

## Adduct Purification of Trimethylgallium using 4-Dimethylaminopyridine

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### Abstract

*1:1 and 2:1 adducts of trimethylgallium (TMGa) with 4-dimethylaminopyridine (DMAP) were synthesized and characterized by <sup>1</sup>H, <sup>13</sup>C NMR, FAB-MS and Trace elemental analyses using ICP-MS. Both adducts are non-pyrophoric, thermally dissociable and easy to handle. FAB-MS study suggests that the adducts are associated in tetrameric forms. TMGa of purity more than 99.999% (5N) was released from these adducts, which shows the adducts are potential candidates to produce high pure metal alkyl sources for Metal-Organic Chemical Vapor Deposition (MOCVD).*

**Keywords:** *Trimethylgallium, pyrophoric, MOCVD precursor, adduct purification technique*

### 1. Introduction

The electronic properties of II-VI and III-V compound semiconducting thin films deposited by MOCVD method are mainly determined by the purity of the precursors [1, 2]. As most of the metal alkyls for MOCVD are volatile and highly reactive pyrophoric liquids, the physical purification methods such as, fractional distillation and low temperature crystallization are difficult to employ and often large amount of metal alkyls need to be discarded to obtain them with high purity. However, these metal alkyls can be purified by 'adduct purification technique', which involves the formation of adducts between the metal alkyl with an appropriate Lewis base, which are easy to handle and can be purified by recrystallization [3, 4, 5]. After removal of non-adducting and weakly-adducting impurities in-vacuo, thermal dissociation of adducts under vacuum releases purified metal alkyls. TMGa has been widely used as a MOCVD precursor for preparing thin films, such as GaAs, GaAlAs, GaN etc. for various electronic applications such as solid state lasers, light emitting diodes, infrared detectors and high mobility transistors [6, 7]. Adducts of TMGa with 4,4'-methylenebis (N,N'-dimethylaniline) and triphenylphosphine [8], N,N,N',N'-tetramethylenediamine [9], ammonia [10], secondary amines [11], (Carbazolyl-methyl)dimethylamine [12], macrocyclic amines [13, 14] and 1,1,3,3-tetramethyldisilazane [15] have been reported. Poly (4-vinylpyridine) was used as a polymeric ligand to react with metal alkyls, Me<sub>n</sub>M (n = 3, M = Al, Ga or In; n = 2, M = Cd or Zn) to form adducts [16]. In this paper, we report the studies on the purification of TMGa using DMAP by following adduct purification technique.

## 2. Experimental Sections

All the reactions were carried out under argon atmosphere following standard Schlenk/vacuum line techniques. Solvents were purified by following standard procedures [17] and were freshly distilled and degassed prior to use. Iodomethane (Aldrich), diethyl ether (Aldrich), 4-dimethylaminopyridine (E-Merck, Germany), nitric acid (E-Merck, Germany), hydrogen peroxide (E-Merck, Germany) and perchloric acid (E-Merck, Germany) are of highest available purity and used as received. Calibration standards for Inductively Coupled Plasma Mass Spectrometer (ICP-MS) were from M/s Accustandard Inc, USA. Gallium-Magnesium alloy (purity, 99.999 %) was obtained from DMRL, Hyderabad, India. TMGa etherate was synthesized in our laboratory by a slight modification of published procedure [18, 19].  $^1\text{H}$  and  $^{13}\text{C}$  NMR were obtained at 400.13 and 100.61 MHz respectively on a Bruker AMX 400 Spectrometer and chemical shifts are cited with respect to  $\text{SiMe}_4$  as internal standard. FAB Mass Spectra (FAB-MS) were recorded on JEOL SX/DA-6000 Mass Spectrometer/data system using Argon (6kv, 10 mA) as FAB gas. The samples for ICP-MS analyses were prepared as per reported procedure [20] and trace-elemental analysis were done using ICP – MS, Thermo elemental VG PQ Excel equipped with a concentric flow nebulizer. The operating parameters of the ICP-MS were set as, Detector mode: Pulse counting; Dwell time: 20 ms; Points/peak: 3; Acquisition time: 100 seconds; Forward power: 1250 W; Cool gas: 14 L  $\text{min}^{-1}$ ; Auxiliary gas: 1.0 L  $\text{min}^{-1}$ ; Carrier gas: 0.98 L  $\text{min}^{-1}$ .

