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

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The structures of trimethylindium (Me_3In) 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-tetraazacyclotetradecane [N_4-aza crown] and 1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazacyclooctadecane [N_6-aza crown] have been determined by single crystal X-ray diffraction. The adducts have the following stoichiometries, $Me_3In{\cdot}2MBDA$ **1**, $2Me_3In{\cdot}MBDA$ **2**, $4Me_3In{\cdot}N_4$-aza crown **3** and $6Me_3In{\cdot}N_6$-aza crown **4**. Compound **1** contains five-coordinate Me_3In 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 Me_3In molecules in a tetrahedral configuration. Compounds **1**–**4** can be used as intermediate adducts in the adduct purification of Me_3In for use in the MOVPE (metal organic vapour phase epitaxy) of InP and related III–V semiconductors.

1 Introduction

Tertiary amine adducts of trimethylindium (Me_3In) 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 Me_3In for subsequent use in MOVPE.[4] For instance, the volatile adducts $Me_3In{\cdot}NR_3$ (R = Me or Et) have been used as precursors for the MOVPE of InP,[2,3] whilst the less volatile adduct $2Me_3In{\cdot}MBDA$ (MBDA = *N*,*N*,*N′*,*N′*-tetramethyl-4,4′-methylenebis(aniline)) has been used for purification of Me_3In 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 $Me_3In{\cdot}NMe_3$, $Me_3In{\cdot}NEt_3$[2,3] and $Me_3In{\cdot}N(CH_2CH_2)_3N$[7] all volatilise without appreciable dissociation. However, quantitative yields of high purity Me_3In have been obtained by thermal dissociation of the $2Me_3In{\cdot}MBDA$ 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 Me_3In, essentially free from oxygen impurities, can be obtained by synthesis of the compound in a hydrocarbon solvent, followed by adduct purification using MBDA.[10] Device data have been reported for a high quality low-oxygen content InAlGaAs GRINSCH laser structure grown by MOVPE using Me_3In purified by thermal dissociation of $Me_3In{\cdot}2MBDA$. In this paper full structural details are given for the adducts $Me_3In{\cdot}2MBDA$ **1** and $2Me_3In{\cdot}MBDA$ **2**.

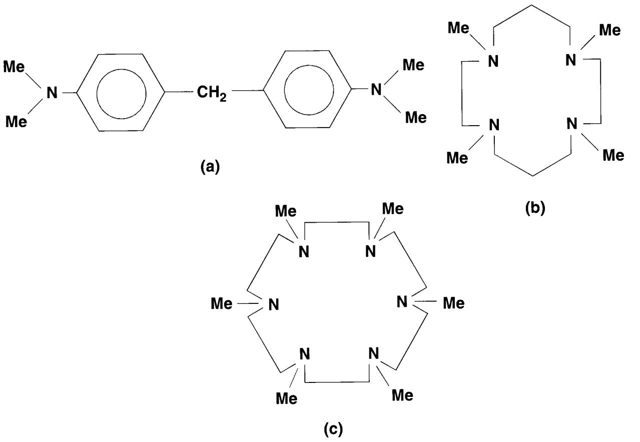

Fig. 1 Bidentate and macrocyclic tertiary amines used in this study: (a) MBDA, (b) N_4-aza crown and (c) N_6-aza crown.

We have previously shown that the macrocyclic amines 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclooctadecane (N_4-aza crown) and 1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazacyclooctadecane (N_6-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, $4Me_3In{\cdot}N_4$-aza crown **3** and $6Me_3In{\cdot}N_6$-aza crown **4**, and show that **1**–**4** also dissociate at relatively low temperature to liberate base-free Me_3In. Although adducts between R_3Ga and R_3Al and macrocyclic amines have been reported,[13–15] very few analogous Me_3In adducts have been reported[16] and structural data are scarce.

