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SYNTHESIS AND CHARACTERIZATION OF ADDUCTS OF R_3M (R = Me, M = Al, Ga In) WITH 5,6-BENZOQUINOLINE: X-RAY CRYSTAL STRUCTURES OF Me_3Ga—BQ AND $ClMe_2Al$—BQ (BQ = 5,6-BENZOQUINOLINE)

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Abstract—The reaction of R_3M and $AlMe_2Cl$ with 5,6-benzoquinoline (BQ) gave the Lewis acid–base adducts R_3M—BQ [R = Me, M = Al (**1**), Ga (**2**), In (**3**)] and $ClMe_2Al$—BQ (**4**). These adducts are much less air- and water-sensitive than the metal trialkyls and $AlMe_2Cl$. All the compounds were characterized by elemental analyses, IR, NMR and mass spectroscopy. The X-ray crystal structures of **2** and **4** showed that gallium and aluminium atoms in the molecule were tetrahedrally coordinated.

The growth of epitaxial layers of semiconductors comprising compounds of Group 13 and 15 by Metal–Organic Chemical Vapour Deposition (MOCVD) has become of major importance to the electronics industry. Coates *et al.*[1,2] and Bradley *et al.*[3,4] have prepared a series of Me_3M—L complexes. Their research showed that these adducts offer potential as precursors to III/V compound semiconductors. We carried out the present research to explore volatile precursors which have the properties of lower toxicity and higher stability.

In this paper we report the syntheses and characterizations of some new MOCVD precursors.

RESULT AND DISCUSSION

Synthesis of the adducts

Reaction of R_3M or $AlMe_2Cl$ with one equivalent of 5,6-benzoquinoline in diethyl ether at room temperature gave high yields of the adducts **1**–**4** (Scheme 1).

$$R_3M(\text{or } AlMe_2Cl) + BQ \xrightarrow{Et_2O} R_3M\text{—}BQ$$

$$\mathbf{1}\ M = Al;\ R = Me \quad \mathbf{3}\ M = In;\ R = Me$$

$$\mathbf{2}\ M = Ga;\ R = Me \quad \mathbf{4}\ ClMe_2Al\text{—}BQ$$

Scheme 1.

Selected analytical data are presented in Table 1.

Stability of the adducts

These white crystal-like adducts are very air- and moisture-sensitive, but much less so than the trialkyl metal and dimethylaluminium chloride. They are easily dissolved in ether and benzene. The adducts could be sublimed at 10^{-1} Torr. The volatility of the adducts increased from **1** to **3** (sublimation temperatures: **1**, 98°C/10^{-1} Torr; **2**, 78°C/10^{-1} Torr; **3**, 65°C/10^{-1} Torr). Adduct **4** was difficult to sublime.

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Table 1. Selected analytical data for R_3M and adducts **1**–**4**

Compound	M.p. (°C)	Yield (%)	^{1}NMR (C_6D_6) δ(Me—M)	Elemental analysis (%)[a] C	H	N
Me_3Al[b]			−0.35			
Me_3Ga[b]			−0.10			
Me_3In[b]			−0.18			
$ClMe_2Al$			−0.32			
1	200 (dec)	95	0.06	76.3 (76.5)	7.3 (7.2)	5.4 (5.6)
2	118	78	0.37	65.0 (65.3)	6.3 (6.2)	4.4 (4.8)
3	102	84	0.30	55.7 (55.7)	5.6 (5.4)	4.1 (4.1)
4	160	76	0.29	66.3 (66.3)	5.5 (5.6)	5.2 (5.2)

[a] Calculated values are given in parentheses.
[b] Reference 5.

Structures of **2** *and* **4**

Molecular structures of **2** and **4** have been determined by X-ray crystallography. The compounds are isostructural with each other; the molecular structures of **2** and **4** are shown in Figs 1 and 2. Selected bond lengths and angles are given in Table 2.

