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Adducts of Gal₃ and Inl₃ with Ph₃P and Ph₃As

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Abstract

Adducts Ph_3PGaI_3 and Ph_3AsGaI_3 obtained by adding the ligands to Et_2OGaI_3 have been investigated by ⁷¹Ga NMR, IR/Raman spectroscopy and X-ray diffraction. Et_2OInI_3 with Ph_3P gives $(Ph_3P)_3(InI_3)_2$. Ph_3As yields $(Ph_3As)_3(InI_3)_2 \cdot H_2O$ as rhombohedral cristals whose structure was solved by X-ray diffraction. Both these indium complexes contain Ph_3EInI_3 molecules alongside five-coordinate adducts $(Ph_3E)_2InI_3$ with the Ph_3E ligands attached in axial sites by long and unequal bonds to a planar InI_3 unit. Vibrational assignments are made for Ph_3PGaI_3 , Ph_3AsGaI_3 , Ph_3EInI_3 and $(Ph_3E)_2InI_3$ (E = P or As). © 1997 Elsevier Science S.A.

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1. Introduction

Adducts with neutral or anionic ligands are a major feature of the chemistry of gallium and indium halides [1-3], those of phosphines and arsines being particularly important in relation to III–V semi-conductor materials [4]. The adducts formed by GaI₃ and InI₃ have received fresh attention recently; the molecular structures of (Me₃Si)₃AsGaI₃ [5], Ph₃AsGaI₃ [6] and (p-MeOC₆H₄)₃AsGaI₃ [7] have been determined by X-ray diffraction, and there have been spectroscopic and crystallographic studies on phosphino complexes of indium(III) iodide [8–10], in which earlier work is reviewed.

The reaction of Ph_3E (E = P or As) with the ether adduct Et_2OGaI_3 is a convenient route to crystalline products in which triphenylphosphine or triphenylarsine is coordinated to gallium through a Ga-E bond [6]. Extending this observation, we have used Et_2OInI_3 to prepare the adducts of InI_3 with Ph_3P and Ph_3As . Here we present crystallographic investigations of these systems together with IR, Raman and NMR spectroscopic results elucidating the structures of gallium(III) iodide and indium(III) iodide adducts with phosphino and arsino ligands.

2. Experimental section

2.1. Preparative work

A solution of Et_2OGaI_3 was prepared by shaking finely powered gallium metal with an equivalent amount of I_2 dissolved in dry diethyl ether until the mixture was colourless [11]. Et_2OInI_3 in Et_2O was obtained similarly, using freshly cut shavings of indium [11,12].

 Ph_3AsGaI_3 1 was obtained as colourless crystals which grew slowly in the mixture formed by adding one equivalent of Ph_3As in Et_2O to a sample of the Et_2OGaI_3 solution. The crystals were rinsed with diethyl ether and dried in air without deterioration. Analysis: calculated for $C_{18}H_{15}AsGaI_3$, C 28.6, H 2.00%; found C 28.2, H 2.61%.

 Ph_3PGaI_3 **2** was prepared similarly. Well developed, colourless crystals are obtained within 15 min at ambient temperature from a solution containing Et₂OGaI₃ plus Ph_3P . Analysis: calculated for $C_{18}H_{15}PGaI_3$, C 30.3, H 2.12%; found, C 30.7, H 1.80%.

 GaI_3 adducts with other phosphine ligands were prepared by reaction of MePh₂P or Me₂PhP with Et₂OGaI₃, followed by collection of the solid product, which was then dissolved in CH₂Cl₂ for NMR investigation. Mixed halides were obtained in situ by the action of IBr or ICl on the GaI₃ adducts.

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 $(Ph_3P)_3(InI_3)_2$ formed rapidly as pale yellow crystals from a dry ether solution containing Ph_3P and Et_2OInI_3 in 2:1 molar proportions. Some of these crystals were heated in cyclohexane to 60°C, whereupon they broke up into a white powder. This product, with small colourless crystals which formed on cooling, was shown by its IR spectrum to be Ph_3PInI_3 . The two solids Ph_3PInI_3 and $(Ph_3P)_3(InI_3)_2$ were identified by investigating a single crystal of each sort by X-ray diffraction. The structures thus determined agreed fully with the recently published findings [10].