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Table 1 Crystal and data collection parameters for $Me_3In{\cdot}2MBDA$ **1**, $2Me_3In{\cdot}MBDA$ **2**, $4Me_3In{\cdot}N_4$-aza crown **3** and $6Me_3In{\cdot}N_6$-aza crown **4**

	1	2	3	4
Empirical formula	$C_{37}H_{53}InN_4$	$C_{23}H_{40}In_2N_2$	$C_{26}H_{64}In_4N_4$	$C_{36}H_{96}In_6N_6$
Formula weight	668.76	574.29	892.22	1302.30
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a/Å	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)
α/°	108.27(3)			
β/°	91.13(4)	106.182(18)	96.714(17)	108.184(17)
γ/°	105.45(4)			
V/Å^3	1732.5(11)	2628.3(6)	1869.5(5)	2696.5(7)
Z	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)
$R1$ [$I > 2\sigma(I)$]	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.

^{1}H 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), N_4-aza crown (0.25 mol equivalent) or N_6-aza crown (0.17 mol equivalent)] to a stirred suspension of Me_3In (1 mol equivalent) in toluene. Removal of the toluene *in vacuo* gave **1**–**4** as crystalline solids which were characterised by ^{1}H NMR, IR spectroscopy, elemental microanalysis and single crystal X-ray diffraction.

$Me_3In{\cdot}2MBDA$ 1. Colourless crystalline solid. mp 71–72 °C. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C): δ −0.19[s, 9H, $InCH_3$], 2.37[s, 24H, NCH_3], 3.75[s, 4H, CCH_2C] and 6.80[m, 16H, C_6H_4]. 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 $C_{37}H_{53}InN_4$: C, 66.45; H, 8.00; N, 8.38%.

$2Me_3In{\cdot}MBDA$ 2. Colourless crystalline solid. mp 79–80 °C. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C): δ −0.19[s, 18H, $InCH_3$], 2.37[s, 12H, NCH_3], 3.75[s, 2H, CCH_2C] and 6.8[m, 8H, C_6H_4]. 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 $C_{23}H_{40}In_2N_2$: C, 48.09; H, 7.03; N, 4.88%.

$4Me_3In{\cdot}N_4$-aza crown 3. Colourless crystalline solid. mp 181–182 °C. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C): δ 0.00[s, 36H, $InCH_3$], 1.25[quintet, 4H, $CH_2C\mathit{H}_2CH_2$], 1.95[s, 4H, NCH_3] and 2.20[broad s, 16H, $NC\mathit{H}_2CH_2C\mathit{H}_2N$, NCH_2CH_2N]. 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 $C_{13}H_{34}In_2N_2$: C, 34.84; H, 7.66; N, 6.25%.

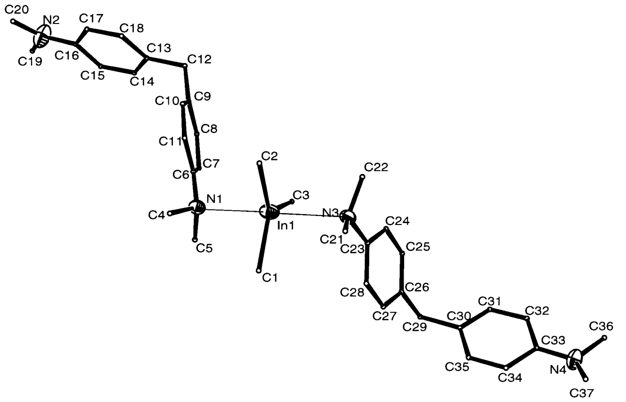

Fig. 2 Crystal structure of $Me_3In{\cdot}2MBDA$ **1**.

