Indium(III) Halide Complexes with Trimethylphosphine Sulphide and Trimethylarsine Sulphide: Structures and Bonding of $[InX_3(Me_3MS)_2]$ (X = Cl or Br, M = P or As) and $[InCl_3(H_2O)(Me_3AsS)_2]$ †

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The crystal structures of four isomorphous compounds $[InX_3(Me_3MS)_2]$, with X = Cl or Br and M = P or As, and of a related octahedral complex $[InCl_3(H_2O)(Me_3AsS)_2]$ are described. In the isomorphous series, the indium is in a distorted trigonal-bipyramidal co-ordination with the thio ligands in apical positions. The distortions, which include small differences in the lengths of the two In–S bonds in each molecule, are produced by a combination of intra- and inter-molecular repulsions. The average In–S bond lengths for each molecule show qualitative decrease with the increasing charge transfer to be inferred from ligand polarity and halogen electronegativity. Comparison with bond lengths in the octahedral complex $[InCl_3(H_2O)(Me_3AsS)_2]$ shows the characteristic lengthening of the apical trigonal-bipyramidal bonds. The M–S bonds of the ligands show the usual lengthening upon co-ordination, with a moderate fall in bond order, *e.g.* from 2.0 to 1.6 in $[InCl_3(Me_3PS)_2]$. ^{31}P N.m.r. spectra also point to a reduction in the π character of the P–S bonds. There is no evidence for the use of In *d* orbitals in the In–S bond.

Compounds of Group 3 elements have commonly been used in studies on electron donor–acceptor interactions. Co-ordination behaviour becomes more varied down the group, with indium readily forming five- and six-co-ordinate complexes.[1] Indium(III), with a d^{10} configuration, has the ability to co-ordinate both oxo and thio ligands.[2] With trimethylphosphine sulphide and trimethylarsine sulphide, indium trichloride and tribromide form compounds $InX_3(Me_3MS)_2$, where X = Cl or Br and M = P or As. Preliminary *X*-ray examination showed the four compounds to be isomorphous and, by analogy with other bis complexes,[3–5] we presumed them to be five-co-ordinate. This encouraged precise structure determinations with the dual aims of finding: (*i*) the co-ordination pattern around indium, as influenced by the bulky Me_3M groups and the angular attachment of thio ligands,[6] and (*ii*) the effects of the P/As and Cl/Br substitutions on bond lengths. As regards the first aim, the structures proved to be distorted trigonal bipyramidal (tbp) with bond angles modified by intra- and inter-molecular approaches. The second aspect enables the strength of ligand bonding, based on bond length variations, to be related to trends in donor–acceptor activity. Within this isomorphous series, bond length comparisons are not impaired by variations in charge, co-ordination number, or other stereochemical features. As a complement to this, evidence on electronic response within the ligand was obtainable from n.m.r. spectra.

The compound $[InCl_3(Me_3AsS)_2]$ undergoes reversible hydration to an octahedral complex, $[InCl_3(H_2O)(Me_3AsS)_2]$, whose structure was also determined. Its structural similarity to the five-co-ordinate series is sufficiently close to enable useful comparison of bond lengths in the corresponding tbp and octahedral situations.

Experimental

Preparation of Compounds.—As a general procedure for $[InCl_3(Me_3PS)_2]$ (**1**), $[InCl_3(Me_3AsS)_2]$ (**2**), and $[InBr_3(Me_3AsS)_2]$ (**4**), solutions of anhydrous indium trihalide and ligand (1 : 2 mmol) in the minimum quantities of dry acetone were mixed, and crystallisation promoted, if necessary, by careful additions of light petroleum (b.p. 50—70 °C) up to, but not beyond, the amount producing permanent separation of a second liquid phase. Initial preparations were made using a vacuum line, but later it was found adequate to use vessels pre-flushed with dry air, and solutions containing 20% (v/v) triethoxymethane (tem) as dehydrating agent. Tabular crystals suitable for *X*-ray diffraction were obtained. Compounds (**1**) and (**4**) also gave crystals of acicular habit [(**1**) when using excess of $InCl_3$, and (**4**) when crystallised from dichloromethane–tem], but these crystals gave the same cell parameters as the respective tabular crystals. Compositions were obtained in the first place from elemental (C, H, and X) analyses.

$[InBr_3(Me_3PS)_2]$ (**3**) was obtained as acicular crystals from concentrated solutions in benzene or dichloromethane containing 20% (v/v) tem. A stumpy needle was used in the *X*-ray analysis.

