FULL PAPER

Synthesis and crystal structures of trimethylindium adducts with bidentate and macrocyclic tertiary amines

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Received 23rd August 2000, Accepted 27th October 2000 First published as an Advance Article on the web 13th December 2000

The structures of trimethylindium (Me₃In) adducts with the bidentate tertiary amine N,N,N',N'-tetramethyl-4,4'-methylenebis(aniline)[MBDA] and the macrocyclic amines 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclo-tetradecane [N₄-aza crown] and 1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazacyclooctadecane [N₆-aza crown] have been determined by single crystal X-ray diffraction. The adducts have the following stoichiometries, Me₃In·2MBDA 1, 2Me₃In·MBDA 2, 4Me₃In·N₄-aza crown 3 and 6Me₃In·N₆-aza crown 4. Compound 1 contains five-coordinate Me₃In in a trigonal bipyramidal configuration and displays the longest In–N bond lengths yet reported (2.720(4), 2.865 Å); 2–4 contain four-coordinate Me₃In molecules in a tetrahedral configuration. Compounds 1–4 can be used as intermediate adducts in the adduct purification of Me₃In for use in the MOVPE (metal organic vapour phase epitaxy) of InP and related III–V semiconductors.

1 Introduction

Tertiary amine adducts of trimethylindium (Me₃In) have been known for many years,¹ but relatively little structural information exists for these compounds. Recently there has been revived interest in trimethylindium–trialkylamine adducts as they are useful both as precursors in the metal organic vapour phase epitaxy (MOVPE) of InP and related III–V semiconductors,^{2,3} and in the purification of Me₃In for subsequent use in MOVPE.⁴ For instance, the volatile adducts Me₃In·NR₃ (R = Me or Et) have been used as precursors for the MOVPE of InP,^{2,3} whilst the less volatile adduct 2Me₃In· MBDA (MBDA = N, N, N', N'-tetramethyl-4,4'-methylenebis-(aniline)) has been used for purification of Me₃In by mild thermal dissociation of the adduct.^{4,5}

The amine ligand used in adduct purification must form a relatively weak donor-acceptor bond with the metal alkyl, allowing thermal dissociation of the adduct at relatively low temperatures (<150 °C) and must also be significantly less volatile than the liberated organometallic compound to allow easy separation.⁶ There are relatively few nitrogen donors which fulfil these criteria, for example the adducts Me₃In·NMe₃, Me₃In·NEt₃^{2,3} and Me₃In·N(CH₂CH₂)₃N⁷ all volatilise without appreciable dissociation. However, quantitative yields of high purity Me₃In have been obtained by thermal dissociation of the 2Me₃In·MBDA adduct.^{4,5}

The rapid growth of MOVPE as a production technology for optoelectronic devices based on AlGaAs, AlGaInAs and AlGaInP is placing increasingly stringent requirements on the purity of the Group III metal organic precursor. Trace oxygen is a particular problem in Al-containing III–V devices, seriously degrading luminescence efficiency,⁸ and diethyl ether (a common solvent in organometallic synthesis) has been identified as a major source of oxygen contamination in III–V materials grown by MOCVD.⁹ It is therefore necessary completely to eliminate diethyl ether from the metal organic synthesis route. Recently we have shown that ultra high purity Me₃In, essentially free from oxygen impurities, can be obtained by synthesis of the compound in a hydrocarbon solvent, followed by adduct



Fig. 1 Bidentate and macrocyclic tertiary amines used in this study: (a) MBDA, (b) N_4 -aza crown and (c) N_6 -aza crown.

purification using MBDA.¹⁰ Device data have been reported for a high quality low-oxygen content InAlGaAs GRINSCH laser structure grown by MOVPE using Me₃In purified by thermal dissociation of Me₃In·2MBDA. In this paper full structural details are given for the adducts Me₃In·2MBDA 1 and $2Me_3In\cdotMBDA 2$.

We have previously shown that the macrocyclic amines 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclooctadecane (N₄-aza crown) and 1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazacyclooctadecane (N₆-aza crown) (Fig. 1) form adducts which dissociate at low/moderate temperatures with triethylgallium,¹¹ triisopropylgallium,¹¹ and dimethylzinc.¹² In this paper we report the synthesis and full structural characterisation of the analogous trimethylindium compounds, 4Me₃In·N₄-aza crown **3** and 6Me₃In·N₆-aza crown **4**, and show that 1–4 also dissociate at relatively low temperature to liberate base-free Me₃In. Although adducts between R₃Ga and R₃Al and macrocyclic amines have been reported ¹⁶ and structural data are scarce.

