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# A structural study of bis-(trimethylamine)alane, $AlH_3 \cdot 2NMe_3$, by variable temperature X-ray crystallography and DFT calculations

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ABSTRACT

The structure of $AlH_3 \cdot 2NMe_3$ has been investigated by single-crystal X-ray diffraction over the range of 296–173 K. Over this temperature range a phase change is observed from *Cmca* to *Pbcm* where the methyl groups convert from a statistically disordered conformation to adopt a mutually eclipsed conformation at lower temperatures. Measurement of the unit cell dimensions shows a decrease in the lengths of the **a** and **b** axes, and an increase in that of the **c** axis as the temperature is lowered, with inflections apparent between 223 and 233 K in the region of the phase change. Low-temperature DSC measurements reveal the change from *Pbcm* to *Cmca* to occur at 218.3 K, with an enthalpy of 107.7 J mol$^{-1}$. The molecular structure of $AlH_3 \cdot 2NMe_3$ is compared with those of related amine adducts of Group 13 hydrides, either measured experimentally or calculated using DFT methods. $^1H$, $^{13}C$ and $^{27}Al$ NMR spectroscopy has also been utilized to characterize $AlH_3 \cdot 2NMe_3$ and its 1:1 counterpart $AlH_3 \cdot NMe_3$.

## 1. Introduction

The binary hydride of aluminum, $AlH_3$ or alane, is a sterically and electronically unsaturated moiety that reacts readily with a range of Lewis donors, leading to 1:1 and 1:2 adducts which are four- or five-coordinate at the Al centre, respectively [1–3]. A wide range of such adducts has been synthesized and characterized over the past 60 years, with donors including carbenes [4–6], phosphines [6–8], amines [9–12], ethers [13–15] and other O-derived functionalities [16].

Amongst these different types of alane adducts, amine complexes are the most widely studied and reported. The simplest amine adducts; viz. $AlH_3 \cdot NMe_3$ and $AlH_3 \cdot 2NMe_3$, were originally reported in 1942 by Wiberg and Stecher [9–11]. For the 1:2 adduct, Wiberg postulated a trigonal bipyramidal (TBP) structure, a prediction that was confirmed by Heitsch et al. in 1963 through a single-crystal X-ray structure determination at room temperature [17]. Heitsch et al. concluded that the complex indeed adopts a TBP structure, with axial amines and equatorial hydrogen ligands, and crystallizes in an orthorhombic space group *Cmca*, with unit cell parameters $a = 10.10$ Å, $b = 8.84$ Å, and $c = 12.94$ Å. Somewhat surprisingly, these authors also reported a dipole moment for the molecule in solution. The molecular structure was corroborated in the same year by Fraser et al., who measured the gas phase IR spectrum of $AlH_3 \cdot 2NMe_3$, and interpreted it in terms of a molecule with $D_{3h}$ symmetry. These authors also concluded that the molecule undergoes partial dissociation in the gas phase, in an equilibrium between the 1:2 and 1:1 adducts and free $NMe_3$ [18]. A subsequent gas electron diffraction (GED) study by Mastryukov et al. confirmed the $D_{3h}$ molecular structure [19]: this study made allowance for the equilibrium described by Fraser et al., but found no significant amounts of $AlH_3 \cdot NMe_3$ or free $NMe_3$ in the GED pattern. The X-ray crystal structure of $AlH_3 \cdot NMe_3$ was reported by Raston et al., who found the compound to be dimeric in the solid state, as postulated by Wiberg [11]. In the gas phase the molecule is monomeric [20]. Other 1:1 alane complexes associate through unsymmetrical bridging hydrides in the crystalline state include the adducts with THF [16], $NMe_2(CH_2Ph)$, 1-methyltetrahydropyridine [21] and $NMe_2(CH_2)_3Cl$ [22].

The preparation of $AlH_3 \cdot 2NMe_3$ is straightforward, and can be achieved by several routes. The original Wiberg synthesis involved the production of $AlH_3$ in $Et_2O$, followed by displacement of the ether ligand by the more basic $Me_3N$ (Eqs. (1) and (2)) [9,10]. Heitsch et al. used a similar approach, substituting $H_2SO_4$ in place of HCl in the first step (Eqs. (3) and 4) [17]. More recently, Ruff and Hawthorne adopted the direct reaction between $LiAlH_4$ and $Me_3NHCl$ in $Et_2O$, thereby employing the ammonium hydrochloride salt as the source of both acid and amine ligand in a single step to form the 1:1 complex (Eq. (5)) [23]. Excess $NMe_3$ must be condensed onto the amine–alane before sublimation to ensure complete production of the 1:2 complex (Eq. (6)). This route was previously employed by Schaeffer for the synthesis of $BH_3 \cdot NMe_3$ using $LiBH_4$ and $NMe_3 \cdot HCl$ [24]. The procedures for preparing the