 $(Ph_3As)_3(InI_3)_2 \cdot H_2O$ 3 was produced as pale yellow crystals when a solution containing Et_2OInI_3 plus Ph_3As (in equimolar proportions) was allowed to stand for several hours. The crystals were rinsed with ether and dried in air. Analysis: calculated for $C_{54}H_{47}As_3In_2I_6O$, C 33.6, H 2.35%; found C 33.8, H 2.07%. The presence of the molecule of H_2O was revealed by the X-ray analysis. Unlike the triphenylphosphine complex, these crystals dissolved fully in hot cyclohexane and returned on cooling without any change in their appearance or in the IR spectrum of the compound.

2.2. Crystallography

Data were collected on a Nonius CAD-4 diffractometer for 1 and 2, and a Siemens SMART diffractometer for 3. Unit cell parameters were gained from setting angles of 25 reflections for CAD-4 data, and all reflections with $I > 10\sigma(I)$ for the SMART data. Intensity data collection on the CAD-4 employed $\omega/2\theta$ scans with scan width $0.80 + 0.347 \tan \theta$. For the SMART data, collection covered a nominal hemisphere of reciprocal space, by a combination of three sets of exposures; each set had a different ϕ angle for the crystal and each exposure covered 0.3° in ω . Crystal alignment and decomposition were monitored throughout the data collection by measuring three reflections on the CAD-4 every 100 measurements, and by repeating the initial frames on the SMART and analysing the duplicate reflections.

The data were corrected for Lorentz and polarisation effects and the empirical absorption corrections were applied using psi scans for the CAD-4 data [13] and employing the method of Blessing [14] for the area collection data. The equivalent reflections for 3 were

Table 1 Crystal data and refinement parameters

	(1)	(2)	(3)
Formula	C ₁₈ H ₁₅ AsGal ₃	C ₁₈ H ₁₅ GaI ₃ P	$C_{54}H_{47}As_{3}I_{6}In_{2}O$
Molecular weight	756.64	712.69	1927.70
Crystal system	Rhombohedral	Rhombohedral	Rhombohedral (Hexagonal axes)
Space group	R-3	R-3	R-3
a (Å)	10.1 94(4)	10.225(5)	15.5059(1)
<i>c</i> (Å)			42.6060(2)
α (deg.)	93.48(2)	93.83(6)	
$V(A^3)$	1053.2(5)	1062(2)	8871.46(9)
Z	2	2	6
$\overline{d(calc)}(g cm^{-3})$	2.386	2.230	2.164
F(000)	692	656	5364
μ (mm ⁻¹)	7.259	5.731	5.612
Radiation Mo $K\alpha$ (Monochromatic) λ (Å)	0.71069	0.71069	0.71069
Temperature (K)	193	293	293
Diffractometer	Nonius CAD-4	Nonius CAD-4	Siemens SMART
Scan technique	$\omega/2\theta$	ω/2θ	Area detector
2θ (min-max) (deg.)	2-60	2-50	3-52
No. of reflections	5326	2058	29613
No. of independent reflections, R(int)	2009, 0.0387	1248, 0.0719	3441, 0.0241
No. of observed reflections $I > 2\sigma(I)$	1842	1065	3084
Crystal size (mm)	$0.30 \times 0.37 \times 0.45$	$0.35 \times 0.45 \times 0.50$	$0.42 \times 0.42 \times 0.56$
A (min-max)	0.69 1.00	0.58 0.98	0.154 0.245
Least squares weights a,b	0.000, 1.336	0.054, 1.244	0.046, 123.50
No. of variables in LS	71	70	199
Goodness of fit on F ²	1.091	1.093	1,119
Function minimised	$\Sigma w (F_0^2 - F_c^2)^2$	$\Sigma w (F_0^2 - F_c^2)^2$	$\Sigma w (F_o^2 - F_c^2)^2$
R and wR2	0.0219 0.0432	0.0421 0.1022	0.0438 0.1109
Peak height in final map (min-max) e (Å ⁻³)	+1.10, -0.41	+0.86, -1.28	+1.24, -2.10
$R = \Sigma F_0 - F_0 / \Sigma F_0 $	$wR2 = \{\Sigma w(F_0^2 - F_0^2)\}$	$^{2}]/\Sigma[w(F_{2}^{2})^{2}])^{1/2}$	
weight = $1.0/[\sigma^{2}(F_{2}^{2}) + a^{*}P^{2} + b^{*}P]$	$P = (F_0^2 + 2F_0^2)/3$		