$[InCl_3(H_2O)(Me_3AsS)_2]$ (**5**) crystallised from solutions of (**2**) which had been exposed to atmospheric moisture. Addition of tem to a solution of (**5**) caused reversion to (**2**). The co-ordinated water in (**5**) contributed a weak broad i.r. band at 3 380 cm^{-1} and a sharp band at 1 620 cm^{-1}. Aqua complexes could not be obtained similarly from (**1**), (**3**), or (**4**), for which exposure to atmospheric moisture caused release of free ligand. The unique behaviour of (**2**) is consistent with the conclusion from the *X*-ray analysis that, with the shortest In–S bonds, it contains the most strongly bound ligand.

Spectra.—N.m.r. spectra were recorded on a Varian XL300 spectrometer, using $CDCl_3$ solutions. Vibrational frequencies were obtained from infrared and Raman spectra (Pye Unicam SP300 for infrared to 200 cm^{-1}, using 'melinex' film calibration[7]

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† Trihalogeno-bis(trimethylphosphine sulphide)indium(III), -bis(trimethylarsine sulphide)indium(III) (halogeno = chloro or bromo), and aquatrichlorobis(trimethylarsine sulphide)indium(III).

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

Table 1. Crystal data, experimental conditions, and refinement

	$[InCl_3(Me_3PS)_2]$ (**1**)	$[InCl_3(Me_3AsS)_2]$ (**2**)	$[InBr_3(Me_3PS)_2]$ (**3**)	$[InBr_3(Me_3AsS)_2]$ (**4**)	$[InCl_3(H_2O)(Me_3AsS)_2]$ (**5**)
M	437.4	525.3	570.8	658.7	543.3
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$Pna2_1$
a/Å	13.818(4)	13.906(6)	14.178(3)	14.227(4)	8.622(1)
b/Å	12.457(4)	12.693(3)	12.786(2)	12.960(3)	11.579(2)
c/Å	9.864(3)[a]	9.941(3)	9.971(2)	10.032(2)	17.564(2)
α/°	90	90	90	90	90
β/°	94.55(3)	93.79(3)	94.94(2)	94.91(2)	90
γ/°	90	90	90	90	90
U/Å^3	1 693(1)	1 751(1)	1 800.7(6)	1 843.0(8)	1 753.5(5)
Z	4	4	4	4	4
F(000)	864	1 008	1 080	1 224	1 040
Crystal size (mm)	0.50 × 0.40 × 0.14	0.50 × 0.20 × 0.10	0.3 × 0.08 × 0.05	0.46 × 0.22 × 0.10	0.40 × 0.13 × 0.10
μ/cm^{-1}	22.57	57.47	82.69	114.67	57.46
Scan mode	ω	ω	ω	ω	ω
Range, 2θ/°	4—52	4—52	4—52	4—52	5—52
Range, h	0—18	0—15	0—18	0—18	0—11
Range, k	0—16	0—14	0—16	0—16	0—15
Range, l	−14—13	−11—11	−13—13	−13—13	0—22
Temperature/°C	−140	−140	−100	−100	−140
Total reflections	3 438	2 375	3 662	3 752	2 068
Unique reflections	3 223	1 905	3 439	3 622	1 813
Observed reflections, $I > 3\sigma(I)$	3 040	1 794	2 451	2 407	1 553
Transmission range	0.400—0.729	0.684—0.855	0.475—0.648	0.702—0.863	0.617—0.881
Parameters refined	199	127	127	127	137
Weighting, g	0.000 43	0.000 78	0.000 39	0.0006	0.000 33
Residual density	0.67, −1.01	1.32, −0.79	0.50, −0.83	1.07, −0.94	0.95, −0.79
R (R')[b]	0.0239 (0.034)	0.0385 (0.0499)	0.0314 (0.0356)	0.0360 (0.0417)	0.0332 (0.0380)

[a] With the acicular form, the needle develops along the c axis. [b] $R = \Sigma(|F_o| - |F_c|)/\Sigma F_o$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{\frac{1}{2}}$.

