Journal of Organometallic Chemistry, 280 (1985) 17–25
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE STRUCTURE OF $C_2H_5InBr_2 \cdot$ tmen, $C_2H_5InI_2 \cdot$ tmen (tmen = *N,N,N′,N′*-TETRAMETHYLETHANEDIAMINE) AND $[(C_6H_5)_4P][C_2H_5InI_3]$ IN SOLUTION AND IN THE SOLID STATE

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(Received May 22nd, 1984)

Summary

The ^1H NMR spectra of $C_2H_5InBr_2 \cdot$ tmen (**1**) $C_2H_5InI_2 \cdot$ tmen (**2**) (tmen = *N,N,N′,N′*-tetramethylethanediamine) and $[(C_6H_5)_4P][C_2H_5InI_3]$ (**3**) show only a broad singlet for the ethyl protons at 60 MHz. Spectra run at 400 MHz resolve these into a triplet + quartet for **1** and **3**. The structure of each compound has been determined by X-ray crystallography; **1** and **2** are five-coordinate species, with InC_2N_2X (X = Br, I) nuclei, while **3** consists of $[(C_6H_5)_4P]^+$ cations and anions whose $InCI_3$ nucleus has C_{3v} symmetry.

Introduction

Organometallic dihalides of indium(III), $RInX_2$, are known for a number of combinations of R and X = Cl, Br, I [1]. A convenient preparation of the iodides, and to a lesser extent the bromides, is by the oxidative insertion reaction of InX and RX [2,3], and it has recently been shown that this process can be carried out by using solutions of InX in non-aqueous media [4]. In this and other methods, the $RInX_2$ products are either obtained as neutral adducts, or may be readily converted to salts of the $RInX_3^-$ anion by treatment with tetraalkylammonium or similar halide.

In the course of our previous work [4], we prepared the neutral adducts $C_2H_5InBr_2 \cdot$ tmen and $C_2H_5InI_2 \cdot$ tmen (tmen = *N,N,N′,N′*-tetramethylethanediamine), and the salt $[(C_6H_5)_4P][C_2H_5InI_3]$ and studied the ^1H NMR spectra of these compounds. At 60 MHz, we observed only a single broad resonance for the ethyl resonance of each compound rather than the expected triplet + quartet. In order to resolve these unusual results, we have determined the structure of each compound by X-ray crystallographic methods, and have also recorded the ^1H NMR spectrum at 400 MHz.

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Experimental

Preparative

The preparation of the three title compounds has been described in an earlier paper [4].

Spectroscopic

^{1}H NMR spectra at 60 MHz were recorded on a Varian EM 360 instrument, and at 400 MHz on the Bruker instrument of the Southwestern Ontario NMR Centre, University of Guelph; ^{13}C spectra were run on a Bruker CXP instrument operating at 22.64 MHz in the F.T. mode.

Crystallographic

X-ray diffraction results for all three compounds were collected on a Syntex P2$_1$ diffractometer by the procedures described previously [5]. A summary of the crystal data is given in Table 1. The following parameters were common in each case: Mo-K_α radiation, λ 0.71069 Å, 2θ 4–50°, scan speed 2.02–4.88 min^{-1}, scan width from $K_{\alpha_1} - 1°$ to $K_{\alpha_2} + 1°$, background time/scan time 0.5.

The compounds $C_2H_5InBr_2 \cdot$ tmen (**1**) and $C_2H_5InI_2 \cdot$ tmen (**2**) (tmen = *N,N,N′,N′*-tetramethylethanediamine) form colourless acicular crystals, samples of which were sealed in capillary tubes; crystals of $[C_6H_5)_4P][C_2H_5InI_3]$ (**3**) are pale yellow prisms which were mounted on a glass fibre. During data collection, the intensity of the three monitor reflections decreased by approximately 14, 15 and 2% for **1**, **2** and **3**, respectively, and appropriate scaling factors were applied. The intensity of the reflections decreased rapidly at the higher $\sin\theta/\lambda$ values for both **1**

