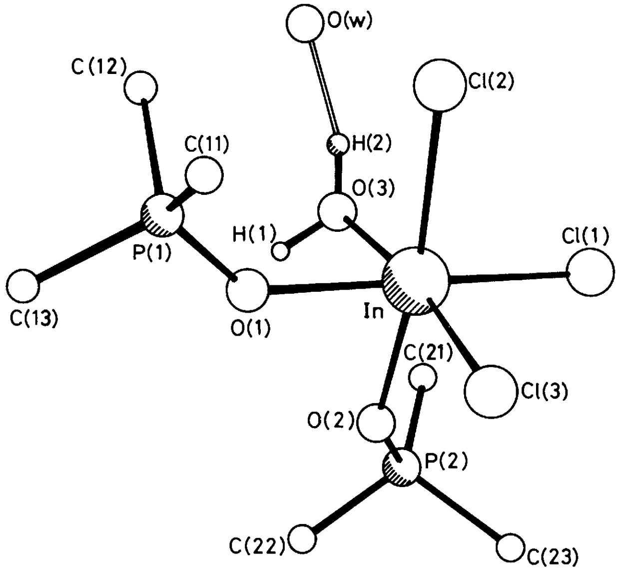

Figure 3. The aqua complex $[InCl_3(Me_3PO)_2(H_2O)]{\cdot}H_2O$ (**3**), with the hydrogen-bond relationship of the water molecules

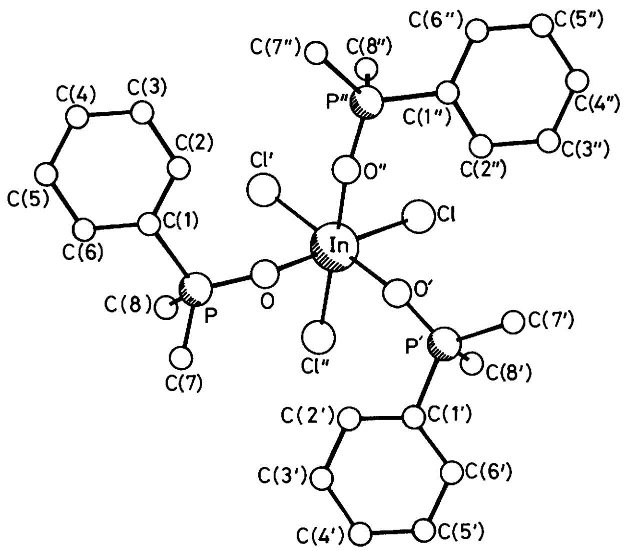

Figure 4. The molecule $[InCl_3(PhMe_2PO)_3]$ (**5**) viewed along its C_3 axis. The ligands of alternate molecules are in right-and left-handed chiral relationship

$[(InBr_3)_2(Me_3AsO)_3]$ (**10**). This molecule is entirely analogous to that of the chloride[3] (**10a**), with three ligand oxo-bridges between the two indium centres (see Table 5), but there is modified packing in the unit cell. The molecules lie with the In–In vector at 8.3° to the body diagonals of the orthorhombic cell. So, unlike the chloride with its trigonal axis lying along cubic cell diagonals, the bromide molecule does not have crystallographically imposed trigonal symmetry. The bridging capacity of arsine oxide stems from its unusually high polarity.[13]

Spectral Features.—With *X*-ray structures available on reference compounds, vibrational spectra in the ν(In–X) ranges (Table 6) can provide definitive evidence for identification of ionic and covalent structures. Thus '$InCl_3(Ph_3PO)_2$' (**7**) gives the same series of ν(In–Cl) bands as the ionic anisole solvate (**7a**), with the $InCl_4^-$ stretching modes[14] at 340 and 320 cm^{-1}. Likewise, '$InBr_3(Ph_3PO)_2$' gives the four Raman bands[15] at 238, 197, 79, and 55 cm^{-1} characteristic of $InBr_4^-$ so indicating the ionic formulation $[InBr_2(Ph_3PO)_4]^+[InBr_4]^-$ corresponding to that found for (**7a**). For the covalent octahedral $[InX_3L_3]$ compounds, the ν(In–X) bands lie at lower