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\mathring{A}^2 \times 10^3$)

	x	У	Z.	U(eq)
(Ph ₃ As)	Gal, 1			
I(1)	4269(1)	2029(1)	5240(1)	35(1)
Ga(1)	3506(1)	3506(1)	3506(1)	24(1)
As(1)	2001(1)	2001(1)	2001(1)	21(1)
C(1)	266(2)	1754(2)	2613(2)	25(1)
C (2)	- 837(2)	1801(2)	1755(3)	31(1)
C (3)	-2081(3)	1635(3)	2225(3)	42(1)
C (4)	- 2221(3)	1416(3)	3532(4)	47(1)
C(5)	-1125(3)	1374(3)	4382(3)	46(1)
C(6)	126(3)	1544(3)	3926(3)	36(1)
(PPh ₃)G	al , 2			
I(1)	3018(1)	749(1)	- 148(1)	65(1)
Ga(1)	1592(1)	1592(1)	1592(1)	46(1)
P(1)	3055(2)	3055(2)	3055(2)	41(1)
C(1)	4679(5)	2455(6)	3234(5)	47(1)
C(2)	5797(6)	3256(7)	3142(6)	55(1)
C(3)	7005(7)	2785(9)	3266(7)	73(2)
C(4)	7114(8)	1463(10)	3490(8)	84(3)
C(5)	6021(8)	662(8)	3571(8)	77(2)
C(6)	4790(7)	1143(7)	3436(7)	64(2)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 3				
Atomic	coordinates $(\times 10^4)$ and	equivalent	isotropic	displacement
paramet	ers $(Å^2 \times 10^3)$ (Ph ₃ As) ₃ (I	nI,), ·H,O,	3	

	x	у	z	U(eq)
In(1)	3333	- 3333	198(1)	50(1)
I(1)	4761(1)	- 1392(1)	184(1)	56(1)
As(1)	3333	3333	900(1)	35(1)
As(2)	3333	- 3333	- 489(1)	50(1)
C(1)	3025(5)	- 2381(5)	1095(2)	40(2)
C(2)	2241(6)	- 2680(6)	1307(2)	48(2)
C(3)	2036(7)	- 1981(7)	1432(2)	60(2)
C (4)	2612(8)	983(8)	1351(2)	68(3)
C(5)	3390(8)	- 681(7)	1144(2)	65(2)
C(6)	3598(6)	- 1379(6)	1012(2)	51(2)
C(7)	3359(7)	- 2189(6)	- 687(2)	57(2)
C(8)	2803(10)	- 1807(9)	~ 552(3)	103(5)
C(9)	2869(11)	- 953(10)	- 678(3)	114(5)
C(10)	3386(9)	- 555(8)	- 943(3)	84(3)
C(11)	3902(8)	- 927(9)	- 1078(2)	84(3)
C(12)	3903(9)	- 1743(8)	- 946(2)	81(3)
In(2)	0	0	1401(1)	43(1)
I(2)	- 602(1)	- 1904(1)	1541(1)	64(1)
As(3)	0	0	762(1)	34(1)
C(13)	242(5)	1245(5)	581(1)	40(2)
C(14)	- 370(6)	1288(6)	353(2)	48(2)
C(15)	- 176(8)	2187(7)	229(2)	65(2)
C(16)	640(8)	3044(7)	331(2)	70(3)
C(17)	1275(7)	3015(6)	558(2)	64(2)
C(18)	1060(6)	2115(6)	683(2)	52(2)
O(1)	3333	- 3333	- 1191(2)	55(2)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 4									
Selected	bond	lengths	(Å)	and	angles	(deg)	for 1	and	2

	(Ph ₃ As)Gal ₃ 1	(PPh3)Gal3 2
Ga-l	2.509(1)	2.518(2)
Ga-E	2.490(1)	2.413(4)
C-E	1.919(2)	1.810(5)
I-Ga-E	102.97(2)	104.60(5)
I-Ga-I	115.11(11)	113.87(3)
GaE-C	113.21(7)	111.4(2)
C-Ga-C	105.49(8)	107.5(2)

E represents As or P in 1 and 2, respectively.

averaged to give the unique data set. Crystal data, collection parameters and refinement details are given in Table 1.