TABLE 1

SUMMARY OF CRYSTAL DATA, INTENSITY COLLECTION AND STRUCTURAL REFINEMENT FOR $C_2H_5InX_2 \cdot$tmen (X = Br, (**1**); X = I (**2**)) AND $[(C_6H_5)_4P][C_2H_5InI_3]$ (**3**)

	(1)	(2)	(3)
Cell constants	*a* 8.054(3), *b* 15.183(4) *c* 11.776(2) Å; β 98.8(2)°	*a* 8.288(5), *b* 15.415(7) *c* 12.254(4)Å; β 97.13(4)°	*a* 14.761(3) Å *c* 13.329(3)Å
Cell volume (Å^3)	1423(1)	1553(1)	2904(1)
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$I4_1/a$ (No. 88)
Z	4	4	4
$F(000)$	808	952	1616
M_r	419.91	513.90	863.99
ρ(calc.) (g cm^{-3})	1.96	2.20	1.98
Abs. coeff. (cm^{-1})	70.15	51.03	30.90
Min./max. abs. correction	1.494/3.178	1.548/1.679	3.193/3.913
Crystal dimens. (mm)	0.07×0.22×0.38	0.11×0.14×0.20	0.19×0.21×0.38
Total reflections measured	2814 ($h,k,\pm l$)	3053 ($h,k,\pm l$)	2929 ($\pm h,k,l$)
Unique av. data [$I > 2\sigma(I)$]	1238	1566	986 = [$R(I) = 0.034$]
Number of parameters	118	118	70
$R = (\Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|)$	0.050	0.039	0.053
$R_w = (\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma wF_o^2)^{1/2}$	0.052	0.040	0.065
max. shift/error in final cycle	0.01	0.1	0.1
Δp(max) (e Å^{-3})	1.2	0.8	1.1

and **2**, accounting for 44% (**1**) and 51% (**2**) of the ‘observed’ reflections; a similar effect was noted during structural studies of the compound $In_2Br_3I \cdot 2$tmen [6]. Each set of data was corrected for Lorentz and polarisation effects, and analytical absorption corrections were applied.

For **1** and **2**, the space group $P2_1/n$ was established from the systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$). The similar crystal morphologies, cell dimensions, and identical space groups suggested that these two compounds might have isomorphous crystal structures, and this was confirmed by the final refinements. The first structure to be solved was that of **1**, with the positions of indium and one bromine atom being obtained from a sharpened Patterson synthesis. The isomorphology between these compounds allow us to locate the analogous atoms in the iodide derivative at approximately the same coordinates. The remaining non-hydrogen atoms were located from subsequent Fourier synthesis, and the structures refined by full matrix least square methods with all the non-hydrogen atoms being treated anisotropically. The refinement converged at $R = 0.057$ and $R_w = 0.061$ for **1** and $R = 0.042$ and $R_w = 0.045$ for **2**. All hydrogen atoms were subsequently included in idealized positions, with C–H 0.95 Å, and thermal parameters assigned values exceeding those for the appropriate carbon atoms by $0.01U$ ($Å^2$). The structures were then refined to convergence, with the final $R = 0.05$ and $R_w = 0.052$ for **1**, and $R = 0.039$ and $R_w = 0.040$ for **2**, for 1238 and 1566 unique ‘observed” reflections respectively.

For compound **3**, the space group $I4_1/a$ was identified from the systematic absences (hkl, $h + k + l = 2n + 1$; $hk0$, h, $(k) = 2n + 1$; $00l$, $l = 4 + i(i = 1–3)$). The positions of the indium and phosphorus atoms, obtained from a sharpened Patterson synthesis, showed $\bar{4}$ site symmetry. Since each indium is coordinated to three iodine atoms and one ethyl group, this site symmetry requires the structure of the anion to be disordered, and the subsequent anisotropic refinement assumed that each ligand at indium could be represented as 75% I, 25% ethyl carbon atoms. This approach