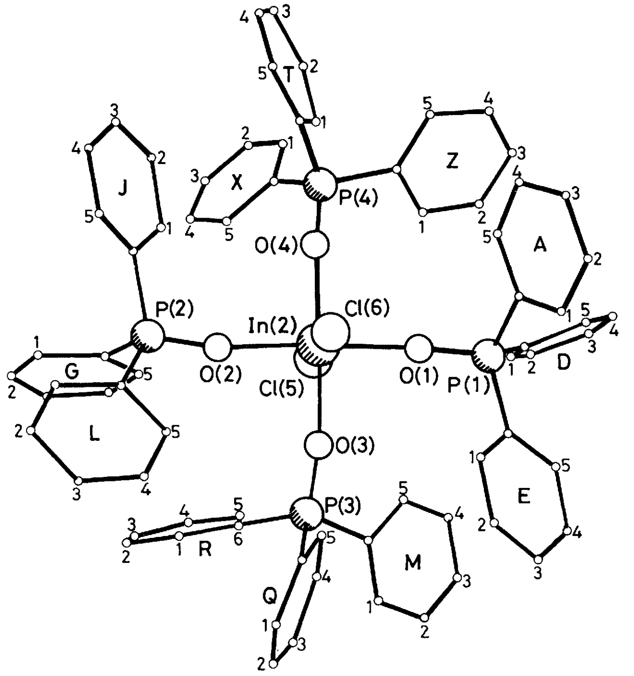

Figure 5. The $[InCl_2(Ph_3PO)_4]^+$ cation of (**7a**). The P(1)—P(4) atoms are respectively +0.47, +0.25, −0.44, and −0.43 Å from the In(2)-O(1)—(4) mean-plane [+towards Cl(6)]. The ring lettering and atom numbering give the C atom designations in the Supplementary Tables

wavenumbers than for their ionic counterparts, ν(In–Cl) in the range 280—250 cm^{-1} and ν(In–Br) below 200 cm^{-1}. As will be seen from Table 6, the spectra provide clear evidence for the covalent nature of $[InCl_3(Ph_2MePO)_3]$ (**6**) and the ionic constitution of '$InBr_3(Ph_2MePO)_2$' (**6a**), quite apart from the significant compositional difference.

The ν(In–X) frequencies are higher for covalent trigonal bipyramidal $[InX_3L_2]$ compounds where the halogen atoms are strongly bonded in the equatorial plane, than for the octahedral $[InX_3L_3]$ class. The trigonal bipyramidal complex $[InCl_3\{(Me_2N)_3PO\}_2]$, for example, shows a single strong band at 327 cm^{-1}. (This is contrary to an earlier report[2] that no such band is present, but in this case the spectrum shown matched that of a hydrolytic decomposition product.)

^{31}P N.m.r. values are included in Table 6. The downfield shifts from the free ligand values are greater than for the thio complexes,[1] and as would be expected, diminish as the number of oxo-ligands linked to the metal centre increases.

Bonding Interactions.—With the present ligands there is no steric impediment to formation of octahedral complexes. Constraints are removed by an increase in oxygen bond angles (see below). For co-ordination of rigid groups, steric effects alone should favour the *mer* configuration.[10] But with the ready enlargement of the In–O–P angle, the predominance of *fac* configurations could simply be a consequence of relative solubilities and crystal packing forces. The appearance of alternative *fac* and *mer* derivatives provides evidence of halogen mobility in solution, probably through ionisation.

Bond lengths in compounds (**1**)—(**3**) show there to be a small *trans* lengthening of In–Cl produced by the phosphine oxide. For (**1**), with its *mer* configuration, In–Cl(3) *trans* to O(1) (Figure 1) is longer (2.495 Å) than the In–Cl(1) and In–Cl(2) bonds (2.459 and 2.478 Å). Moreover in (**2**) and (**3**), of *fac* configuration, the In–Cl bonds *trans* to the weakly co-ordinating MeOH and H_2O molecules (Figures 2 and 3) are shorter than those lying *trans* to the more strongly co-ordinating phosphine oxide. The effect can be ascribed to electrostatic repulsion between the oxo ligand and the In *d* electrons, which is transmitted across the indium centre to increase Cl repulsion. Both the In–O and the In–Cl bond lengths in (**1**)—(**3**) and (**5**) would indicate that the field strengths associated with the ligands are in the order $Me_3PO > Me_2SO > MeOH \approx H_2O$. This positioning of Me_3PO and Me_2SO accords with the estimated dipole moments of their P–O and S–O bonds, 3.2[16] and 2.7 D[17] respectively.