Table 2. Atomic co-ordinates (× 10^4) with e.s.d.s in parentheses

	$[InCl_3(Me_3PS)_2]$ (**1**)			$[InCl_3(Me_3AsS)_2]$ (**2**)			$[InBr_3(Me_3PS)_2]$ (**3**)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
In	4 484(1)	7 304(1)	7 325(1)	4 471(1)	7 205(1)	7 309(1)	4 530(1)	7 356(1)	7 287(1)
M(1)	6 895(1)	8 876(1)	7 163(1)	6 846(1)	8 837(1)	7 185(1)	6 951(1)	8 828(1)	7 102(2)
S(1)	6 415(1)	7 383(1)	7 457(1)	6 358(2)	7 274(2)	7 520(2)	6 434(1)	7 411(1)	7 460(2)
C(11)	8 087(2)	8 794(3)	6 587(3)	8 110(7)	8 744(8)	6 567(10)	8 070(4)	8 687(6)	6 444(7)
C(12)	6 997(3)	9 653(3)	8 692(3)	6 925(8)	9 662(9)	8 788(10)	7 161(5)	9 586(6)	8 609(7)
C(13)	6 144(2)	9 608(3)	5 918(3)	6 054(7)	9 573(8)	5 871(11)	6 216(5)	9 572(5)	5 910(7)
M(2)	1 783(1)	7 917(1)	7 199(1)	1 786(1)	7 946(1)	7 194(1)	1 859(1)	7 933(1)	7 187(1)
S(2)	2 691(1)	6 667(1)	7 560(1)	2 706(2)	6 611(2)	7 553(3)	2 765(1)	6 730(1)	7 492(2)
C(21)	610(2)	7 408(2)	6 601(3)	554(6)	7 441(8)	6 552(10)	732(4)	7 420(5)	6 581(7)
C(22)	1 654(2)	8 688(2)	8 705(3)	1 665(7)	8 727(8)	8 822(8)	1 721(4)	8 647(5)	8 698(6)
C(23)	2 158(2)	8 818(2)	5 938(3)	2 204(7)	8 885(7)	5 866(9)	2 191(4)	8 845(5)	5 964(6)
X(1)	4 329(1)	9 001(1)	8 438(1)	4 303(2)	8 889(2)	8 394(3)	4 392(1)	9 074(1)	8 517(1)
X(2)	4 307(1)	7 432(1)	4 897(1)	4 316(2)	7 404(2)	4 897(2)	4 347(1)	7 504(1)	4 754(1)
X(3)	4 866(1)	5 628(1)	8 433(1)	4 831(2)	5 513(3)	8 335(3)	4 912(1)	5 601(1)	8 370(1)

	$[InBr_3(Me_3AsS)_2]$ (**4**)			$[InCl_3(H_2O)(Me_3AsS)_2]$ (**5**)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
In	4 515(1)	7 276(1)	7 263(1)	5 737(1)	5 050(1)	7 500
M(1)	6 911(2)	8 809(1)	7 100(1)	4 432(1)	8 602(1)	8 042(1)
S(1)	6 380(1)	7 312(2)	7 503(2)	5 558(1)	7 786(3)	8 417(3)
C(11)	8 104(6)	8 642(7)	6 406(9)	4 235(7)	8 900(14)	6 516(10)
C(12)	7 109(8)	9 617(7)	8 687(9)	4 309(6)	10 603(13)	8 836(12)
C(13)	6 118(7)	9 569(7)	5 813(10)	3 659(6)	7 329(12)	8 727(10)
M(2)	1 846(1)	7 955(1)	7 172(1)	7 031(1)	1 490(1)	7 064(1)
S(2)	2 782(1)	6 673(2)	7 485(2)	5 877(1)	2 181(3)	6 872(3)
C(21)	639(6)	7 437(8)	6 529(10)	7 165(6)	−499(12)	6 449(10)
C(22)	1 726(6)	8 687(7)	8 813(8)	7 284(7)	1 252(14)	8 724(9)
C(23)	2 219(6)	8 915(6)	5 877(8)	7 736(6)	2 886(13)	6 328(11)
X(1)	4 365(1)	9 008(1)	8 441(1)	6 997(1)	5 284(3)	8 478(3)
X(2)	4 329(1)	7 461(1)	4 735(1)	4 393(1)	4 575(3)	6 883(3)
X(3)	4 890(1)	5 508(1)	8 294(1)	6 169(1)	6 084(3)	5 631(2)
O(w)				5 377(4)	4 152(8)	9 301(7)

at low frequencies; Raman from Victoria University of Wellington, using Spectra-Physics Kr^+ ion laser, Spex 1400 double monochromator, neon calibration).

X-Ray Structure Determinations.—These were performed on a Nicolet R3M four-circle diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å), 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, with the proportionality of cell dimensions providing evidence of isomorphism for (**1**)—(**4**); crystal and instrument stability monitored using three standards every 97 reflections, but no significant variations; Lorentz-polarisation correction included, absorption corrections applied [based on ψ scans for (**2**)—(**5**), and crystal shape for (**1**)].

The In, As(1), and As(2) atoms were located from Patterson maps and remaining non-hydrogen atoms from difference Fourier syntheses, but independent location of atoms was unnecessary for isomorphous compounds; least-squares refinement with anisotropic thermal parameters; function minimised, $\Sigma w(|F_o| - |F_c|)^2$, with reflection weights $w = [\sigma^2|F_o| + gF_o^2]^{-1}$; for (**1**), H-atoms were located and their positions and thermal parameters refined, and likewise for one H(w) atom of the water molecule in (**5**), but in all other cases H-atoms were introduced at idealised positions with fixed thermal parameters. Other details for the individual compounds are given in Table 1. Final atomic co-ordinates are listed in Table 2.