The structures were solved by direct methods using SHELXS [15]. Refinement was by full-matrix least squares on F^2 using SHELXL-93 [16] with scattering curves for neutral atoms. All non-hydrogen atoms were allowed to refine anisotropically. Hydrogen atoms, except those of the water molecule, were placed geometrically and refined with a riding model and with U_{iso} constrained to be 20% greater than U_{eq} of the carrier atom. Final atomic coordinates are given in Table 2 for 1 and 2, and in Table 3 for 3. Relevant interatomic distances and angles are given in Tables 4 and 5 for 1 and 2, and 3, respectively. Further details of the crystal-lographic data for compounds 1–3 are available from the Director of the Cambridge CF2 1EZ, UK.

Table 5 Selected bond lengths (Å) and angles (deg) for $(Ph_3As)_3(InI_3)_2 \cdot H_2O$,

3		
$\overline{\ln(1)-I(1)}$	2.7024(5)	
$\ln(1) - As(2)$	2.926(2)	
$\ln(1) - As(1)$	2.990(2)	
As(1)-C(1)	1.950(7)	
As(2)-C(7)	1.947(8)	
In(2)-I(2)	2.6811(6)	
$\ln(2)$ -As(3)	2.7238(13)	
As(3)-C(13)	1.933(7)	
I(1)#1-In(1)-I(1)	119.949(2)	
I(1) - In(1) - As(2)	88.70(2)	
I(1) - In(1) - As(1)	91.30(2)	
C(1) - As(1) - In(1)	115.2(2)	
C(7) - As(2) - In(1)	115.7(2)	
I(2)#2-In(2)-I(2)	115.22(2)	
I(2) - In(2) - As(3)	102.82(2)	
C(13) - As(3) - In(2)	113.4(2)	

Symmetry transformations used to generate equivalent atoms: #1 -y,x-y-1,z; #2 -y,x-y,z.

2.3. Spectroscopy

NMR measurements were made on a Bruker AM400 spectrometer at 298 K. ³¹P and ⁷¹Ga spectra were run using a 10 mm broad-band probe, as described else-where [17].

IR spectra were recorded on samples as nujol mulls between CsI plates, or in pressed polythene discs, using Perkin-Elmer Paragon 1000PC and Bio-Rad FTS60V or FTS6000 spectrometers. Raman spectra of crystalline samples were obtained with a Jobin Yvon U1000 spectrometer, employing the green 514 nm line of a Spectra Physics 2016 argon-ion laser at 20 mW.

3. Results and discussion

3.1. Synthesis

Past preparation of phosphino complexes of gallium tribalides [18] and indium triiodide [7-10] has usually involved the prior synthesis and purification of these highly reactive halides, which were then combined with the chosen ligand in a suitable solvent to yield the adduct. The method employed here makes use of a simple route to Et₂OMI₃ [11,12] involving the rapid oxidation of the metal by iodine in anhydrous ether solution. The existence of MI₃ in ether as the molecular adduct Et₂OGaI₃ has been proven by NMR in the case of gallium [17], with only a trace of dissociation to the ionic product $[GaI_2(Et_2O)_2]^+[GaI_4]^-$. Addition of a ligand L, which is a more powerful donor than diethyl ether, results in the displacement of Et_2O to form LGaI₃, readily detected in solution by ⁷¹Ga NMR (and ³¹ P NMR for phosphino complexes). Similar behaviour occurs when indium is used to prepare Et, OInI, and then treated with Ph₃P or Ph₃As, although the resulting complex may now contain more than one molecule of the ligand L (see below). The adducts of Gal, and Inl, with the phosphine or arsine are only slightly soluble in the ether solution and produce well formed, analytically pure crystals soon after introducing the ligand.