Published on 13 December 2000. Downloaded on 26/10/2014 05:01:27

DOI: 10.1039/b008600m

 $Table 1 Crystal and data collection parameters for Me_{3}In \cdot 2MBDA 1, 2Me_{3}In \cdot MBDA 2, 4Me_{3}In \cdot N_{4} - aza crown 3 and 6Me_{3}In \cdot N_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot N_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parameters for Me_{3}In \cdot M_{6} - aza crown 4 Crystal and data collection parame$

	1	2	3	4
Empirical formula	C37H53InN4	$C_{23}H_{40}In_2N_2$	C ₂₆ H ₆₄ In ₄ N ₄	C ₃₆ H ₉₆ In ₆ N ₆
Formula weight	668.76	574.29	892.22	1302.30
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	ΡĪ	$P2_1/c$	$P2_1/n$	$P2_1/c$
aĺÅ	10.641(5)	18.113(3)	7.8656(11)	10.6624(16)
b/Å	10.763(4)	8.3668(7)	18.871(3)	22.856(3)
c/Å	16.634(4)	18.058(3)	12.6821(18)	11.6461(17)
$a/^{\circ}$	108.27(3)			
βl°	91.13(4)	106.182(18)	96.714(17)	108.184(17)
y/°	105.45(4)			
V/Å ³	1732.5(11)	2628.3(6)	1869.5(5)	2696.5(7)
Ζ	2	4	4	2
μ/mm^{-1}	0.637	1.621	2.266	2.355
Reflections collected	9330	16126	10131	16905
Reflections unique (R_{int})	4310 (0.0813)	4152 (0.0506)	2531 (0.0581)	4251 (0.0443)
$R1 \left[I > 2\sigma(I) \right]$	0.0370	0.0317	0.0640	0.0256
wR2 (all data)	0.0809	0.0805	0.1780	0.0580

2 Experimental

General techniques

Trimethylindium was supplied by Epichem Limited. The nitrogen donor ligands used were MBDA, N_4 -aza crown and N_6 -aza crown. All were purchased from Aldrich Chemical Co., dried by distillation off sodium wire and deoxygenated before use.

¹H NMR spectroscopy was carried out using a Bruker 300 spectrometer and infrared spectroscopy on a Perkin-Elmer 1000 infrared Fourier Transform spectrometer using Nujol mulls between NaCl plates. Elemental microanalyses were carried out by the Chemistry Department service at Liverpool University.

Adduct synthesis

The same general synthesis method was used for compounds 1–4. This involved addition of the amine [MBDA (0.5 mol equivalent, 2 mol equivalent), N₄-aza crown (0.25 mol equivalent) or N₆-aza crown (0.17 mol equivalent)] to a stirred suspension of Me₃In (1 mol equivalent) in toluene. Removal of the toluene *in vacuo* gave 1–4 as crystalline solids which were characterised by ¹H NMR, IR spectroscopy, elemental microanalysis and single crystal X-ray diffraction.

Me₃In·2MBDA 1. Colourless crystalline solid. mp 71–72 °C. ¹H NMR (C₆D₆, 300 MHz, 20 °C): δ –0.19[s, 9H, InCH₃], 2.37[s, 24H, NCH₃], 3.75[s, 4H, CCH₂C] and 6.80[m, 16H, C₆H₄]. IR (cm⁻¹): 1613s, 1514s, 1347m, 1272w, 1221w, 1164m, 1142s, 947w, 920m, 852m, 810m, 795m and 677s. Found: C, 66.7; H, 8.10, N, 8.6%. Calc. for C₃₇H₅₃InN₄: C, 66.45; H, 8.00; N, 8.38%.

2Me₃In·MBDA 2. Colourless crystalline solid. mp 79–80 °C. ¹H NMR (C₆D₆, 300 MHz, 20 °C): δ –0.19[s, 18H, InCH₃], 2.37[s, 12H, NCH₃], 3.75[s, 2H, CCH₂C] and 6.8[m, 8H, C₆H₄]. IR (cm⁻¹): 1613s, 1514s, 1347m, 1272w, 1221w, 1164m, 1142s, 947w, 920m, 852m, 810m, 795m and 677s. Found: C, 47.77; H, 7.07; N, 4.79%. Calc. for C₂₃H₄₀In₂N₂: C, 48.09; H, 7.03; N, 4.88%.