The SHELXTL (version 4) package used[8] included atomic scattering factors and all programs required 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

Aquatrichlorobis(trimethylarsine sulphide)indium(III) (**5**).—The molecular structure of this somewhat distorted octahedral complex is shown in Figure 1. The arsine sulphide ligands are *trans*-co-ordinated through sulphur, and O(w) of the water molecule is almost coplanar with the chlorine atoms. The arsenic atoms are mutually *trans* and lie close to the mean plane through In,Cl(1),Cl(2),S(1),S(2). The enlarged angles S(1)–In–Cl(2), 98.7, and S(2)–In–Cl(1), 96.9° (Table 3) indicate repulsive effects between the chlorine atoms and adjacent methyl groups, but it is also apparent that the methyl groups avoid approach to the protons of the water molecule even at the cost of these repulsions. The closest intermolecular approaches to O(w) are by Cl (Table 4, footnote *c*).

The In–S(1) and In–S(2) bonds, 2.606 and 2.589 Å, are just distinguishable, but the In–S(1)–As(1) and In–S(2)–As(2) angles, 109.0 and 109.2° are equivalent. The In–O(w) bond length is long, 2.313 Å, but this value lies between those reported for $[InCl_5(H_2O)]^{2-}$, 2.22,[9] and $[InBr_5(H_2O)]^{2-}$, 2.344 Å.[10] The four angles adjacent to the weak In–O(w) bond are less than 90°, probably due to reduced VSEPR (valence-shell electron-pair repulsion) effects.[11] Variations in intramolecular non-bonded distances can be related to intermolecular 'contacts'. Thus the C(13) atom which has five intermolecular distances below 4 Å makes a closer approach to Cl(2), 3.447 Å, than does C(11), 3.763 Å, with only two such intermolecular distances (see Table 4, footnote *a*).

Complexes $[InX_3(Me_3MS)_2]$ [X = Cl, M = P (**1**) *or* As (**2**); X = Br, M = P (**3**) *or* As (**4**)].—The molecular structure for

Table 3. Bond lengths (Å) and selected angles (°)

	$[InCl_3(Me_3PS)_2]$ (**1**)	$[InCl_3(Me_3AsS)_2]$ (**2**)	$[InBr_3(Me_3PS)_2]$ (**3**)	$[InBr_3(Me_3AsS)_2]$ (**4**)	$[InCl_3(H_2O)(Me_3AsS)_2]$ (**5**)
In–X(1)	2.400(2)	2.412(3)	2.531(3)	2.554(3)	2.495(4)
In–X(2)	2.393(2)	2.406(3)	2.524(3)	2.539(3)	2.500(3)
In–X(3)	2.396(2)	2.417(4)	2.529(3)	2.552(3)	2.461(4)
In–$X_{av.}$	2.396	2.412	2.528	2.548	2.485
In–S(1)	2.663(3)	2.620(3)	2.691(3)	2.643(3)	2.606(4)
In–S(2)	2.630(3)	2.594(4)	2.653(3)	2.615(3)	2.589(4)
In–$S_{av.}$[a,b]	2.647	2.607	2.672	2.629	2.598[b]
M(1)–S(1)	2.003(2)	2.130(3)	1.998(3)	2.133(3)	2.144(4)
M(2)–S(2)	2.014(3)	2.140(3)	2.010(3)	2.136(3)	2.125(3)
M–$S_{av.}$	2.009	2.135	2.004	2.135	2.135
In–O(w)					2.313(8)
Bond angles[c]					
X(1)–In–X(2)	113.1(1)	110.4(1)	114.6(1)	111.9(1)	168.8(1)
X(1)–In–X(3)	125.7(1)	128.5(1)	125.9(1)	128.6(1)	95.6(1)
X(2)–In–X(3)	121.1(1)	121.1(1)	119.6(1)	119.3(1)	95.7(1)
X(1)–In–S(1)	94.1(1)	93.5(1)	93.8(1)	93.7(1)	81.3(1)
X(1)–In–S(2)	96.1(1)	95.5(1)	96.4(1)	96.1(1)	96.9(1)
X(2)–In–S(1)	93.9(1)	95.7(1)	94.5(1)	96.2(1)	98.7(1)
X(2)–In–S(2)	95.0(1)	95.8(1)	94.8(1)	95.4(1)	81.5(1)
X(3)–In–S(1)	80.0(1)	79.5(1)	79.6(1)	78.8(1)	93.9(1)
X(3)–In–S(2)	82.6(1)	82.7(1)	82.4(1)	82.1(1)	94.0(1)
In–S(1)–M(1)	117.7(1)	110.3(1)	113.2(1)	111.6(1)	109.0(1)
In–S(2)–M(2)	109.2(1)	108.2(1)	110.6(1)	109.6(1)	109.2(1)
S(1)–In–S(2)	162.6(1)	162.0(1)	162.0(1)	160.7(1)	172.0(1)