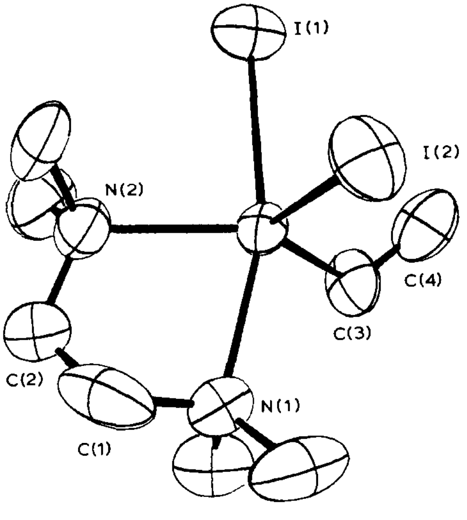

Fig. 1. The molecular structure of $C_2H_5InI_2 \cdot$tmen.

TABLE 2

ATOMIC COORDINATES AND THERMAL PARAMETERS FOR NON-HYDROGEN ATOMS

	x	y	z	$\bar{U}$ (Å^2 × 10^3)
(a) $C_2H_5InBr_2 \cdot$ tmen				
In	0.0959(1)	0.2152(1)	0.1561(1)	40.9
Br(1)	0.1789(3)	0.3385(1)	0.0109(2)	82
Br(2)	−0.1050(3)	0.1367(1)	0.0027(2)	84
N(1)	0.1068(15)	0.0868(7)	0.2879(10)	51
N(2)	0.3539(15)	0.1520(8)	0.1515(10)	50
C(1)	0.2358(26)	0.0309(11)	0.2507(16)	86
C(2)	0.3886(22)	0.0810(11)	0.2353(15)	71
C(3)	−0.0139(21)	0.3010(10)	0.2713(13)	59
C(4)	−0.1250(20)	0.3650(10)	0.2166(13)	58
C(11)	0.1587(23)	0.1142(10)	0.4065(13)	69
C(12)	−0.0502(21)	0.0352(12)	0.2794(17)	81
C(21)	0.4846(21)	0.2181(13)	0.1807(15)	84
C(22)	0.3582(23)	0.1206(12)	0.0345(14)	81
(b) $C_2H_5InI_2 \cdot$ tmen				
In	0.0842(1)	0.2190(1)	0.1605(1)	47.3
I(1)	0.1667(1)	0.3545(1)	0.0105(1)	85
I(2)	−0.1222(1)	0.1361(1)	0.0007(1)	75
N(1)	0.0940(12)	0.0935(6)	0.2829(8)	58
N(2)	0.3413(12)	0.1598(7)	0.1557(8)	65
C(1)	0.2260(22)	0.0402(9)	0.2427(11)	99
C(2)	0.3746(17)	0.0891(10)	0.2319(11)	78
C(3)	−0.0232(18)	0.3000(9)	0.2766(11)	78
C(4)	−0.1315(20)	0.3649(9)	0.2280(13)	98
C(11)	0.1391(21)	0.1200(9)	0.398(12)	97
C(12)	−0.0526(18)	0.0418(10)	0.2783(11)	97
C(21)	0.4731(18)	0.2221(11)	0.1839(12)	101
C(22)	0.3508(16)	0.1284(9)	0.0375(11)	87
(c) $[(C_6H_5)_4P][C_2H_5InI_3]$				
In	0.0	0.0	0.5000	92
P	0.0	0.0	0.0	51
I	0.1317(1)	0.0869(1)	0.6051(1)	93
C(11)	0.0630(4)	0.0754(5)	0.0786(5)	55
C(12)	0.0725(5)	0.1659(5)	0.0570(6)	69
C(13)	0.1237(6)	0.2203(6)	0.1166(8)	85
C(14)	0.1697(7)	0.1836(8)	0.1993(8)	100
C(15)	0.1621(7)	0.0940(8)	0.2209(7)	95
C(16)	0.1081(7)	0.0405(6)	0.1610(7)	87
C(1)	−0.0488(36)	0.1289(34)	0.4346(41)	88 (11)
C(2)	−0.1232(37)	0.0895(41)	0.3667(41)	60 (7)

gave unreasonable distances and geometry for the C–C group, but when the C(1)–C(2) distance was constrained at 1.54 Å, the refinement yielded chemically reasonable positions. In the final cycle of refinement, In, I and P atoms and the phenyl carbon atoms were refined anisotropically, and the constrained C(1) and C(2) atoms were refined isotropically. The hydrogen atoms of the phenyl groups were included in the idealized positions (C–H 0.95 Å) and were assigned isotropic temperature factors 0.01U Å^2 greater than those for the appropriate carbon atoms.