4Me₃In·N₄-aza crown 3. Colourless crystalline solid. mp 181–182 °C. ¹H NMR (C₆D₆, 300 MHz, 20 °C): δ 0.00[s, 36H, InCH₃], 1.25[quintet, 4H, CH₂CH₂CH₂], 1.95[s, 4H, NCH₃] and 2.20[broad s, 16H, NCH₂CH₂CH₂N, NCH₂CH₂N]. IR (cm⁻¹): 2267w, 1608w, 1388m, 1329w, 1285w, 1215m, 1183m, 1148s, 1138m, 1089m, 1036s, 1027s, 1022m, 948w, 883w, 832w and 682s. Found: C, 34.73; H, 7.47; N, 5.80%. Calc. for C₁₃H₃₄In₂N₂: C, 34.84; H, 7.66; N, 6.25%.



Fig. 2 Crystal structure of Me₃In·2MBDA 1.

6Me₃In·N₆-aza crown 4. Colourless crystalline solid. mp 103–104 °C. ¹H NMR (C₆D₆, 300 MHz, 20 °C): δ –0.12[s, 36H, InCH₃], 1.95[s, 18H, NCH₃] and 2.51[broad s, 24H, NCH₂-CH₂N]. IR (cm⁻¹): 2274w, 1648w, 1302m, 1285w, 1210m, 1142m, 1121w, 1091m, 1067w, 1022m, 992m, 947w, 917m, 858w, 787w and 685s. Found: C, 33.30; H, 7.50; N, 6.7%. Calc. for C₆H₁₆InN: C, 33.19; H, 7.44; N, 6.45%.

Single crystal X-ray diffraction

Single crystals of compounds 1–4 suitable for X-ray diffraction were obtained by slow recrystallisation of each adduct from toluene. Crystallographic data were recorded on a STOE-IPDS diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å), T = 200 K. Structures were solved by Direct Methods and refined by full-matrix least squares against F^2 using all data.¹⁷ Crystal and data collection parameters are given in Table 1.

CCDC reference number 186/2258.

See http://www.rsc.org/suppdata/dt/b0/b008600m/ for crystallographic files in .cif format.

3 Results and discussion

Structures of Me₃In·2MBDA 1 and 2Me₃In·MBDA 2

The crystal structures of compounds 1 and 2 are shown in Figs. 2 and 3, whilst selected bond lengths and angles are given in Table 2.

The structure of compound 1 is noteworthy in that the Me₃In moiety is five-coordinate with the longest In–N bond lengths (2.720(4), 2.865(4) Å) reported to date. Only a few five-coordinate alkylindium adducts have been reported, and these

Table 2 Selected bond lengths (Å) and angles (°) for Me₃In·2MBDA 1 and 2Me₃In·MBDA 2

1		2	
In(1)–C(3)	2.157(5)	In(1)–C(1)	2.167(4)
In(1)-C(1)	2.164(5)	In(1)-C(2)	2.155(5)
In(1)-C(2)	2.189(5)	In(1)-C(3)	2.172(4)
In(1) - N(1)	2.720(4)	In(2)-C(4)	2.168(5)
In(1) - N(3)	2.865(4)	In(2)-C(5)	2.165(5)
		In(2)-C(6)	2.171(6)
		In(1)-N(1)	2.446(3)
		In(2)-N(2)	2.462(4)
C(3)-In(1)-C(1)	121.1(2)	C(2)-In(1)-C(3)	120.17(19)
C(3) - In(1) - C(2)	121.5(2)	C(2) - In(1) - C(1)	116.2(2)
C(2) - In(1) - C(2)	117.3(2)	C(3) - In(1) - C(1)	116.35(18)
C(3) - In(1) - N(1)	90.99(16)	C(4) - In(2) - C(5)	117.4(3)
C(1)-In(1)-N(1)	90.82(16)	C(4) - In(2) - C(6)	118.5(2)
C(2)-In(1)-N(1)	92.03(16)	C(5) - In(2) - C(6)	117.2(3)
C(3) - In(1) - N(3)	89.51(16)	N(1) - In(1) - C(1)	101.42(14)
C(1) - In(1) - N(3)	88.72(16)	N(1)-In(1)-C(2)	98.69(15)
C(2)-In(1)-N(3)	87.91(16)	N(1)-In(1)-C(3)	97.07(14)
N(1)-In(1)-N(3)	179.45(12)	N(2)-In(2)-C(4)	100.13(18)
		N(2)-In(2)-C(5)	97.0(2)
		N(2)-In(2)-C(6)	99.26(18)