### 2.1 Synthesis of 4-dimethylaminopyridine.trimethylgallium Adduct (I):

Trimethylgallium etherate (7 g, 37 mmol) was added drop wise to a stirred solution of DMAP (4.53 g, 37 mmol) dissolved in 50 mL of benzene by means of a cannula. The reaction mixture was refluxed for 3 Hrs and cooled to room temperature followed by addition of excess petroleum ether, which yielded white crystals of adduct I. The compound was filtered, dried and recrystallised from chloroform. Yield: 8.43g (96%).

### 2.2 Synthesis of hexamethyl- $\mu$ -[4-dimethylaminopyridine] digallium (II):

The above procedure was followed to synthesize II using 2 mole equiv. of trimethylgallium etherate (14 g, 74 mmol). The white crystals obtained were recrystallised from chloroform. Yield: 12.39 g (95%).

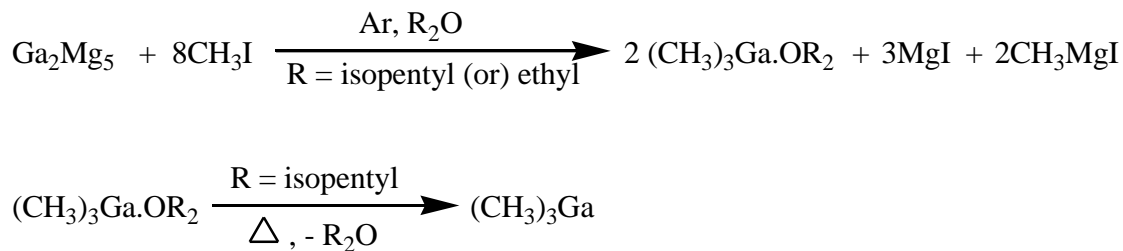
### 2.3 Thermal Cracking of Adducts to Release TMGa:

A known weight of adduct (I or II) was taken in a flask equipped with vacuum distillation assembly. The reaction flask was immersed in an oil bath and heated slowly above the melting point of the adduct, as given in Table 2, under static vacuum, while keeping the receiving flask immersed in liquid nitrogen (ca.  $-196\text{ }^\circ\text{C}$ ). The process was continued until the white fumes of TMGa stops releasing from adduct and pure TMGa collected were packed under argon atmosphere.

## 3. Results and Discussion

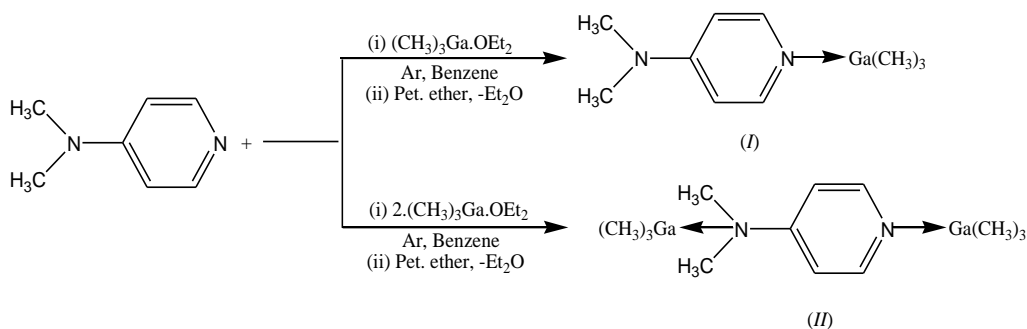
Diethylether adduct of TMGa was synthesized by one pot reaction of iodomethane with gallium-magnesium alloy of stoichiometric ratio  $\text{Ga}_2\text{Mg}_5$  using diethyl ether as solvent (Figure 1) [18, 19]. Best yields are obtained from homogeneous phase of  $\text{Ga}_2\text{Mg}_5$ , whereas inhomogeneous alloys often leads to the formation of Grignard reagent and gallium metal [21]. Reaction in high boiling ether such as isopentyl ether instead of diethyl ether yields dry TMGa, as isopentyl ether adduct of TMGa breaks nearly at the boiling point of isopentyl

ether. On the other hand, diethyl ether adduct of TMGa distills at 99 °C without breaking, which is far higher than dry TMGa (bp. 56 °C) [22].