3.2. Crystallography

The structure of Ph_3AsGaI_3 1 has been described in our preliminary communication [6]. Ph_3PGaI_3 2 is isostructural and isomorphous with 1 whose structure is shown therein [6]. Table 4 compares selected bond lengths and angles of the two compounds. Coordination at Ga and As (or P) is pyramidal. The phenyl substituents are staggered with respect to the iodine atoms. The internal C-C bond lengths and angles in the phenyl rings of both compounds are within the expected ranges and the C-As or C-P bond distances agree with those of kindred systems [19-22]. The Ga-I distance of 2.518(2) Å in Ph_3PGal_3 is slightly longer that of Ph_3AsGal_3 (2.509(1) Å).

The Ga–P bond length in Ph₃PGaI₃ is 2.413 Å. This value is bracketed by 2.35 Å in Me₃PGaCl₃ [23] and 2.45 Å in (Me₃Si)₃PGaClPh₂ [24]. The Ga–As bond distance of 2.490 Å in Ph₃AsGaI₃ may be compared with 2.423 Å in (Me₃Si)₃AsGaI₃ [5] and 2.509 Å in (*p*-MeOC₆H₄)₃AsGaI₃ [7]. Other Ga–As distances in adducts are 2.55 Å in R₃AsGa(C₆F₅)₃ [25], 2.57 Å in R₃AsGaPh₃ [25], and 2.63 Å in R₃AsGaCl (*neopentyl*)₂ [26] (R = Me₃Si). The mean of these six values is 2.53 Å, whereas the Ga–As covalent radius sum is 2.45 Å [2].

We examined both of the crystalline $InI_3 + Ph_3P$ adducts by X-ray diffraction. A recent study [10] matches ours and therefore we need only to summarise the main findings. Colourless Ph_3PInI_3 exists as a simple 1:1 adduct in which the In-P distance is 2.603 Å. Its precursor is a pale yellow solid in which both Ph_3PInI_3 and $(Ph_3P)_2InI_3$ are present. The latter component has a bipyramidal structure comprising planar InI_3 with weakly attached ligands forming In-P bonds of 2.86(1) and 2.99(1) Å. We have not found the separate 2:1 adduct of Ph_3P with InI_3 mentioned in some reports [27-29].

The behaviour of InI_3 with triphenylarsine is akin to that with triphenylphosphine, but there are significant differences. A pale yellow product is obtained on adding Ph₃As to Et₂OInI₃, and this can be recrystallised from cyclohexane without change. The yellow crystals **3** possess equal numbers of Ph₃AsInI₃ and (Ph₃As)₂InI₃ molecules, and also contain a single, adventitious molecule of H₂O which is not attached to either of the indium species. Fig. 1 shows the structures concerned and Table 5 gives the important bond lengths and angles. Within Ph₃AsInI₃ the indium atom has distorted tetrahedral coordination. (Ph₃As)₂InI₃ has a bipyramidal skeleton consisting of a trigonal planar InI₃ unit with the arsine ligands in axial positions. The In–I



Fig. 1. The molecular structures of the 2:1 and 1:1 adducts of Ph_3As with InI_3 which co-crystallise in **3**.

bonds of 2.702 Å are slightly less than in the kindred phosphine adduct (2.707 Å [10]). Once again, the distances from indium to the donor ligands are unequal being 2.926(2) and 2.990(2) Å for the Ph₃As-In links. The In-As bond of the discrete Ph₃AsInI₃ molecule is much shorter and measures 2.724 Å, which is close to the In-As covalent radius sum (2.70 Å) [2]. Similarly, the In-I bonds of Ph₃AsInI₃ which measure 2.681 Å are shorter than in (Ph₃As)₂InI₃.