Fig. 3 Crystal structure of 2Me₃In·MBDA 2.

generally involve chelating donor ligands (*e.g.* Me₃In·Me₂-NCH₂NMe₂¹⁸ and Me₂InCl·2,2'-bipy¹⁹) and structural data are scarce. The In–N bond lengths are significantly greater than those in the adducts Me₃In·NHCMe₂(CH₂)₃CMe₂ and Me₃In·NHMe(CH₂)₂NHMe·InMe₃ which are 2.502(5) and 2.369(7) Å, respectively.⁷ In 1 the Me₃In moiety is in a trigonal bipyramidal configuration with a linear N–In–N bond angle of 179.45(12)°, similar to the Me₃In configuration in the polymeric complex [Me₃In·N(CH₂CH₂)₃N]_x, which also displays very long In–N bond lengths (2.62 Å).⁷ The C–In–C bond angles in 1 of close to 120° are very close to those in pure unadducted Me₃In, in which the Me₃In exists in the trigonal planar configuration, providing further evidence of the very weak In–N interactions in 1.

The long In–N bond lengths in five-coordinate trigonal bipyramidal adducts such as 1 and $[Me_3In \cdot (NCH_2CH_2)_3N]_x$ have been attributed⁷ to the In being sp³d hybridised (*i.e.* donation of nitrogen lone pairs into a combination of $5p_z$ and $5d_{z^2}$ orbitals on In). These will be weaker interactions than donation into a single vacant sp³ hybrid orbital on In, as occurs in four-coordinate Me₃In·L adducts.

In compound **2** the In–N lengths of 2.446(3) and 2.462(4) Å are significantly shorter than in **1**, indicating a stronger In–N interaction. The Me₃In is four-coordinate and exists in a distorted tetrahedral environment with N–In–C bond angles ranging from 97.0(2)° to 101.42(14)°, similar to those in Me₃In·NHMe(CH₂)₂NHMe·InMe₃ (98.8(4)–101.4(3)°) and Me₃In·NHMCMe₂(CH₂)₃CMe₂ (92.8(2)–109.3(2)°). The C–In–C bond angles in **2** (≈116°) are similar to those in Me₃In·NHMe(CH₂)₂NHMe·InMe₃ (≈116°) and Me₃In·NHCMe₂-(CH₂)₃CMe₂ (≈116°) and Me₃In·NHCMe₂-(CH₂)₃CMe₂ (≈116°) and Me₃In·NHCMe₂-(CH₂)₃CMe₂ (≈116°) and Me₃In·NHCMe₂-(CH₂)₃CMe₂ (≈117.6°),⁷ which also display comparable In–N bond distances (2.37–2.50 Å).

The similarity in chemical shifts in the ¹NMR data for 1 and 2 suggests that both compounds may be present in mixtures of



Fig. 4 Crystal structure of $4Me_3In \cdot N_4$ -aza crown 3.



Fig. 5 Crystal structure of $6Me_3In \cdot N_6$ -aza crown 4.

 Me_3In and MBDA in solution. This may be similar to the case of mixtures of Et_3Ga and N_6 -aza crown in which two separate species, $4Et_3Ga \cdot N_6$ -aza crown and $6Et_3Ga \cdot N_6$ -aza crown, were isolated from the same solution and characterised by X-ray diffraction.¹¹

Structures of $4Me_3In \cdot N_4$ -aza crown 3 and $6Me_3In \cdot N_6$ -aza crown 4

The crystal structures of compounds **3** and **4** are shown in Figs. 4 and 5, respectively and selected bond distances and angles are given in Table 3. Each adduct displays the expected 4:1 and 6:1 Me₃In:ligand stoichiometries. In the case of **4** this contrasts with N₆-aza crown complexes involving more bulky R₃Ga moieties, such as $4Pr^{i}Ga \cdot N_{6}$ -aza crown where steric constraints limit the stoichiometry at 4:1.¹¹