[a] Differences in average In–S values: between (**2**) and (**1**), 0.040; (**4**) and (**3**), 0.043; (**3**) and (**1**) 0.025; (**4**) and (**2**), 0.022 Å. The consistency of these differences shows the regularity of the effects arising from the Cl/Br and P/As replacements. [b] For comparison, the In–S distances for the octahedrally co-ordinated In in the spinel-type lattice of In_2S_3 is 2.601 Å, A. Likforman, M. Guittard, A. Tomas, and J. Flahaut, *J. Solid State Chem.*, 1980, **34**, 353. See also R. K. Chadha, P. C. Hayes, H. E. Mabrouk, and D. G. Tuck, *Can. J. Chem*, 1987, **65**, 804. [c] For (**5**), bond angles adjacent to In–O(w): X(1)–In–O, 82.0(2); X(2)–In–O, 86.8(2); X(3)–In–O, 177.2(2); S(1)–In–O, 84.4(2); S(2)–In–O, 87.7(2)°.

Table 4. Selected intra- and inter-molecular non-bonded distances (Å)[a]

	(1)		**(2)**		**(3)**		**(4)**		**(5)**	
	intra[b]	inter[b]	intra	inter	intra	inter	intra	inter	intra	inter[c]
S(1) ··· X(1)	3.667		3.709		3.813		3.793		3.325	
S(1) ··· X(2)	3.729		3.701		3.830		3.857		3.873	
S(1) ··· X(3)	3.223		3.258		3.343		3.298		3.703	
S(2) ··· X(1)	3.708		3.744		3.866		3.845		3.807	
S(2) ··· X(2)	3.712		3.705		3.810		3.813		3.322	
S(2) ··· X(3)	3.313		3.323		3.415		3.394		3.696	
X(1) ··· C(12)	3.765	3.873	3.771	3.844	3.974	4.133	3.970	4.112		
X(1) ··· C(13)	3.746		3.713		3.874		3.851			3.581
X(1) ··· C(21)		3.883		3.874		3.949		3.927		3.800
X(1) ··· C(22)	3.746		3.726		3.846		3.827		3.526	
X(1) ··· C(23)	3.736		3.724		3.865		3.823		3.481	
X(2) ··· C(11)		3.869		3.894		3.932		3.904		3.763
X(2) ··· C(13)	3.794	3.814	3.748	3.939	3.849	3.868	3.827	3.932	3.447	
X(2) ··· C(21)		3.844		3.849		3.866		3.856		
X(2) ··· C(22)		3.801		3.787		3.901		3.905		
X(2) ··· C(23)	3.652		3.669		3.791		3.803			3.661
X(3) ··· X(3)		3.459		3.560		3.584		3.655		
X(3) ··· C(11)		3.637		3.635		3.757		3.733		3.507
X(3) ··· C(22)		3.741		3.671		3.877		3.807		
X(3) ··· C(23)		3.683		3.634		3.836		3.793		

[a] The X ··· C intermolecular distances listed are generally those below 4 Å. X ··· C is used rather than X ··· H, since only for **(1)** could H positions be refined. For **(1)** the average of closest (< 3 Å) X ··· H intramolecular distances is 0.85 Å less than for the corresponding X ··· C; and for intermolecular distances this difference is 0.88 Å. [b] For the series **(1)**—**(4)** the average intramolecular X ··· C distance is 0.048 Å less than the listed intermolecular X ··· C distances. [c] Other intermolecular distances for **(5)** are: Cl(3) ··· C(12), 3.630; Cl(3) ··· C(13), 3.961; Cl(3) ··· C(21), 3.556; O(w) ··· Cl(2), 3.210; O(w) ··· Cl(3), 3.128; H(w) ··· Cl(3), 2.223 Å.