3.3. NMR studies

We have investigated the formation of gallium(III) halide adducts by NMR, employing both ⁷¹Ga and ³¹P resonances [30,31]. The ⁷¹Ga spectrum of an ether solution of Et₂OGaI₃, with added Ph₃P, was recorded after removal of the crystals of Ph₃PGaI₃. Two signals were observed; a broad feature at -228 ppm due to unreacted Et_2OGaI_3 [17], and a doublet at -157.8 ppm which is attributable to Ph₃PGaI₃. The splitting (450 Hz) arises from coupling to phosphorus and its existence shows that the Ga-P bond is long-lived. Similarly, the ³¹P spectrum contains a quartet at -30.2 ppm due to the attachment of phosphorus to quadrupolar gallium, both ⁶⁹Ga and ⁷¹Ga nuclei having I = 3/2. This phosphorus shift is close to the value of -28.2ppm recently deduced for Ph₃PInI₃ during an investigation of the dissociation of (Ph₃P)₂InI₃ [10]. In solutions subject to hydrolysis, for example by atmospheric moisture, we observed an additional ³¹P resonance as a doublet at 4.8 ppm (split by 510 Hz), which is due to [Ph₃PH]⁺. A further signal at 45 ppm was sometimes present and this probably belongs to [Ph₃PI]⁺. The counter-ion to these species is $[GaI_4]^-$, revealed by a sharp signal at -458 ppm in the ⁷¹Ga spectrum.

NMR data for the adducts of GaI₃ with Ph₃P, MePh₂P and Me₂PhP are summarised in Table 6. Addition of PhPCl₂ to Et₂OGaI₃ gave no evidence of adduct formation. The ⁷¹Ga resonance of Ph₃AsGaI₃ is detected as a very broad signal with w_{1/2} = 3400 Hz, owing to unresolved coupling with the quadrupolar ⁷⁵As nucleus. This signal occurs at -220 ppm, compared

Table 6 NMR data for Gal, adducts in CH₂Cl₂ solution

Adduct	$\delta(^{71}\text{Ga})$	$^{1}J(^{71}Ga - ^{31}P)$	δ(³¹ P)
	(ppm)	(Hz)	(ppm)
Ph ₃ PGal ₃	-157.9	452	- 30.2
MePh, PGal	- 141.5	464	28
Me, PhPGal,	- 126.6	476	-42
Ph.PGaBrI,	-43.1	549	- 30
Ph, PGaCll,	11.9	586	- 30
Ph, AsGal,	-220 broad		
Ph ₃ AsGaBrl ₂	- 106 broad		
PhAsGaCIL	- 35 broad		

^aIn Et₂O solution.

Tuble	7
I adle	1

IR and Raman bands (below 600 cm⁻¹) of 1:1 Ph₃EMI₃ adducts

Ph ₃ PGaI ₃		Ph ₃ AsGal ₃		Ph 3PIr	1 ₃	Assignment ^a
IR	Raman	IR	Raman	IR	Raman	
				45 m	43 s	$\delta_{as}(\ln l_3)$
				54 s	54 m	δ (InI 1)
60 m	64 w	55 m	59 w			$\delta_{as}(Gal_3)$
70 m	75 m	68 w	72 m	72 m	67 m	bending
83 m	89 s	86 w	84 s			$\delta_{s}(Gal_{3})$
				85 w	85 m	bending
100 w	98 w	95 vw	92 sh	96 w	94 s	modes
				145 w	145 vs	v.(in1)
144 m	148 vs	142 w	141 vs			v (Ga-I)
				157 s	158 m	ν(InP)
		175 m	176 vw			v(Ga-As)
187 m	185 m	185 w	183 w	185 w	190 vw	x
198 m	197 m	202 m	198 w			x
				202 vs	203 m	v _{as} (In–I)
216 m	21 i m			215 w	213 m	บ
		232 w	234 w			u
				245 w	247 w	u
246 vs	245 s	246 s	249 m			$\nu_{\rm av}({\rm Ga-I})$
266 w	265 m			266 w	266 w	บ
		310 w				t (Ph ₃ As)
		331 m	333 vw			t (Ph ₁ As)
97 w	395 vw	397 w	392 w	397 w	395 vw	w
21 w	423 w			421 w	420 w	t (Ph ₁ P)
42 w	441 w			439 w	441 w	t (Ph ₃ P)
		445 w				y (Ph ₃ As)
		462 s	464 w			y (Ph, As)
96 s	498 w			493 s	495 vw	y (Ph ₃ P)
25 s	520 w			519 s	523 m	y (Ph,P)
545 w	545 vw			540 w	545 vw	v (Ph ₁ P)

^aPhenyl ring modes are assigned according to Whiffen's notation (see text).

with -158 ppm for Ph₃PGaI₃, demonstrating that arsenic has a greater shielding influence upon gallium than does phosphorus.