TABLE 3a

INTERATOMIC DISTANCES (Å) AND ANGLES (°), WITH esd's IN PARENTHESES, FOR $C_2H_5InX_2$·tmen (X = Br, I)

	X = Br (**1**)	X = I (**2**)		X = Br	X = I
(a) Interatomic distances			*(b) Angles*		
In–X(1)	2.688(2)	2.919(1)	X(1)–In–X(2)	93.9(1)	93.3(0)
In–X(2)	2.531(2)	2.750(1)	X(1)–In–N(1)	162.8(3)	163.9(3)
In–N(1)	2.49(1)	2.44(1)	X(1)–In–N(2)	87.8(3)	88.7(3)
In–N(2)	2.30(1)	2.33(1)	X(1)–In–C(3)	98.3(4)	98.6(5)
In–C(3)	2.17(1)	2.17(1)	X(2)–In–N(1)	92.0(3)	92.3(2)
N(1)–C(1)	1.46(2)	1.50(2)	X(2)–In–N(2)	105.6(3)	106.9(3)
N(1)–C(11)	1.46(2)	1.47(2)	X(2)–In–C(3)	116.9(4)	117.7(4)
N(1)–C(12)	1.48(2)	1.45(2)	N(1)–In–N(2)	75.0(4)	75.2(4)
N(2)–C(2)	1.46(2)	1.44(2)	N(1)–In–C(3)	93.4(5)	92.2(5)
N(2)–C(21)	1.46(2)	1.46(2)	N(2)–In–C(3)	136.4(5)	134.1(5)
N(2)–C(22)	1.46(2)	1.54(2)	In–N(1)–C(1)	103.1(9)	101.7(8)
C(1)–C(2)	1.48(2)	1.46(2)	In–N(1)–C(11)	110.7(9)	110.8(8)
C(3)–C(4)	1.41(2)	1.42(2)	In–C(3)–C(4)	115 (1)	115 (1)
			In–N(1)–C(12)	115.2(9)	116.8(9)
			In–N(2)–C(2)	111.9(9)	112.5(9)
			In–N(2)–C(21)	109 (1)	113.3(9)
			In–N(2)–C(22)	108 (1)	115 (1)
			N(1)–C(1)–C(2)	112 (1)	114 (1)
			N(2)–C(2)–C(1)	113 (1)	111 (1)

TABLE 3b

INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR 3 [a]

(a) Interatomic distances		*(b) Angles*	
In–I	2.718(1)	I–In–I [a]	117.9(1)
C(1)–C(2)	1.54 (constrained)	I–In–C(1)	112.1(2)
C(11)–C(12)	1.37(1)	C(11)–P–C(12) [a]	108.3(4)
C(12)–C(13)	1.36(1)	P–C(11)–C(12)	122.4(6)
C(14)–C(15)	1.36(1)	C(11)–C(12)–C(13)	120.7(8)
In–C(1)	2.213(9)	C(13)–C(14)–C(15)	120.2(8)
P–C(11)	1.790(7)	C(15)–C(16)–C(11)	121.7(9)
C(11)–C(16)	1.38(1)	I–In–I [b]	105.4(1)
C(13)–C(14)	1.40(1)	In–C(1)–C(2)	98.0(5)
C(15)–C(16)	1.38(1)	C(11)–P–C(11) [c]	110.1(2)
		P–C(11)–C(16)	118.9(6)
		C(12)–C(13)–C(14)	119.9(9)
		C(14)–C(15)–C(16)	118.8(9)

Symmetry equivalent positions: [a] is $-x, -y, 2$ [b] is $-y, x, l-2$ [c] is $-y, x, -2$.

The refinement converged with the final $R = 0.053$, and $R_w = 0.065$ for 986 unique 'observed' reflections.