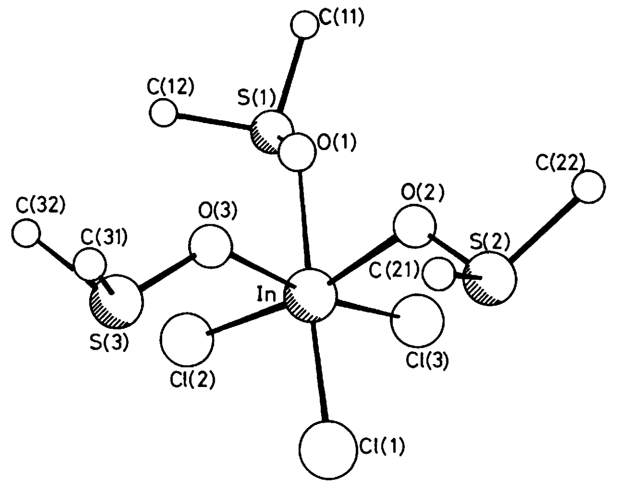

Figure 6. The $[InCl_3(Me_2SO)_3]$ (**8**) molecule. For (**8**) and the bromide (**9**) the largest differences in torsion angles involve S(2), C(21), and C(22), with values for (**8**), (**9**): X(1)-In-O(2)-S(2), 30.0, 12.6; In-O(2)-S(2)-C(21), −111.0, −95.4; In-O(2)-S(2)-C(22), 146.8, 161.6°

The In–Cl bond lengths in (**1**) provide evidence against any significant d_π–d_π component to these bonds, for otherwise there would be a mutual *trans*-lengthening effect shown by the diametrically opposite Cl(1) and Cl(2) atoms.

Appearance of Ionic Structures.—It is clear that several factors can influence the development of ionic structures. (*i*) Crystallisation of the ionic (**4**) (with an $InCl_4^-$ anion), as opposed to the covalent (**1**) requires a lower ligand:$InCl_3$ ratio (Scheme), and so arises from the predominance of an equilibrium effect. (*ii*) It can be inferred from the structure of cation (**7a**) (Figure 5) that formation of the (unobtainable) *mer* derivative $[InCl_3(Ph_3PO)_3]$ should be sterically possible. However the structure of the complex cation, with nesting of each of its two Cl atoms within a set of six phenyl rings, is significant. In the cell, phenyl rings of other cations complete the enclosure of these Cl(5) and Cl(6) atoms. Even at the observed approach distances Cl ··· H, 2.8—3.1 Å, and Cl ··· C, 3.55—3.85 Å, there will be some local neutralisation of charge, with enhancement of the stability of the ionic structure. (*iii*) Development of ionic structures can be influenced by the halide: *viz*. the ionic '$InBr_3(Me_3PO)_2$' (**4a**), but the absence of a Br analogue of $[InCl_3(Me_3PO)_3]$ (**1**); $[InX_3(Me_2SO)_3]$ (**8**) and (**9**), but an ionic iodide $[InI_2(Me_2SO)_2]^+I^-$;[18] $[InCl_3(Ph_2MePO)_3]$ (**6**), but an ionic bromide $[InBr_2(Ph_2MePO)_4]^+[InBr_4]^-$ (**6a**). These examples point to a preferential formation of ionic derivatives by a heavier halogen, but present information does not permit systematic discussion.

Oxygen Bond Angles.—In the present trimethylphosphine oxide compounds the oxygen angles are in the range 137—142°, and so are always much higher than the sulphur angles, 109—112°, in the trimethylphosphine sulphide complexes. High, and

Table 6. Spectroscopic data

Compound	In–X Vibrational modes/cm^{-1}[a]	^{31}P N.m.r.[b]	
		δ/p.p.m.[c]	Shift from ligand[c]
(**1**) [$InCl_3(Me_3PO)_3$]	283s, 252ms	50.3	9.3
(**2**) [$InCl_3(Me_3PO)_2(MeOH)$][d]	285 (sh), 272s, 252s	53.7	12.7
(**3**) [$InCl_3(Me_3PO)_2(H_2O)$]·H_2O[e]	288 (sh), 280s, 265m, 246m	54.5	13.5
(**4**) '$InCl_3(Me_3PO)_2$'	336s,[f] 320w (sh)[f]	50.0	9.0
(**4a**) '$InBr_3(Me_3PO)_2$'	*238*m,[f] *197*vs,[f] *78*s,[f] *56*s[f]	[g]	
(**5**) [$InCl_3(PhMe_2PO)_3$]·H_2O	273m, 248s	42.5	8.1
(**6**) [$InCl_3(Ph_2MePO)_3$]	277ms, 265ms	43.2, 41.1, 34.7[h]	12.5, 11.4, 5.0
(**6a**) [$InBr_2(Ph_2MePO)_4$]$^+$[$InBr_4$]$^-$	*240*m,[f] *198*s,[f] *165*m, *80*w,[f] *55*w[f]	39.1	9.4
(**7**)[i] [$InCl_2(Ph_3PO)_4$]$^+$[$InCl_4$]$^-$	340s,[f] 320w,[f] 302ms[j]	35.0	6.4
(**8**) [$InCl_3(Me_2SO)_3$]	280m, 257vs		
(**9**) [$InBr_3(Me_2SO)_3$]	*186*s, *175*w, *152*w		