$6Me_3In{\cdot}N_6$-aza crown 4. Colourless crystalline solid. mp 103–104 °C. ^{1}H NMR (C_6D_6, 300 MHz, 20 °C): δ −0.12[s, 36H, $InCH_3$], 1.95[s, 18H, NCH_3] and 2.51[broad s, 24H, NCH_2CH_2N]. 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 $C_6H_{16}InN$: 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-Kα 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 $Me_3In{\cdot}2MBDA$ 1 and $2Me_3In{\cdot}MBDA$ 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 Me_3In 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 $Me_3In\cdot 2MBDA$ **1** and $2Me_3In\cdot MBDA$ **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)

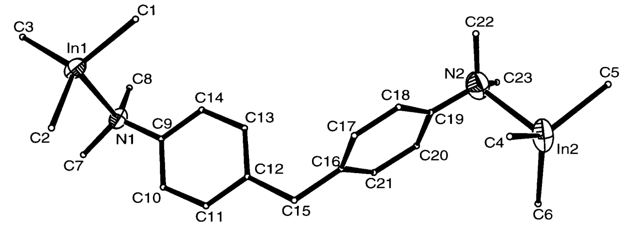

Fig. 3 Crystal structure of $2Me_3In\cdot MBDA$ **2**.

generally involve chelating donor ligands (*e.g.* $Me_3In\cdot Me_2NCH_2NMe_2$[18] and $Me_2InCl\cdot 2,2'$-bipy[19]) and structural data are scarce. The In–N bond lengths are significantly greater than those in the adducts $Me_3In\cdot\overline{NHCMe_2(CH_2)_3C}Me_2$ and $Me_3In\cdot NHMe(CH_2)_2NHMe\cdot InMe_3$ which are 2.502(5) and 2.369(7) Å, respectively.[7] In **1** the Me_3In moiety is in a trigonal bipyramidal configuration with a linear N–In–N bond angle of 179.45(12)°, similar to the Me_3In configuration in the polymeric complex $[Me_3In\cdot N(CH_2CH_2)_3N]_x$, 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 Me_3In, in which the Me_3In 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 attributed[7] to the In being sp^3d 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 sp^3 hybrid orbital on In, as occurs in four-coordinate $Me_3In\cdot L$ 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 Me_3In 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 $Me_3In\cdot NHMe(CH_2)_2NHMe\cdot InMe_3$ (98.8(4)–101.4(3)°) and $Me_3In\cdot\overline{NHCMe_2(CH_2)_3C}Me_2$ (92.8(2)–109.3(2)°). The C–In–C bond angles in **2** (≈116°) are similar to those in $Me_3In\cdot NHMe(CH_2)_2NHMe\cdot InMe_3$ (≈116°) and $Me_3In\cdot NHCMe_2(CH_2)_3CMe_2$ (≈117.6°),[7] which also display comparable In–N bond distances (2.37–2.50 Å).

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

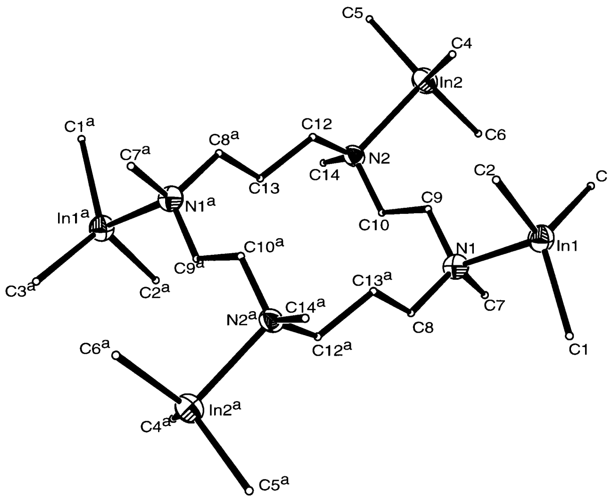

Fig. 4 Crystal structure of $4Me_3In\cdot N_4$-aza crown **3**.