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1:1 and 1:2 adducts are almost identical, except that the latter requires addition of an excess of $NMe_3$ prior to sublimation to guard against dissociation to the 1:1 complex.

$$LiAlH_4 + HCl \xrightarrow{Et_2O} AlH_3 \cdot Et_2O + LiCl + H_2 \qquad (1)$$

$$AlH_3 \cdot Et_2O + 2NMe_3 \rightarrow AlH_3 \cdot 2NMe_2 + Et_2O \qquad (2)$$

$$LiAlH_4 + H_2SO_4 \xrightarrow{THF} AlH_3 \cdot THF + LiSO_4 + H_2 \qquad (3)$$

$$AlH_3 \cdot THF + 2NMe_3 \rightarrow AlH_3 \cdot 2NMe_2 + THF \qquad (4)$$

$$LiAlH_4 + NHMe_3Cl \xrightarrow{Et_2O} AlH_3 \cdot NMe_3 + LiCl \qquad (5)$$

$$AlH_3 \cdot NMe_3 + NMe_3 \rightarrow AlH_3 \cdot 2NMe_3 \qquad (6)$$

The 1:1 and 1:2 adducts are white, air-sensitive crystalline materials that sublime readily at ambient temperature, and which as described above exist in equilibrium in the gas phase [18,25,26]. Under thermolysis, they decompose readily into crystalline Al, and $Me_3N$ and $H_2$ gases [9]. The availability of high purity Al in this manner has prompted a large body of research into the use of these adducts in various types of methods of chemical vapour deposition (CVD) to produce Al thin films [27–29].

In the solid state, $AlH_3{\cdot}2NMe_3$ is known to crystallize in at least two phases. In their earlier X-ray diffraction study, Heitsch et al. reported the existence of a phase change at −35 °C [17]. In this paper, we report an improved room temperature crystal structure for $AlH_3{\cdot}2NMe_3$, a determination of the low temperature structure for the first time, and characterization of the phase transition between them by low-temperature DSC. In addition, variable temperature single-crystal X-ray diffraction has been conducted between −100 °C and room temperature in 10 °C increments, permitting us to monitor the temperature dependence of the crystal and molecular structure of $AlH_3{\cdot}2NMe_3$. Finally, the $^{1}H$, $^{13}C$ and $^{27}Al$ NMR data for $AlH_3{\cdot}2NMe_3$ are reported and compared with the corresponding values for the 1:1 adduct $AlH_3{\cdot}NMe_3$.

## 2. Experimental

### 2.1. General considerations

All manipulations were performed using standard Schlenk or drybox techniques in vacuo or under an atmosphere of purified nitrogen or argon ($H_2O$ and $O_2$ < 1 ppm). Solvents were dried and deoxygenated using a Grubbs-type solvent dispensing system, degassed prior to use, and stored under argon. All starting materials were reagent grade from Sigma–Aldrich and were used as received, with the exception of $LiAlH_4$, which was purified by recrystallization from THF. The NMR spectra for $AlH_3{\cdot}NMe_3$ and $AlH_3{\cdot}2NMe_3$ were recorded in toluene-$d_8$. $^{13}C$ spectra for both complexes and the $^{1}H$ spectrum for $AlH_3{\cdot}NMe_3$ were measured using a Varian 300 NMR spectrometer. $^{27}Al$ spectra for both complexes and the $^{1}H$ spectrum for $AlH_3{\cdot}2NMe_3$ were recorded using a Varian 400 spectrometer. $^{13}C$ NMR spectra were referenced to the toluene-$d_8$ singlet at 137.86 ppm and $^{1}H$ spectra were referenced to the H NMR were referenced to the toluene-$d_8$ singlet at 7.09 ppm. $^{27}Al$ NMR were referenced using $Al(NO_3)_3$ in $D_2O$ (1.1 mol/L) as an external standard. DSC measurements were conducted using a TA Instruments DSC Q200 with Perkin-Elmer Volatile Aluminum pans. The purge gas was UHP 5.0 He at 25 mL/min. Data were collected at 0.1 s/point. The method used included a temperature equilibration at −100 °C, isothermal for 1 min, followed by a temperature ramp of 2 °C/min to 400 °C.