Both gallium and aluminium are four-coordinated. Their stereochemistry can be described as distorted tetrahedral. Compound **2** is distorted more significantly than compound **4** toward a trigonal pyramid. The base of the pyramids is defined by the three metal–methyl carbon atoms in **2** and the two metal–methyl carbon and chlorine atoms in **4**. The Ga—C and Al—C bond lengths are close in value, but the Ga—N bond is significantly longer than the Al—N bond, implying stronger bonding of BQ to $AlMe_2Cl$ than to $GaMe_3$.

NMR spectra

The ^{1}H NMR spectrum of 5,6-benzoquinoline showed six peaks: 8.85 (d, 1H), 8.32 (d, 1H), 8.20 (m, 2H), 7.58 (m, 2H), 7.34 (m, 2H), 6.93 (m, 1H). The ^{1}H NMR spectra of the adduct compounds are listed in the Experimental section. Usually, coordination of a Lewis base would be expected to increase the electron density on the metal and hence produce more shielding of the alkyl protons. For this aromatic Lewis base, however, the delocalization of electron density from the metal to the BQ rings causes deshielding of the alkyl protons.

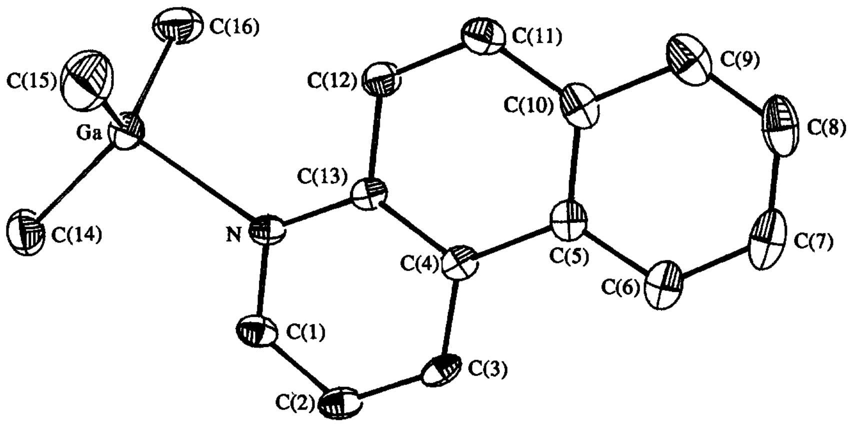

Fig. 1. Molecular structure of Me_3Ga—BQ (**2**). Thermal ellipsoids are drawn at the 30% level, and hydrogen atoms are omitted for clarity.

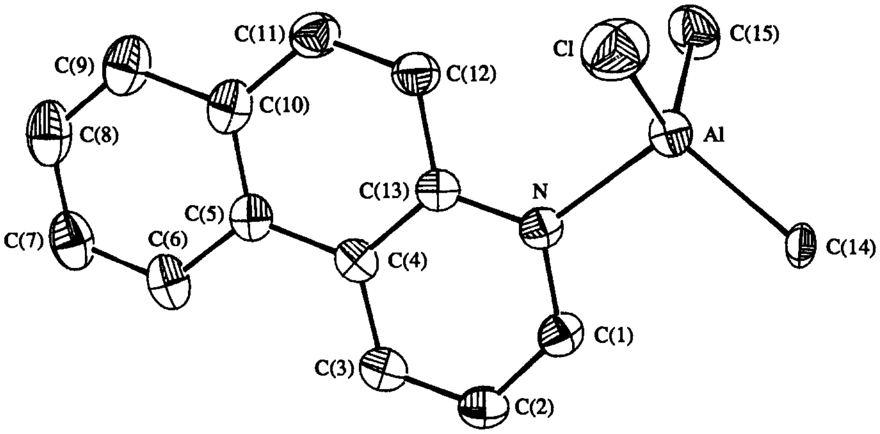

Fig. 2. Molecular structure of ClMe$_2$Al—BQ (**4**). Thermal ellipsoids are drawn at the 30% level, and hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°)