In compounds 3 and 4 the Me₃In molecules exhibit distorted tetrahedral geometry, with C–In–N bond angles ranging from 95.6(6) to $104.2(5)^{\circ}$ in 3 and $95.27(14)-101.85(17)^{\circ}$ in 4, significantly less than the tetrahedral angle of 109° . These are entirely typical of C–In–N bond angles in tetrahedrally coordinated Me₃In adducts, as shown by the comparative data for a range of Me₃In–tertiary amine adducts given in Table 4. The In–N bond lengths in 3 and 4 are close to the In–N bond length in 2, and fairly typical for In–N bond lengths in an sp³ hybridised tetrahedral configuration (see Table 4). The In–N bond length in 2, 3 and 4 are significantly shorter than the In–N length in the sp³d hybridised complex 1. The In–N bond distance in 4 is very slightly longer than that in 3, presumably

due to a slight increase in steric hindrance in the $6Me_3In \cdot N_6$ -aza crown complex.

The Me₃Al and Me₃Ga analogues to $\mathbf{2}$ have been structurally characterised,^{13,14} and this allows us to make a direct comparison of M-N, M-C bond lengths, and various intramolecular angles in the R₃M molecule (see Table 5). The most notable feature is that the M-N adduct bond length decreases in the order In > Ga > Al, in line with increasing Lewis acidity of the metal centre.²⁰ The M-C bond lengths show a similar trend, decreasing in the order $In > Ga \approx Al$, broadly consistent with increasing strength of the metal-carbon bond. The M-C bond lengths in the $4Me_3Ga \cdot N_4$ -aza crown and $4Me_3In \cdot N_4$ -aza crown adducts are close to those in the unadducted compounds, Me₃Ga(g) (M-C: 1.967(2) Å)²¹ and Me₃In(s) (M-C: 2.16(4)-2.25(6) Å).^{22,23} However, the Al-C bond lengths of 1.960(5)-1.966(6) Å in 4Me₃Al·N₄-aza crown are slightly shorter than the terminal Al-C distances in the Me₃Al dimer (1.99 Å).²⁴ The C-M-N bond angle decreases in the order Al > Ga >In, with an increasing deviation from the tetrahedral angle of 109°.

Dissociation of Me₃In-aza crown adducts

Complex 2 has previously been shown to liberate base free

Table 3 Selected bond lengths (Å) and angles (°) in $4Me_3In\cdot N_4\text{-}aza$ crown 3 and $6Me_3In\cdot N_6\text{-}aza$ crown 4

3		4	
In(1)–C(1)	2.169(16)	In(1)–C(1)	2.166(4)
In(1)-C(2)	2.158(17)	In(1)-C(2)	2.169(4)
In(1)-C(3)	2.175(16)	In(1)-C(3)	2.170(5)
In(2)-C(4)	2.170(17)	In(2)-C(4)	2.168(5)
In(2)-C(5)	2.162(18)	In(2)-C(5)	2.166(5)
In(2)-C(6)	2.180(17)	In(2)-C(6)	2.169(6)
In(1)-N(1)	2.433(12)	In(1)-N(1)	2.490(3)
In(2)-N(2)	2.427(11)	In(2)-N(2)	2.462(3)
		In(3)-N(3)	2.449(3)
C(1)–In(1)–C(2)	118.1(7)	C(1)-In(1)-C(2)	118.7(2)
C(1)-In(1)-C(3)	121.3(7)	C(1)-In(1)-C(3)	113.97(19)
C(2)-In(1)-C(3)	113.8(8)	C(2)-In(1)-C(3)	122.16(18)
C(6)-In(2)-C(5)	120.8(8)	C(7)-In(3)-C(8)	120.4(2)
C(6)-In(2)-C(4)	120.9(7)	C(7)-In(3)-C(9)	119.5(2)
C(4)-In(2)-C(5)	111.7(8)	C(8)-In(3)-C(9)	113.1(2)
N(1)-In(1)-C(1)	95.9(6)	N(1)-In(1)-C(1)	99.79(15)
N(1)-In(1)-C(2)	104.2(5)	N(1)-In(1)-C(2)	97.86(14)
N(1)-In(1)-C(3)	96.4(6)	N(1)-In(1)-C(3)	95.27(14)
N(2)-In(2)-C(4)	101.1(5)	N(2)-In(2)-C(4)	101.85(17)
N(2)-In(2)-C(5)	99.3(6)	N(2)-In(2)-C(5)	100.44(15)
N(2)–In(2)–C(6)	95.6(6)	N(2)-In(2)-C(6)	97.87(16)