**Figure 1. Preparation of TMGa etherate and TMGa**

As diethyl ether adduct of TMGa is non-pyrophoric compared to dry TMGa [23], in the present study, the former has been synthesized in diethyl ether as solvent and subsequently used for the preparation of the adducts (Figure 2). Moreover, diethyl ether is a good leaving group during adduct formation and consequently acts as solvent.



**Figure 2: Preparation of Adducts I and II**

The physical and analytical data of adducts I and II are given in Table 1.  $^1\text{H}$  NMR resonance signal due to methyl groups of TMGa appeared in high fields, which can be attributed to the coordination of the lone pair electron from aromatic nitrogen atom of DMAP to gallium atom. The observed chemical shift values are comparable to those reported for the adducts of TMGa and trimethylindium (TMIn) with 4,4'-methylenebis (N,N'-dimethylaniline) [24]. For adduct II, the appearance of two signals for methyl groups of TMGa at high fields confirms the formation of 2:1 adducts of TMGa with DMAP. The  $^1\text{H}$  NMR resonance signal due to methyl groups of DMAP for adduct II appearing at lower field as compared to adduct I further indicate its coordination reaction with second TMGa. Similarly  $^{13}\text{C}$  NMR signals due to methyl groups of TMGa and DMAP showed similar trends.

**Table 1: Physical and NMR Data for I and II**

| Adduct | m.p and Spectral data  |
|--------|--|
| I      | m.p (°C): 90-92  |
|        | $^1\text{H}$ NMR ( $\text{CDCl}_3$ ), $\delta$ : 0.16 (s, Ga- $\text{CH}_3$ ), 2.08 (s, N- $\text{CH}_3$ ), 5.70 & 7.90 (d, Ar-H)<br>$^{13}\text{C}$ NMR ( $\text{CDCl}_3$ ), $\delta$ : -6.0 (Ga- $\text{CH}_3$ ), 39.2 (N- $\text{CH}_3$ ), 106.7, 146.9 & 155.1 (Ar-C)                        |
| II     | m.p (°C): 60-62  |
|        | $^1\text{H}$ NMR ( $\text{CDCl}_3$ ), $\delta$ : -0.05, 0.06 (s, Ga- $\text{CH}_3$ ), 3.05 (s, N- $\text{CH}_3$ ), 6.6 & 7.9 (d, Ar-H)<br>$^{13}\text{C}$ NMR ( $\text{CDCl}_3$ ), $\delta$ : -2.63 to -2.59 (merged, Ga- $\text{CH}_3$ ), 39.5 (N- $\text{CH}_3$ ), 106.5, 137.6 & 156.5 (Ar-C) |

The ‘thermal cracking’ details of adducts I and II are given in Table 2. A sample of TMGa released was diluted with diethyl ether and characterized by <sup>1</sup>H NMR, which showed signal due to methyl group of TMGa at -0.18 (δ ppm, C<sub>6</sub>D<sub>6</sub>, TMS) [24].

**Table 2. Thermal Cracking Data for I and II**

| Adduct    | Temperature (°C) | Vacuum (mm Hg)   | Yield (%) |
|-----------|------------------|------------------|-----------|
| <i>I</i>  | 90-105           | 10 <sup>-2</sup> | 87        |
| <i>II</i> | 60-80            | 10 <sup>-2</sup> | 88        |

The origin of major fragmentation peaks due to FAB-MS with the corresponding e/m values are given in Table 3. The FAB-MS spectrometry of both adducts reveals that the compounds may be associated as tetramers. Further m/e values higher than tetrameric associations were not observed in FAB-MS, which may be due to steric effect of methyl groups.