2		**4**	
Ga—C(14)	1.972(5)	Al—C(14)	2.061(3)
Ga—C(15)	1.984(6)	Al—C(15)	1.976
Ga—C(16)	1.982(5)	Al—Cl	2.137(2)
Ga—N	2.152(3)	Al—N	2.016(3)
N—C(1)	1.318(4)	N—C(1)	1.330(5)
C(14)—Ga—C(15)	114.7(2)	C(14)—Al—C(15)	115.8(2)
C(14)—Ga—C(16)	113.1(2)	C(14)—Al—Cl	109.4(1)
C(15)—Ga—C(16)	119.2(2)	C(15)—Al—Cl	115.1(2)
C(14)—Ga—N	102.2(2)	C(14)—Al—N	105.6(1)
C(15)—Ga—N	101.0(2)	C(15)—Al—N	106.2(2)
C(16)—Ga—N	103.4(2)	Cl—Al—N	103.5(1)

Therefore, the chemical shifts of the metal methyl protons have a significant downfield shift when the adducts are formed.

Mass spectra

The fragments: $[M-CH_3]^+$, BQ^+ and MMe_2 were found in the adducts and the additional fragments $[AlMeCl]^+$ and $[M-CH_3-Cl]^+$ were found for **4**. None of the adducts showed a parent molecular ion $[M]^+$.

EXPERIMENTAL

All experiments were carried out under specially dried oxygen-free nitrogen using Schlenk tubes and a glove box. All solvents were carefully dried by distillation from sodium diphenyl ketone under nitrogen before use. ^1H NMR spectra were obtained using a Bruker AM500 spectrometer using C_6D_6 as solvent. Chemical shifts were measured by internal reference to TMS. Mass spectra were obtained using a ZAB-MS instrument. Elemental analyses were recorded on a Carlo Erba 1106 elemental analyser. TMAl, TMGa, TMIn and AlMe$_2$Cl were provided by the Special Gas Institute of Nanjing University.

Trimethyl(5,6-*benzoquinoline*) *aluminium*(III) (**1**)

TMAl (2.3 cm^3, 23.4 mmol) was added to a solution of 5,6-benzoquinoline (3.5 g, 19.5 mmol) in Et$_2$O (60 cm^3), immediately giving a white precipitate. The reaction mixture was continuously stirred for 5 h at room temperature. About half of the solvent was removed *in vacuo*. The white precipitate was filtered off and washed with Et$_2$O. After recrystallization from cyclohexane–benzene (5 : 2), colourless needle crystals were obtained (4.6 g, 95% based on BQ). It could be sublimed at 98°C/10^{-1} Torr. ^{1}H NMR, δ: 0.06 (s, 9H, Al—Me), 6.56 (d, 1H), 7.13 (s, 1H), 7.27 (t, 2H), 7.37 (t, 2H), 7.87 (d, 1H), 8.05 (d, 1H), 8.60 (d, 1H), 8.84 (br, 1H, BQ). MS, *m/z*: 236 ($M-CH_3$), 179 (BQ), 57 ($AlMe_2$).

Trimethyl(5,6-*benzoquinoline*)*gallium*(III) (**2**)

TMGa (2.5 cm^3, 25.05 mmol) was added to a stirred solution of 5,6-benzoquinoline (3 g, 16.7 mmol) in Et_2O (60 cm^3). The clear colourless solution was stirred at room temperature for 5 h. Ether was removed *in vacuo* and the white solid residue was recrystallized from cyclohexane; colourless needle crystals suitable for X-ray crystallography were obtained (3.8 g, 78% based on 5,6-benzoquinoline). Sublimed at 78°C/10^{-1} Torr. ^{1}H NMR, δ: 0.37 (s, 9H, Ga—Me), 6.69 (t, 1H), 7.31 (m, 2H), 7.46 (m, 2H), 7.98 (d, 1H), 8.14 (d, 1H), 8.48 (d, 1H), 8.82 (d, 1H, BQ). MS, *m/z*: 278 ($M-CH_3$), 179 (BQ), 99 ($GaMe_2$), 84 (GaMe).