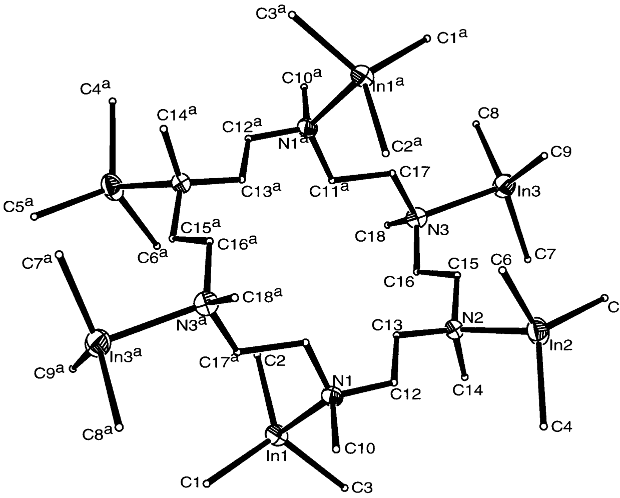

Fig. 5 Crystal structure of $6Me_3In\cdot N_6$-aza crown **4**.

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 Me_3In:ligand stoichiometries. In the case of **4** this contrasts with N_6-aza crown complexes involving more bulky R_3Ga moieties, such as $4Pr^iGa\cdot N_6$-aza crown where steric constraints limit the stoichiometry at 4:1.[11]

In compounds **3** and **4** the Me_3In molecules exhibit distorted tetrahedral geometry, with C–In–N bond angles ranging from 95.6(6) to 104.2(5)° in **3** and 95.27(14)–101.85(17)° in **4**, significantly less than the tetrahedral angle of 109°. These are entirely typical of C–In–N bond angles in tetrahedrally coordinated Me_3In adducts, as shown by the comparative data for a range of Me_3In–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 sp^3 hybridised tetrahedral configuration (see Table 4). The In–N bond lengths in **2**, **3** and **4** are significantly shorter than the In–N length in the sp^3d 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 Me_3Al and Me_3Ga analogues to **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 R_3M 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 ≈ 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, $Me_3Ga(g)$ (M–C: 1.967(2) Å)[21] and $Me_3In(s)$ (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 $4Me_3Al{\cdot}N_4$-aza crown are slightly shorter than the terminal Al–C distances in the Me_3Al 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 Me_3In–aza crown adducts

Complex **2** has previously been shown to liberate base free Me_3In when heated at 80–130 °C *in vacuo*.[4] Complexes **1**, **3** and **4** were also found to liberate base-free Me_3In (confirmed by ^1H NMR spectroscopy) when heated at relatively low temperatures 80–115 °C under vacuum. A sample of crude Me_3In 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 Me_3In,[4] but removal of the organic impurity MeI is a useful additional advantage of tertiary amines in adduct purification processes.

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

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 four-coordinate 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.

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Table 4 Bond lengths (Å) and angles (°) for some Me_3In–tertiary amine adducts

Compound	In–N	In–C	C–In–C	C–In–N	Reference
$Me_3In{\cdot}2MBDA$ **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
$2Me_3In{\cdot}MBDA$ **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
$4Me_3In{\cdot}N_4$-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
$6Me_3In{\cdot}N_6$-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
$Me_3In{\cdot}NHCMe_2(CH_2)_3CMe_2$	2.502(5)	2.170(5)–2.174(6)	109.3(3)–118.9(3)	92.8(2)–109.3(2)	7
$Me_3In{\cdot}NHMe(CH_2)_2NHMe{\cdot}InMe_3$	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
$[Me_3In{\cdot}N(CH_2CH_2)_3N]_x$	2.62	2.172(7)–2.176(5)	119.4(2)	—	7

Table 5 Bond lengths (Å) and angles (°) for $Me_3M{\cdot}N_4$-aza crown adducts (M = Al, Ga or In)

Compound	M–N	M–C	C–M–C	C–M–N	Reference
$4Me_3Al{\cdot}N_4$-aza crown	2.093(3), 2.102(3)	1.960(5)–1.966(6)	—	102.8(2)–107.1(2)	13
$4Me_3Ga{\cdot}N_4$-aza crown	2.182(4), 2.202(4)	1.970(6)–1.973(6)	113.0(3)–118.1(3)	101.0(2)–105.9(2)	14
$4Me_3In{\cdot}N_4$-aza crown	2.433(12), 2.427(11)	2.158(17)–2.180(17)	111.7(8)–121.3(7)	95.6(6)–104.2(5)	This work

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