[a] Raman values italicised. [b] Against 20% H_3PO_4 as standard. [c] Corresponding values for [$GaCl_3(Me_3PO)$] 69.7, 28.7; [$GaCl_3(Me_3PS)$] 43.0, 12.6 p.p.m. [d] OH band at 3 320 cm^{-1}. [e] H_2O bands at 3 550, 3 460, and 1 620 cm^{-1}. [f] InX_4^- modes. [g] Solubility too low for measurement. [h] Evidence of solution equilibrium, *cf.* ionic bromide (**6a**). [i] Compound (**7a**) gives the same i.r. spectrum, but with anisole bands at 1 590, 1 250, and 1 045 cm^{-1}. [j] May be ν(In–Cl) from cation.

often rather variable, oxygen angles are characteristic of adducts between oxo ligands and metal centres generally. This can be related in the first place to the more ionic (electrostatic) nature of the metal–oxygen linkage (with the likelihood that susceptibility to deformation increases with loss of covalent character). There is thus a sharp contrast with the specificity of the S–In orbital interaction which maintains the low sulphur angle.[1]

For the structures under consideration, including those of [$InCl_3\{(Me_2N)_3PO\}_2$] (153° angle) and the cation (**7a**), it is found that the oxygen angles assume values just large enough to prevent intramolecular distances falling below the sum of the van der Waals radii (3.6 Å for $Cl\cdots CH_3$ and $CH_3\cdots CH_3$). This implies that the preferred angles are probably lower than those actually developed, but that they are easily enlarged without appreciable loss of bond strength. It is this increase in P–O–In angles, to *ca.* 160° in (**7a**), that enables co-ordination of so large a ligand as triphenylphosphine oxide, and in a way that contributes to the cation stability. It is significant that triphenylphosphine sulphide, with its low sulphur angle requirement, fails to react with $InCl_3$. The case of $(Me_2N)_3PO$ in *tbp* [$InCl_3\{(Me_2N)_3PO\}_2$] is unusual, because the ligand molecule is a downwards-spreading umbrella. Reference to a model shows that no increase in oxygen bond angle from its value of 153.3, even to 180°, would enable bonding approach of more than two ligands to positions related by O–In–O angles close to 90°, as would be required in the known types of indium halide complexes. There would still be a clash of umbrella spokes. For dimethyl sulphoxide complexes, lower oxygen angles could be expected to be associated with the lower steric demand of the ligand. This is found to be so for (**8**) and (**9**), with angles of 123—125°.

To the extent that valence-shell electron-pair repulsion (VSEPR) effects[19] might exert some residual influence on oxygen (In–O–M) angles, they would particularly favour enlargement of phosphine oxide angles, over those of most other oxo ligands. The high p_π–d_π component of the O–P bond at once increases electron density in that bond, reduces the p character of σ-bonding hybrids, and reduces electron density in the third (sp^2) bonding position around oxygen. A short survey of complexes formed by dimethyl sulphoxide, pyridine N-oxide, urea, and aldehydes showed that their oxygen bond angles are generally lower than for phosphine oxides.

Angles in the Methanol and Aqua Complexes, (**2**) *and* (**3**).—Refinement of the structures of (**2**) and (**3**) included hydroxylic protons. In each case the positions of those protons became sufficiently defined to establish the ligand orientation. For co-ordination of water, reviewed by Ferraris and co-workers,[20a,b] there is a tendency towards colinearity of the OH_2 axis (OA) and the M–O vector, but with tilting of the HOH plane and an in-plane skewing of the molecule influenced by hydrogen bond contacts. In the case of (**3**), the tilt is 12—13°, and the skewing is also 12—13°. The angle In–O–A is *ca.* 18°. For comparison, neutron diffraction data on 36 structures where *both* protons of co-ordinated water molecules were considered as interacting with acceptors[20a] showed a mean deviation from colinearity of 13°, with a median of *ca.* 9°.

The methanol molecule in compound (**2**) is likewise oriented so that there is an approach to colinearity of the In–O vector and the C–O–H bisecting axis. The tilt is 6.2°, skewing angle 2.3°, and In–O(3)–A 6.7°. The methyl group lies rather symmetrically between the other two ligands with H(1) beyond the range of interaction with either O(1) or O(2).

It is evident that, as with ligands presenting a singly σ-bonded (spearhead) oxygen to the metal centre, the oxygen atoms of water and methanol also offer a quasi-ionic field. Protons are turned away from the metal and there is no apparent tendency of these oxygen atoms to form directed tetrahedral bonds. At the same time however, there seems to be a tendency for directed bonds to develop between the more polarisable hydroxide ion and metal centres, as in $In(OH)_3$[21] and $K_3[Cr(OH)_6]$.[22]

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