Trimethyl(5,6-*benzoquinoline*)*indium*(III) (**3**)

Compound **3** was prepared in a similar manner to **2** using TMIn (3.2 g, 20 mmol) and 5,6-benzoquinoline (3 g, 16.7 mmol). Compound **3** was obtained as colourless needle crystals (4.7 g, 84% based on 5,6-benzoquinoline). Sublimed at 65°C/10^{-1} Torr. ^{1}H NMR, δ: 0.30 (s, 9H, In—Me), 6.73 (m, 1H), 7.35 (m, 2H), 7.56 (m, 2H), 8.10 (m, 2H), 8.21 (d, 1H), 8.85 (d, 1H, BQ). MS, *m/z*: 324 ($M-CH_3$), 179 (BQ) 145 ($InMe_2$), 130 (InMe), 115 (In).

Chlorodimethyl(5,6-*benzoquinoline*)*aluminium*(III) (**4**)

Compound **4** was prepared in a similar manner to **1** using $ClAlMe_2$ (1.9 cm^3, 33.4 mmol) and 5,6-benzoquinoline (3 g, 16.7 mmol). Compound **4** was obtained as colourless needle crystals after recrystallization from benzene (3.4 g, 76% based on 5,6-benzoquinoline). ^{1}H NMR, δ: 0.29 (s, 6H, Al—Me), 6.69 (br, 2H), 7.41 (t, 2H), 7.51 (t, 2H), 8.02 (d, 1H), 8.19 (d, 1H), 8.72 (d, 1H, BQ). MS, *m/z*: 256 ($M-CH_3$), 220 ($M-CH_3-Cl$), 179 (BQ), 91 ($AlMe_2Cl-1$).

Table 3. Crystal data, details of intensity measurements and structural refinement data for compounds **2** and **4**

Compound	**2**	**4**
Formula	$C_{16}H_{18}NGa$	$C_{15}H_{15}NClAl$
Molecular weight	294.04	271.72
Crystal system	Monoclinic	Monoclinic
a (Å)	7.24(1)	7.219(4)
b (Å)	14.614(4)	14.609(2)
c (Å)	13.836(7)	13.522(2)
β (°)	97.81(9)	97.07(4)
V (Å^3)	1449(2)	1415.2
Space group	$P21/c$	$P21/c$
Z value	4	4
D_{calc} (g cm^{-3})	1.35	1.28
$F(000)$	608	568
μ(Mo-K_α cm^{-1})	18.73	3.11
$2\theta_{max}$ (°)	49.9	49.9
Range of h, k, l	0–8, 0–17, -16 to 16	0–8, 0–17, -16 to 16
No. of reflections measured	2894	2824
No. of independent reflections	2673	2617
No. of observed reflections	2089	2004
No. of reflections used in refinement	1917	1717
No. of parameters refined	164	164
Weighting scheme	$w = 1/\sigma^2(F)$	$w = 1/\sigma^2(F)$
R	0.046	0.063
R_w	0.053	0.076
$\Delta\rho_{min}$	-0.74	-0.28
$\Delta\rho_{max}$	0.66	0.26

X-Ray crystallography

X-Ray measurements for both compounds were made on crystals mounted in glass capillaries using an Enraf–Nonius CAD4 diffractometer operating in the ω–2θ scan mode with graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å). Both structures were solved by direct methods and refined by the full-matrix least-squares method. Atomic scattering factors and anomalous dispersion terms were taken from ref. 6. All calculations were carried out on a MICRO VAX3100 computer using the TEXSAN program.

Crystal data, details of the intensity measurement and refinement data are given in Table 3. All other data are included in the supplementary material.

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