Mixed halide data in Table 6 were obtained by introducing a chloride or bromide ligand to the gallium complex through the addition of IBr or ICl to the solution of Ph_3PGaI_3 or Ph_3AsGaI_3 . The observed trend in ⁷¹Ga chemical shift to a more positive value as iodine is replaced by bromine or chlorine is normal for such complexes of gallium, for example, the diethyl ether adducts [17].

3.4. Vibrational spectra

Far IR data for adducts of GaI_3 [18,32,33] and InI_3 [28,29] are of long standing. We have extended these and have also recorded the Raman spectra of the various crystalline products of GaI_3 and InI_3 with Ph_3P or Ph_3As as ligands. Structure-sensitive bands occur particularly in the region below 600 cm⁻¹ and are presented in Tables 7 and 8, where internal modes of the ligands are assigned according to Whiffen's notation [34].

Table 8

IR and Raman Bands (below 600 cm⁻¹) of 3:2 Ph_3E/MI_3 adducts

(Ph ₃ P) ₂ InI ₃ :Ph ₃ PInI ₃		(Ph ₃ As) ₂ InI ₃ :Ph ₃ AsInI ₃ Assignment ^{a,b}			
IR	Raman	IR	Raman		
46 m	45 w	48 w	46 w	$\delta_{as}(\ln I_3) C_{fr}$	
58 m	55 m	58 m	56 w	$\delta_{s}(\ln I_{3}) C_{jv}$	
66 w	64 m	63 m	63 m	$\delta(\ln I_3) D_{3h}$	
80 vw	82 w	85 vw	85 w	bending	
105 w	104 w	100 w	100 w	modes	
		124 m	125 sh	v(ln–As)	
	133 vs		133 vs	$v_{s}(In-I) D_{3h}$	
148 m	148 sh	152 s	154 s	$v_{s}(\ln - l) C_{3v}$	
160 s	160 w			$\nu(In-P)$	
	185 w	185 sh	187 w	x	
191 vs	197 s	195 vs	197 s	$\nu_{\rm as}$ (In–I) D_{3h}	
		205 sh	202 m	$v_{as}(In-I) C_{3}$	
216 w	215 w			u	
		230 w	237 w	u	
246 w	250 w	245 vw	248 vw	u	
		308 w	309 w	t (Ph ₃ As)	
		323 m	325 w	t (Ph ₃ As)	
397 vw	394 w	397 vw	395 vw	w	
415 vw	417 m			t (Ph ₃ P)	
434 m	435 vw			t (Ph ₃ P)	
442 w	443 w			t (Ph,P)	
		464 s	465 w	y (Ph ₃ As)	
		475 m	475 vw	y (Ph. As)	
492 s	495 vw			y (Ph ₃ P)	
514 m				y(Ph,P)	
520 s	519 s			y (Ph ₁ P)	
537 s				y (Ph ₃ P)	

^aPhenyl ring modes are assigned according to Whiffen's notation (see text).

^b The InI₃ group has C_{3v} symmetry in Ph₃EInI₃ and D_{3h} symmetry in (Ph₃E)₂InI₃.

Table 7 contains IR and Raman spectra of the 1:1 adducts Ph_3EGaI_3 (E = P or As) and Ph_3PInI_3 . The GaX₃ modes of gallium trihalide complexes with O, S and N ligands were located by Greenwood in early work [32]. For Et₂OGaI₃, symmetric stretching appears at 165 cm⁻¹ and antisymmetric stretching at 252 cm⁻¹, and similar ν (Ga–I) frequencies were found with the ligands Me₂S, Et₂S or pyridine. For Me₃PGaI₃ the values are 157 and 252 cm⁻¹ [18,35]. The present findings are 148 and 246 cm⁻¹ for the Ph₃P adduct, or 141 and 248 cm⁻¹ for the Ph₃As adduct, which extend the series, showing the influence of the nature of the ligand especially upon the symmetric mode. The 246 cm⁻¹ band of Ph₃PGaI₃ was reported and assigned by Carty [33] in an IR study of the spectra of GaX, complexes with triarylphosphine ligands covering the range 600-200 cm⁻¹. This band was unaltered in dichloromethane solution, but shifted to 226 cm^{-1} in acetone, which calls into question the integrity of the complex in this solvent. For Ph₃PInI₃, we see ν_{as} (In-I) at 202 cm^{-1} (in agreement with a previous report of the IR spectrum [29]) and find a strong Raman signal at 145 cm⁻¹, which is naturally assigned to v_s (In–I). The IR

spectrum attributed elsewhere to the 2:1 adduct $(Ph_3P)_2InI_3$, with a strong band at 184 cm⁻¹ and broad features at 132 and 121 cm⁻¹ [29], has not been observed in our investigations.