In all cases, the function minimised in the least squares refinement was $((|F_o| - |F_c|)^2$. Unit weights were used in the initial stages, while in the final cycles the weights were derived from the counting statistics. Computer programmes, and the sources of scattering factors, were those reported previously [7].

Positional and thermal parameters for non-hydrogen atoms are given in Table 2,

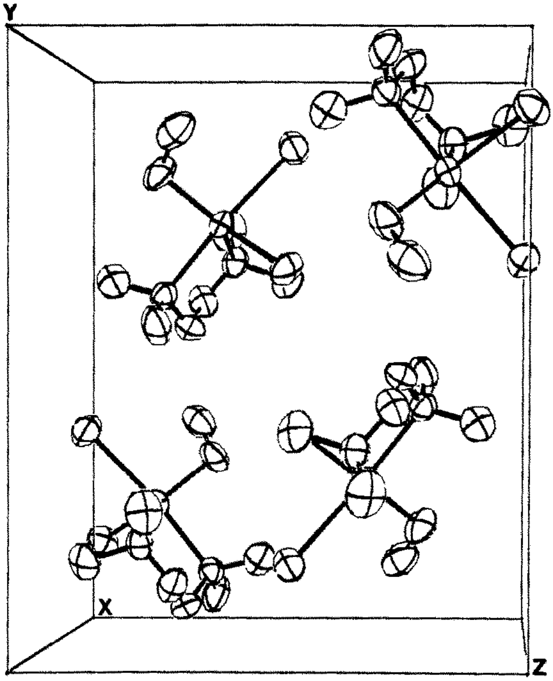

Fig. 2. The cell packing of $C_2H_5InI_2 \cdot$tmen.

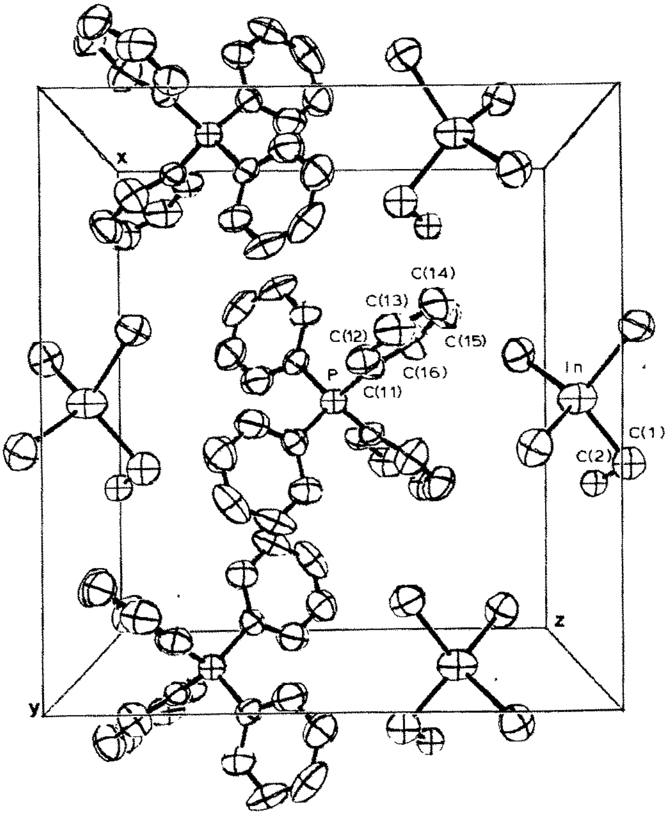

Fig. 3. The cell packing of $[(C_6H_5)_4P][C_2H_5InI_3]$.

and interatomic distances and angles in Table 3. Figure 1 shows the molecular structure of **2** (and by analogy, of **1**), with the atomic numbering scheme, and Fig. 2 shows the cell packing for the same species. Figure 3 shows the crystal packing and atomic numbering scheme for **3**. The In atoms pack in layers at 0.0 and 0.5 in this structure, and only one such layer at 0.5 is shown for the sake of clarity; hydrogen atoms are excluded for the same reason. The anion disorder is not shown.