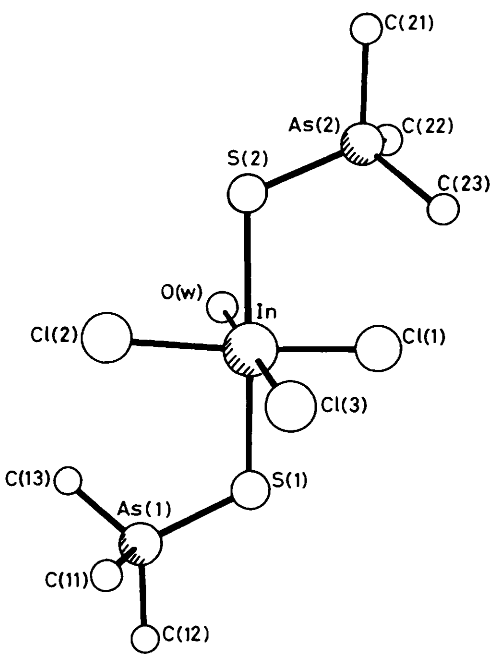

Figure 1. The molecule of the octahedral complex [$InCl_3(H_2O)(Me_3AsS)_2$]

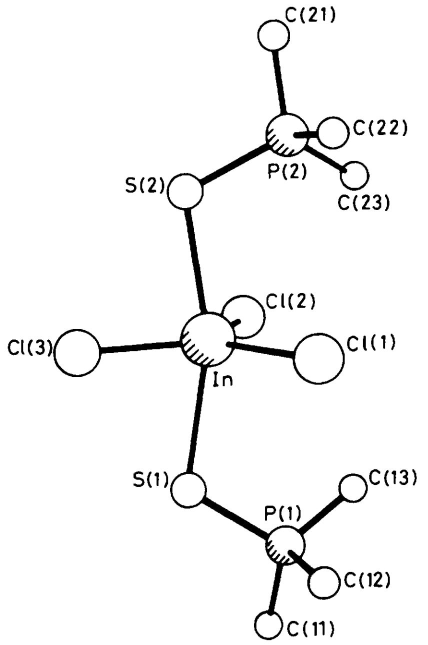

Figure 2. The complex [$InCl_3(Me_3PS)_2$], representative of the isomorphous series [$InX_3(Me_3MS)_2$] (X = Cl or Br, M = P or As). P(1) and P(2) lie between the arms In–Cl(1) and In–Cl(2). There is similarity of C(12), C(22) ··· Cl(1), C(13), C(23) ··· Cl(1), and C(13), C(23) ··· Cl(2) distances

these complexes is shown in Figure 2, and the molecular packing in Figure 3. The effect of steric pressure is apparent from the 'backwards bending' of the In–S(1) and In–S(2) bonds towards X(3) to give S(1)–In–S(2) angles of 160—162.6° (Table 3). As viewed from a direction normal to the X(1),X(2),X(3) plane, the Me_3M groups lie in almost eclipsed postions with the M atoms staggered with respect to the In–X(1) and In–X(2) bonds.*

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* In terms of intermolecular effects, there seems no reason why the eclipsed configuration should be preferred over a staggered one, with say M(2) lying between the arms In–X(2) and In–X(3), but the more symmetrical eclipsed form apparently offers more efficient molecular packing.