A mode of particular interest in coordination complexes is that of metal-ligand stretching. Such M-L modes can prove difficult to locate, but fortunately a recent study of trimethylphosphine-gallium halide complexes provides secure ground [35]. For Me₃PGaI₃, the Ga-I stretching mode occurs at 355 cm^{-1} and shifts to 326 cm⁻¹ upon deuteration of the methyl groups. Using this behaviour as a model, and assuming the Ga-P force constant remains approximately the same, the change in mass from Me₃P to Ph₃P might be expected to lower the Ga-L frequency by a factor of $(262/78)^{1/2}$ or 1.83, which leads to a predicted value of 194 cm⁻¹ for Ph₃PGaI₃. Accordingly, we assign the band at 187 cm^{-1} , which has medium intensity in both IR and Raman spectra, to gallium-phosphorus stretching, ν (Ga-PPh₃). Internal vibrations of the Ph₃P ligand occur in this vicinity, but are normally rather weak. For indium-phosphorus stretching, ν (In-PPh₃), there is a plausible band of Ph_3PInI_3 at 157 cm⁻¹, although its closeness to the band at 145 cm⁻¹ attributed to In-I symmetric stretching means that the designation is somewhat arbitrary. The corresponding assignment for $Ga-AsPh_3$, stretching involves a band at 175 cm⁻¹ with a weak Raman counterpart. Otherwise, this moderately strong band of Ph₃AsGaI₃ has no obvious origin, since ν_s (Ga-I) is assigned at 141 cm⁻¹ and ν_a (Ga-I) at 246 cm⁻¹ for this complex. Bands at lower frequency can be assigned to the bending modes of GaI₃ or InI₃ in the Ph₃EMI₃ series, using the prior knowledge of the spectra of LMX₃ and $[MX_4]^-$ [18,36,37] for guidance.

The IR and Raman spectra of the complexes $(Ph_3P)_3(InI_3)_2$ and $(Ph_3As)_3(InI_3)_2 \cdot H_2O$ are given in Table 8. For the former, our results are in agreement with the limited data previously available [28]. The internal ligand bands associated with Ph₃P or Ph₃As present a similar picture to those of the 1:1 adducts, although the pattern is more complicated owing to the presence of both strongly and weakly coordinated ligands. Other bands will be due to the InI₃ moieties and here the situation appears relatively straightforward. The very intense Raman band at 133 cm^{-1} is likely to be that of symmetric In-I stretching of the planar InI, unit in the five-coordinate species. It has the same frequency in each case, which is not surprising since the phosphine or arsine ligands are only weakly attached. This mode is inactive in the infrared. The antisymmetric In-I stretching mode is allowed in IR and Raman spectra and is assumed to produce the strong 195 cm⁻¹ band. For comparison, the free InI₃ molecule in the gas phase exhibits ν_s at 151 and ν_{as} at 200–230 cm⁻¹ [37]. Other bands in the 100–200 cm⁻¹ region can be plausibly associated with the four-coordinate Ph₃EInI₃

molecules which crystallise alongside those of the fivecoordinate kind. The appropriate assignments are given in Table 8. These include the $\nu(ln-I)$ modes shown, along with $\nu(ln-As)$ at 124 cm⁻¹ and $\nu(ln-P)$ at 160 cm⁻¹ (to be compared with 157 cm⁻¹ for Ph₃PInI₃ in the pure crystalline 1:1 compound). Assignments of the InI₃ bending modes of both planar and pyramidal species are included, although these can only be tentative because of complications due to other bending and possible lattice modes. Overall, the spectroscopic data form a useful complement to the X-ray findings. These results provide further evidence of the structural diversity which is a feature of the coordination chemistry of the Group 13 elements, especially indium.

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