Supplementary material on deposition includes tables of hydrogen coordinates, anisotropic thermal factors and observed and calculated structure factors for **1**, **2** and **3**.

Results and discussion

Crystal structure of $C_2H_5InX_2 \cdot$ *tmen* $(X = Br, I)$

The results in Table 3a show that compounds **1** and **2** are mononuclear complexes, with quasi-trigonal bipyramidal geometry for the $InCX_2N_2$ nucleus, so that compounds are members of the increasingly large group of five-coordinate organoindium(III) species.

The interatomic distances are in good agreement with earlier results. The In–C distance of 2.17(1) Å is close to that in other organoindium(III) halides [8], where the range is 2.06–2.23 Å. The axial and apical In–Br distances differ significantly (2.531(2) and 2.688(2) Å, respectively), with the longer of these being similar to the In–Br distances in $[(CH_3)_2InBr_2]^-$ (2.644(2) and 2.635(2) Å) [8,9]. There do not appear to be any In–I bond length results for organoindium(III) compounds, other than $C_2H_5InI_3^-$ (see below). The In–N bond lengths again show differences between axial (N(2)) and apical (N(1)) positions, with similar values in both **1** and **2**. In the compound $ClIn(2\text{-}Me_2NCH_2C_6H_4)_2$, in which the donor nitrogen atoms occupy apical sites in a distorted trigonal bipyramid [5], the In–N bond lengths are 2.422(3) and 2.482(3) Å in good agreement with the present results, and with the few earlier measurements (see ref. [8]).

We have drawn attention elsewhere [6] to the unusually short C–C and C–N

TABLE 4

NMR SPECTRA OF SOME ORGANOINDIUM HALIDES (ppm from TMS)

Compound	^1H, 60 MHz [a]	^1H, 400 MHz (a)	^{13}C [b]	Assignment
$C_2H_5InBr_2 \cdot$tmen	2.75 (s, 4H)	2.76 (s, 4H)	56.20 (t)	$N\text{-}CH_2$
	2.59 (s, 12H)	2.57 (s, 12H)	47.34(q)	$N\text{-}CH_3$
	1.24 (m, 5H)	1.27 (t, 3H)	−0.19 (q)	$In\text{-}CH_2\mathit{CH_3}$
		1.11(q, 2H)	13.00 (t)	$In\text{-}\mathit{CH_2}CH_3$
$C_2H_5InI_2 \cdot$tmen	2.72 (s, 4H)	2.80 (s, 4H)	56.33	$N\text{-}CH_2$
	2.58 (s, 12H)	2.61 (s, 12H)	47.76	$N\text{-}CH_3$
	1.23 (s, 5H)	1.20 (s, 5H)	−0.05	$In\text{-}CH_2\mathit{CH_3}$
			12.29	$In\text{-}\mathit{CH_2}CH_3$
$[C_6H_5)_4P][C_2H_5InI_3]$	7.4–8.0 (m, 4H)	7.63–7.94 (m, 20H)		C_6H_5
	1.1 (m, 1H)	1.16 (q, 2H)	–	$In\text{-}\mathit{CH_2}CH_3$
		1.03 (t, 3H)	–	$In\text{-}CH_2\mathit{CH_3}$

[a] In CD_2Cl_2. [b] In $CDCl_3$.

bond distances in coordinated tmen in the compound $In_2Br_3I \cdot 2tmen$. These results are part of a number of examples of such behaviour, reviewed earlier by Maslen and Waters [10]; more recent examples involving copper complexes are noted in ref. 6. As in our earlier work, the accuracy of the results is rather low, since the atoms in question contribute relatively little to the overall X-ray scattering; nevertheless, the average lengths of 1.47 Å for both C(1)–C(2) and $C-N_{tet}$ are shorter than the "normal" lengths of these bonds.

In view of the NMR results discussed below, it is worth noting that the In–C–C angles of 115(1)°, and C–C bond length show the normal features of an ethyl group σ-bonded to a metal.