### 2.2. Syntheses

#### 2.2.1. $AlH_3{\cdot}2NMe_3$

*2.2.1.1. Method A.* A preliminary qualitative reaction was conducted using a solution of $AlH_3$ prepared as described by Brown and Yoon [30]. THF (50 mL) was added to purified $LiAlH_4$ (1.5 g; 40 mmol), and left to stir overnight. The suspension was cooled in an ice bath whilst conc. $H_2SO_4$ (2.0 g; 20 mmol) was added dropwise. A white precipitate of $Li_2SO_4$ quickly formed and $H_2$ evolution was apparent. The reaction mixture was stirred for 6 h and left to stand overnight, allowing the precipitate to settle. The supernatant solution was then filtered into a Schlenk tube. The concentration of the resulting $AlH_3$ solution was ca. 0.8 M. A 10 mL aliquot of this solution was transferred into an H-tube equipped with a magnetic stirrer flea and a coarse sintered glass frit between the two limbs. The vessel was cooled to −196 °C and partially evacuated, and gaseous $Me_3N$ (9.0 g; 150 mol) was condensed on top of the frozen solution. Upon warming, the solution melted and a white precipitate was observed. The whole procedure was repeated one more time to ensure complete reaction, then the THF solution was transferred via cannula into a separate Schlenk flask and the THF was removed in vacuo, leaving a white powder on the bottom and colourless, irregular shaped crystals that had sublimed on the side of the flask. The remaining white powder in the H-tube was dissolved in toluene and washed through the frit: this solution deposited cubic crystals that decomposed rapidly on exposure to air.

*2.2.1.2. Method B.* $LiAlH_4$ (2.2 g; 58 mmol) and $Me_3NHCl$ (4.5 g; 47 mmol) were introduced into a Schlenk flask, which was then cooled to −78 °C. $Et_2O$ (100 mL) was added, and the contents were stirred and allowed to warm to room temperature. After 1 h, the solvent was then removed in vacuo, leaving a pasty white residue. To guarantee the 2:1 complex, $NMe_3$ gas was condensed into the flask and the contents were allowed to stir for 20 min. The flask was then warmed to 50 °C, and the contents sublimed into a separate flask cooled to −78 °C. A white crystalline powder thus obtained was stored at −37 °C in a glove box.

*Yield*: 3.4 g (98%). $^{1}H$ NMR (toluene-$d_8$): $\delta$ (ppm) = 3.42 (br, 3H, $AlH_3$), 2.13 (s, 18H; $CH_3$). $^{27}Al$ NMR (toluene-$d_8$): $\delta$ (ppm) = 111.49. $^{13}C$ NMR (toluene-$d_8$): $\delta$ (ppm) = 47.39 (N–$CH_3$). The unit cell was measured by single-crystal X-ray diffraction, which confirmed the material as $AlH_3{\cdot}2NMe_3$.

#### 2.2.2. $AlH_3{\cdot}NMe_3$

$AlCl_3$ (3.78 g, 28 mmol) and $LiAlH_4$ (3.69 g, 97 mmol) were introduced into an H-tube whose two limbs were separated by a sintered glass frit. The apparatus was cooled in an ice bath and pentane (100 mL) was added. $NMe_3$ (9 g; 152 mmol) was condensed onto the slurry, which was then allowed to warm to room temperature and stirred overnight. The resulting solution was filtered through the frit and the vessel was stored at −40 °C for 24 h, to afford a white crystalline powder. The pentane solvent was removed in vacuo, leaving a pasty white residue. The flask was then warmed to 50 °C, and the contents sublimed into a collection vessel cooled to −78 °C. The white powder thus obtained was stored at −37 °C in a glove box.

*Yield*: 1.092 g (10.8%). $^{1}H$ NMR; $\delta$ (ppm) = 3.92 (br, 3H, $AlH_3$), 1.89 (s, 9H; $CH_3$). $^{27}Al$ NMR; $\delta$ (ppm) = 139.81. $^{13}C$ NMR; $\delta$ (ppm) = 47.76 ($CH_3$).

### 2.3. X-ray crystal structure determinations

Crystals of $AlH_3{\cdot}2NMe_3$ were grown by sublimation in vacuo at room temperature. A suitable single crystal of dimensions (mm) 0.60 × 0.50 × 0.40 was selected in a glovebox, fixed in a glass capillary without oil and mounted on a Bruker AXS P4/SMART 1000 diffractometer. A hemisphere of data was collected using graphite monochromated Mo-K$\alpha$ radiation ($\lambda$ = 0.71073 Å) and $\omega$- and $\theta$-scans with a scan width of 0.3°. The unit cell parameters were obtained by least-squares refinement of 4579 reflections (low-temperature study at 173 K, LT) and 1780 reflections