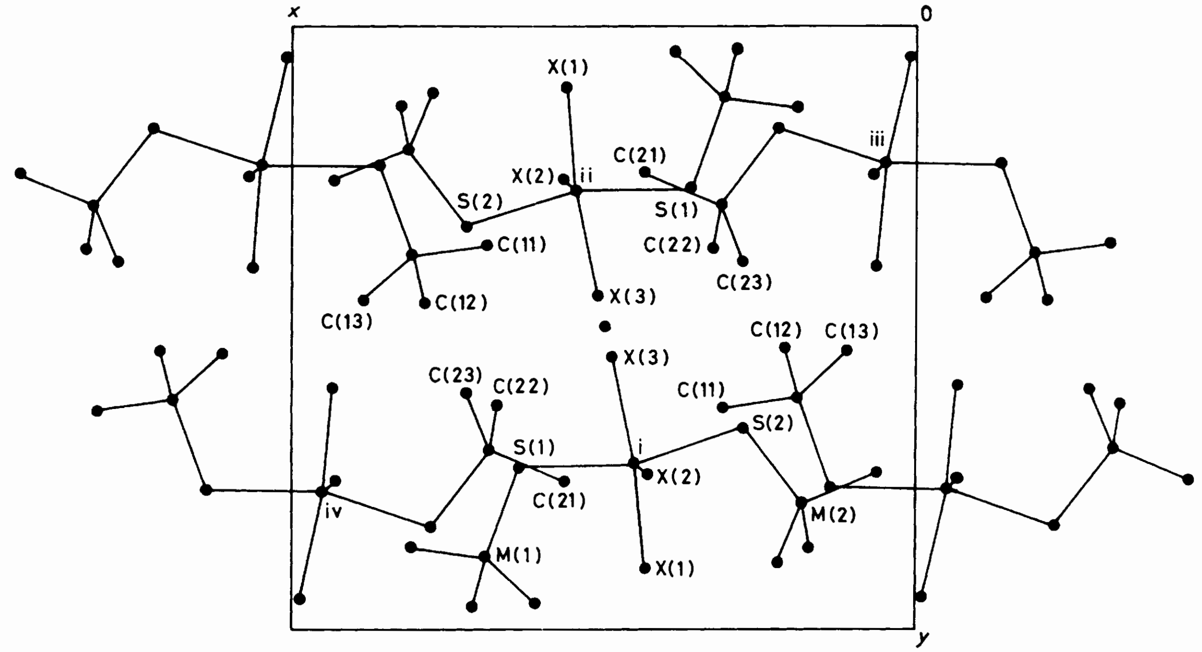

Figure 3. Packing of the [$InX_3(Me_3MS)_2$] molecules in the unit cell, as projected onto the 001 plane. Symmetry codes for the molecules shown are: (i) x, y, z; (ii) $1 - x, 1 - y, 1 - z$; (iii) $0.5 - x, y - 0.5, 1.5 - z$; (iv) $0.5 + x, 1.5 - y, z - 0.5$. The closest X(3) ··· X(3′) approach is between molecule (i) and molecule (ii′) $1 - x, 1 - y, 2 - z$. X(3) of molecule (i) is displaced towards S(1) by the predominance of repulsions from C(21), C(22), and C(23) of molecule (iii)

The molecules are disposed in the cell with their longest dimension almost in the x direction but with necessarily differing contacts at either end, which accounts for the lack of symmetry between the two segments of the molecule. Within each molecule torsion angles about the In–S and S–M vectors adjust to produce six quite similar intramolecular C(12) ··· X(1), C(13) ··· X(1),X(2) and C(22) ··· X(1), C(23) ··· X(1),X(2) distances (Table 4 and Figure 2). This minimises the aggregate of the X ··· Me_3M repulsions, since repulsive forces rise steeply as interatomic distance falls.[12] The halogen atoms are subject to displacement from fully symmetric tbp positions. The atoms X(1) and X(2) transmit the repulsive forces across the molecule, and X(3) is exposed to intermolecular contacts. It shows a particularly marked displacement in the equatorial plane through an X(3) ··· X(3′) approach from a direction which causes a large increase in the X(1)–In–X(3) angle. There is also a smaller, but very significant, axial displacement of X(3) towards S(1) caused by intermolecular approach of a $(CH_3)_3M(1)$ group, see Figure 3 and Table 4. This latter displacement causes the S(1) ··· X(3) and S(2) ··· X(3) distances to be unequal and, mainly for the same reason, In is not coplanar with X(1),X(2),X(3), but lies *ca.* 0.04 Å towards S(2) throughout the series of complexes.

The deformation of S(1)–In–S(2) has reduced the S(1) ··· X(3) and S(2) ··· X(3) distances, *e.g.* in (**1**) to 3.223 and 3.313 Å respectively. These S ··· X(3) distances have fallen well below the sum of the van der Waals radii ($\nless$ 3.60 for chlorides and 3.75 Å for bromides). This means that repulsive forces are rising rapidly and that effects of the distance inequality might become significant. The atom S(1) is more constrained against backwards bending and further decrease in S(1)–In–X(3). By way of compensation, M(1)–S(1)–In is spread more than M(2)–S(2)–In. Again, since the S(1) ··· X(3) repulsion is greater than S(2) ··· X(3), In–S(1) shows greater lengthening than In–S(2), with the inequality becoming greater as the bond length increases (bond strength decreases) through the series.

The geometry of these molecules in the crystal lattice can thus be attributed to the effects of intra- and inter-molecular repulsions. In tbp structures both apical and equatorial atoms are prone to displacement, the former through their relatively weak bonding[13,14] and the latter from the ease with which equatorial angles can be deformed.[15,16]

Charge Transfer and Bond Lengths.—Using the average bond lengths in the octahedral complex (**5**) as a point of reference (see Table 3) it is evident that the In–Cl bonds in the tbp molecule (**2**) are considerably shorter (by *ca.* 0.07 Å). Some shortening could be expected from the decreased co-ordination number and the removal of electron in-flow from O(w). On the other hand, the In–S bonds are slightly longer in (**2**) than in (**5**); but this reversal of the order only appears because of the characteristically long bonding to atoms in axial positions of tbp molecules.[13,14] In indium(III)–dithizonate (dithizonate = 1,5-diphenyl-3-mercaptoformazanate) where anionic S atoms occupy equatorial positions, the In–S bonds are shorter, 2.477 and 2.467 Å.[17]

The bonding in these five-co-ordinate complexes is consistent with the indium s orbital contributing preferentially to the equatorial bonds at the expense of the apical ones.[18] For bonding in apical directions a three-centre four-electron bond has been suggested.[16b,13,14] In the case of indium this would involve the $5p_z$ orbital without significant contribution from the (outer) $5d_{z^2}$ oribital.