Table 4 Bond lengths (Å) and angles (°) for some Me₃In-tertiary amine adducts

Compound	In–N	In–C	C–In–C	C–In–N	Reference
Me ₃ In·2MBDA 1	2.720(4), 2.865(4)	2.157(5)-2.189(5)	117.3(2)-121.5(2)	87.91(16)-92.03(16)	This work
2Me ₃ In·MBDA 2	2.446(3), 2.462(4)	2.165(5) - 2.172(4)	116.2(2)-120.17(19)	97.0(2)-101.42(14)	This work
4Me ₃ In·N₄-aza crown 3	2.427(11)-2.433(12)	2.158(17) - 2.180(17)	111.7(8)-121.3(7)	95.6(6)-104.2(5)	This work
$6Me_{3}In\cdot N_{6}$ -aza crown 4	2.449(3)-2.490(3)	2.166(4)-2.170(5)	113.1(2)-122.6(18)	95.27(14)-103.13(16)	This work
Me ₃ In·NHCMe ₂ (CH ₂) ₃ CMe ₂	2.502(5)	2.170(5)-2.174(6)	109.3(3)-118.9(3)	92.8(2)-109.3(2)	7
Me ₃ In•NHMe(CH ₂) ₂ NHMe• InMe ₃	2.369(7), 2.393(7)	2.147(10)-2.183(9)	113.0(4)–120.2(4)	96.3(3)-101.4(3)	7
$[Me_{3}In \cdot N(CH_{2}CH_{2})_{3}N]_{x}$	2.62	2.172(7)-2.176(5)	119.4(2)	_	7

Table 5	Bond length	ıs (A) an	d angles (°	') for	Me ₃ M	∙N₄-aza	crown adducts	: (M =	Al,	Ga o	r In)
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Compound	M–N	М–С	С–М–С	C-M-N	Reference
4Me₃Al∙N₄-aza crown	2.093(3), 2.102(3)	1.960(5)–1.966(6)		102.8(2)–107.1(2)	13
4Me₃Ga∙N₄-aza crown	2.182(4), 2.202(4)	1.970(6)–1.973(6)		101.0(2)–105.9(2)	14
4Me₃In∙N₄-aza crown	2.433(12), 2.427(11)	2.158(17)–2.180(17)		95.6(6)–104.2(5)	This work

Me₃In when heated at 80–130 °C *in vacuo.*⁴ Complexes 1, 3 and 4 were also found to liberate base-free Me₃In (confirmed by ¹H NMR spectroscopy) when heated at relatively low temperatures 80–115 °C under vacuum. A sample of crude Me₃In containing high levels of MeI (18000 ppm, deriving from the Grignard-based synthesis route) was purified by thermal dissociation of the adducts 1–4 and it was shown that, in each case, the iodide impurity level was reduced to <10 ppm. Such a dramatic reduction can be attributed to formation of the involatile quaternary ammonium salt, $R_4N^+I^-$, resulting from reaction between the tertiary amine and MeI.²⁵ It has previously been shown that MBDA is highly effective in removing trace metal impurities (*e.g.* Si, Zn, Mg) from Me₃In,⁴ but removal of the organic impurity MeI is a useful additional advantage of tertiary amines in adduct purification processes.

4 Conclusion

The crystal structures of $Me_3In \cdot 2MBDA 1$, $2Me_3In \cdot MBDA 2$, $4Me_3In \cdot N_4$ -aza crown 3 and $6Me_3In \cdot N_6$ -aza crown 4 have been determined. Compound 1 is one of only two reported adducts containing five-coordinate Me_3In , whereas 2–4 contain fourcoordinate Me_3In in a distorted tetrahedral configuration. The adducts 1–4 all liberate base-free Me_3In at low/moderate temperatures and are suitable for adduct purification of Me_3In for electronic applications.

Acknowledgements

We are very grateful to Epichem Limited for funding the work and for providing samples of Me_3In . We also thank Mr S. A. Apter (University of Liverpool, UK) for provision of the microanalytical data.

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