**Table 3: FAB-MS Fragmentation Data for I and II**

| Adduct   | m/z (M <sup>+</sup> )   |
|--|---|
| <i>I</i>   | 916 ([Me <sub>3</sub> Ga.NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> ] <sub>4</sub> - 2Me] <sup>+</sup> )   |
|  | 832 ([Me <sub>3</sub> Ga.NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> ] <sub>4</sub> - GaMe <sub>3</sub> ] <sup>+</sup> )  |
|  | 768 ([Me <sub>3</sub> Ga.NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> ] <sub>4</sub> - [NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> & 4Me] <sup>+</sup> )  |
|  | 735 ([Me <sub>3</sub> Ga.NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> ] <sub>4</sub> - [NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> & 6Me] <sup>+</sup> )  |
|  | 643 ([Me <sub>3</sub> Ga.NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> ] <sub>4</sub> - [2NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> & 4Me] <sup>+</sup> )   |
|  | 530 ([Me <sub>3</sub> Ga.NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> ] <sub>4</sub> - [2NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> & GaMe <sub>3</sub> & 4Me] <sup>+</sup> )                     |
|  | 486 ([Me <sub>3</sub> Ga.NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> ] <sub>4</sub> - [2NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> & GaMe <sub>3</sub> & 7Me] <sup>+</sup> )                     |
|  | 221 ([Me <sub>3</sub> Ga.NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> - Me] <sup>+</sup> )   |
|  | 122 ([Me <sub>3</sub> Ga.NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> - GaMe <sub>3</sub> ] <sup>+</sup> )   |
| <i>II</i>  | 1423 ([Me <sub>3</sub> Ga.NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> .GaMe <sub>3</sub> ] <sub>4</sub> + Me] <sup>+</sup> )  |
|  | 1377 ([Me <sub>3</sub> Ga.NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> .GaMe <sub>3</sub> ] <sub>4</sub> - 2Me] <sup>+</sup> )   |
|  | 1025 ([Me <sub>3</sub> Ga.NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> .GaMe <sub>3</sub> ] <sub>4</sub> - [NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> & 2GaMe <sub>3</sub> & 2Me] <sup>+</sup> ) |
|  | 946 ([Me <sub>3</sub> Ga.NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> .GaMe <sub>3</sub> ] <sub>4</sub> - [NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> & 2GaMe <sub>3</sub> & 6Me] <sup>+</sup> )  |
|  | 574 ([Me <sub>3</sub> Ga.NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> .GaMe <sub>3</sub> ] <sub>2</sub> - [GaMe <sub>3</sub> & Me] <sup>+</sup> )  |
|  | 439 ([Me <sub>3</sub> Ga.NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> .GaMe <sub>3</sub> ] <sub>2</sub> - [GaMe <sub>3</sub> .NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> & 2Me] <sup>+</sup> )    |
|  | 399 (Me <sub>3</sub> Ga.NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> .GaMe <sub>3</sub> & 3Me] <sup>+</sup> )  |
| 276 (Me <sub>3</sub> Ga.NC <sub>5</sub> H <sub>4</sub> NMe <sub>2</sub> .GaMe <sub>3</sub> - 3Me] <sup>+</sup> ) |   |

Trace elemental impurities data obtained from ICP-MS analyses are given in Table 4. Purities of TMGa reported are calculated based on the trace elemental impurities of I and II and their respective residues left back in the thermal cracking flask after complete release of TMGa.

**Table 4. Purity of TMGa by ICP-MS Analysis**

| TMGa from | Elements (concentration in ppm, wt/wt)  | Purity (%) |
|-----------|---|------------|
| I         | Al (0.0467), As (0.0643), B (0.4547), Be (0.0008), Cd (0.0184), Fe (< 1 ppb), Ge (0.00049), Na (0.5533), Pb (0.118), S (0.705), Se (0.003), Si (< 1 ppb), Sn (0.015), Sr (0.106), Te (0.029), Zn (0.3936), Cr (1.829), Ni (0.0134), Co (0.00129), Li (0.00334), Cu (0.147), Ca (< 1ppb) | 99.99950   |
| II        | Al (0.438), As (0.0042), B (0.0530), Be (< 1ppb), Cd (0.15), Fe (0.473), Ge (< 1ppb), Na (1.2), Pb (0.164), S (0.299), Se (< 1ppb), Si (0.359), Sn (0.006), Sr (< 1ppb), Te (0.0677), Zn (0.503), Cr (0.475), Ni (0.848), Co (0.00622), Li (0.0041), Cu (0.27), Ca (< 1ppb)             | 99.99945   |

## 5. Conclusions

A convenient method has been followed to synthesize 1:1 and 2:1 adducts of TMGa with DMAP in good yields. Both adducts are non-pyrophoric, non-hygroscopic and easier to handle and were studied by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and FAB-MS. Trace elemental analyses studies by ICP-MS method suggest that these adducts may be potentially used for the purification of TMGa to electronic grade purity for MOCVD applications.

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