For each of the thio ligands, the In–S bonds are shorter for the chlorides than for the bromides. In the simplest terms, this is consistent with the chloride promoting greater charge transfer into the In–S bonding region. As between the ligands, the arsine sulphide gives the shorter In–S bonds, corresponding to the higher polarity of As–S than P–S.[19] Conversely, where charge in-flow from S becomes greater, the effective radius of the In atom is increased and the In–X bond should be longer, as is found for both the chlorides and the bromides. Consistent with this, the respective ν(In–X) frequencies (Table 5) are higher for the phosphine sulphide than the arsine sulphide compounds [but similar reliance cannot be placed on ν(In–S) frequencies

Table 5. Spectroscopic data

	I.r. bands/cm^{-1}				N.m.r. (δ/p.p.m.)[b]				
Compound	ν(In–X)	ν(In–S)	δ(P/As–S)[a]	ν(P/As–S)[a]	^{31}P[c]	^{13}C	J(C–P)	^{1}H	^{2}J(H–P)
Me_3PS			283m	563s	30.57	22.58	55.4	1.787	13.2
(**1**) $[InCl_3(Me_3PS)_2]$	319s, 310s	253m br	280mw	541s	36.85	21.03	54.5	1.977	13.2
(**3**) $[InBr_3(Me_3PS)_2]$	228s, 186s[d]	251m	303m	536s	37.09	20.93	54.5	1.996	13.2
Me_3AsS			228m	476s		20.03		1.753	
(**2**) $[InCl_3(Me_3AsS)_2]$	308s, 300s (sh)	277m	229m	452s		19.34		2.032	
(**4**) $[InBr_3(Me_3AsS)_2]$	218s, 172s[d]	265m	228 (sh)	448s		19.22		2.060	
(**5**) $[InCl_3(H_2O)(Me_3AsS)_2]$	278s	262s br[e]	227m	451s					

[a] Me_3PS and Me_3AsS assignments based on Raman analysis, H. Rojhantalab and J. W. Nibler, *Spectrochim. Acta, Ser. A*, 1976, **32**, 519, 947. [b] In $CDCl_3$ solution, J in Hz. [c] Against 20% H_3PO_4 as standard. [d] Value from Raman spectrum of complex. [e] This band may also contain a ν(In–Cl) component. A barely resolved band at 245 cm^{-1} may represent ν[In–O(w)].

which are likely to be strongly coupled with δ(M–S)]. Thus, although In–X bond lengths can be related broadly to co-ordination number and net resultant charge,[20,21] the significance of charge distribution is also evident from the present results.

As regards bonding around sulphur, the small valence angles, 108—113°, indicate strong repulsion from an unshared electron pair. We therefore suggest that the sulphur atom uses essentially sp^2 hybrid orbitals for σ-bonding to M, σ-bonding to In, and for lone-pair accommodation. Estimates of the M–S bond order (n) from Pauling's relationship[22] $l_n = l_1 - 0.6 \log n$, gives n = 1.65 in (**1**) and 1.55 in (**2**). The bond orders, though reduced from those in the free ligands (2.0 and 1.9 respectively[19]) remain high. Hence the remaining p_z orbital of S is still mainly involved in the p_π–d_π bonding to M. This interpretation accords with the n.m.r. evidence for the compounds in solution.

The ^{31}P n.m.r. absorption (Table 5) shows a moderate downfield shift upon complex formation. This reflects the lower screening through reduced S–P π-bonding.[19,23] The ^{1}H spectra are likewise still subject to marked downfield end-of-chain shift transmitted through the C atoms. On the other hand, the ^{13}C resonances show upfield displacement from the free ligand position. In the absence of evidence from related series of compounds, the simplest interpretation seems to be that a 'γ-effect'[24] (as counted from In) is operating. There is no significant modification of the geometry of the Me_3P or Me_3As groups[19] upon co-ordination, beyond a small decrease in the average S–M–C bond angles attributable to reduction in the M–S bond order.

Overall, there is no indication of involvement of In d orbitals in the In–S bonding. Pauling bond orders for In–S, using $\Sigma r_{\text{cov.}} = 2.54$, give n no higher than 0.77 for (**2**) and 0.60 for (**3**). This virtually excludes σ-bond strengthening through use of $5d_{z^2}$, or π-bond development from use of $4d^{10}$ electrons. The reduction in ^{31}P shielding is additional evidence against the latter.

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