Crystal structure of $[(C_6H_5)_4P][C_2H_5InI_3]$

The structure of **3** consists of independent mononuclear $(C_6H_5)_4P^+$ cations and $C_2H_5InI_3^-$ anions. The former requires no comment since the bond lengths and angles all show conventional values. The bond lengths and angles of the anion are not as accurate as those for **1** and **2** because of the disorder problem noted in the Experimental Section, and the e.s.d.'s may be unrealistically low for the same reason. The $InCI_3$ nucleus of the anion has C_{3v} symmetry, and the indium–carbon bond distance is again within the range of reported values [8]. The indium–iodine bond is shorter than either of those in **2**, and this result is similar to that found in inorganic indium(III) halide species, where In–X bond length increases with increasing coordination number [11,12]. The present value is close to that reported for the InI_4^- anion (2.71 Å) [13].

As in compounds **1** and **2**, the $In-C_2H_5$ group shows no unusual bond angles; the C–C bond length was not independently determined (see Experimental).

NMR studies

Table 4 shows the ^1H NMR spectra of compounds **1**, **2** and **3** at 60 and 400 MHz. The assignments are straightforward, and the most important point is that the C_2H_5 resonances in **1** and **3**, which appear as singlets at 60 MHz, are resolved into the normal triplet plus quartet spectrum at 400 MHz. For **2**, in contrast, even the 400 MHz spectrum fails to separate the CH_2 and CH_3 resonances. We also note that the compound $C_2H_5InI_2 \cdot 2dmso$ prepared earlier [4] showed an unresolved multiplet centred at 1.27 ppm ($CDCl_3$ solution) in a 60 MHz spectrum. For compounds **1** and **3** the coupling constants obtained from the pseudo first order spectra at 400 MHz give J(HH) 7.8 Hz.

The ^1H NMR spectra of C_2H_5 groups attached to atoms other than carbon have been discussed by a number of authors. The classical triplet + quartet pattern of organic chemistry is a fortuitous simplification of a multi-component spectrum, with complex spectra found in the more general case. Various theoretical treatments [14–16] permit the assignment of both the H–H coupling constants and $\Delta\delta$, the difference between the CH_2 and CH_3 chemical shifts, in the latter; the magnitude and sign of $\Delta\delta$ vary from the conventional value of ca +2 ppm through zero to negative values of a few ppm. A number of organometallic compounds of elements close to indium have been studied in this respect, including diethylzinc ($\Delta\delta$ −0.85 ppm) [16], ethylaluminum chlorides ($\Delta\delta$ negative, and halide dependent) [17–19], triethylgallium [20], tetraethylgermanium ($\Delta\delta$ −0.31 ppm) [20], organotin halides ($\Delta\delta$ positive, and substituent dependent) [21–23] and tetraethyllead ($\Delta\delta$ 0) [17]. The

J(HH) values in all these cases are 8 ± 0.5 cps. Discussions of the value of $\Delta\delta$ have generally focussed on the effective electronegativity of the metal plus substituents [24], although Lorbeth and Vahrenkamp [22] suggest that neighbour anisotropy effects are a dominant factor. The present results show that $\Delta\delta$ for compounds **1** and **3** is +0.16 and +0.13 Hz respectively, while for **2**, $\Delta\delta$ 0. These results clearly cannot of themselves lead to any discussion of the electronic factors which affect $\Delta\delta$, although they are clearly compatible with those summarised above.

The ^{13}C spectra of **1** and **2** call for little comment insofar as the tmen carbon atoms are concerned; the resonances are very similar to those observed in other tmen adducts of indium halides and of the neutral ligand ($\delta(NCH_2)$ 57.24, $\delta(NCH_3)$ 46.08 ppm from TMS) [25]. The CH_2 and CH_3 resonances of the ethyl group bonded to indium are to lower field than in many organic molecules, but the $\Delta\delta$ values of 13.19(1) and 12.34(2) ppm are in the conventional range, so that the effects on $\Delta\delta$ noted for proton resonances are not reflected in ^{13}C NMR spectroscopy of these compounds.

Acknowledgement

This work was supported in part by Operating Grants (to DGT) from the Natural Sciences and Engineering Research Council of Canada.

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