

Note

Crystal structure of $\text{Al}(\text{tBu})_3(\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph})$: A molecular "slinky"

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The molecular structure of $\text{Al}(\text{tBu})_3(\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph})$ is determined by the crystal packing of the phenyl rings and the pseudo spherical $\text{Al}(\text{tBu})_3$ units, and may be viewed as a layered structure consisting of double sheets of the phenyl rings and the $\text{Al}(\text{tBu})_3$ units. The Al–N–C–C linkage shows severe disorder as a result of its flexibility. The structure of $\text{Al}(\text{tBu})_3(\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph})$ can be likened to a molecular "slinky," in which the rigid ends are fixed in space by molecular packing forces, leaving the interior link to adopt multiple orientations. Crystal data: orthorhombic, $Cmca$, $a = 13.282(9)$, $b = 25.01(1)$, $c = 13.210(9)$ Å, $V = 4388(10)$ Å³, $Z = 4$, $R = 0.0957$, $R_w = 0.0957$.

KEY WORDS: Molecular "slinky;" molecular structure; crystal packing; aluminum; amine.

Introduction

Recent work in our laboratory has been concerned with the relationship between molecular structure and crystal packing of organometallic compounds of aluminum, gallium, and indium. As part of this study we have investigated the effects on crystal packing in dimeric alkoxide compounds $[(\text{tBu})_2\text{Ga}(\mu\text{-OR})]_2$ of the length of the alkoxide carbon chain.¹ The geometry of the Ga_2O_2 core is found to be essentially independent of the substituents at oxygen; however, the conformation adopted by the alkoxide group may be modified, from that expected, by steric interactions with the gallium *tert*-butyl groups. The crystal packing of $[(\text{tBu})_2\text{Ga}(\mu\text{-OR})]_2$ for substituents with carbon chains of C_5 or lower is only dependent on the packing of the organometallic $(\text{tBu})_2\text{Ga}(\mu\text{-O})_2\text{Ga}(\text{tBu})_2$ core; whereas, for longer carbon chains the amphiphilic intermolecular interactions dominate the packing, and consequently provide for the possibility of liquid crystalline behavior. Thus, in the case of the dimeric gallium alkoxides,

the crystal packing is determined by structure of molecule. However, we have shown that in the presence of strong intermolecular interactions (e.g., $\text{Ph} \cdots \text{Ph}$ π -interactions) severe distortions in the inorganic cores can occur,² and the molecular structure is controlled by the crystal packing. Furthermore, the physical properties of gallium chalcogenide cubane compounds, $[(R)\text{GaE}]_4$ ($E = \text{S}, \text{Se}, \text{Te}$), may be controlled by the crystal packing as well as the organic substituents.³ In each of the examples studied to date we have limited the molecule to a single rigid unit (e.g., a Ga_2O_2 or Ga_4S_4 core). In an effort to understand the molecular consequences of two rigid subunits being joined by a flexible spacer, as is found in our carboxylate alumoxanes,⁴ we have investigated the structure of small molecular models. One such model is the Lewis acid–base complex between $\text{Al}(\text{tBu})_3$ and phenethylamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph}$), in which the $\text{Al}(\text{tBu})_3$ and phenyl moieties are expected to control the crystal packing.

Experimental

Synthesis of $\text{Al}(\text{tBu})_3(\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph})$

To a hexane (50 mL) solution of $\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph}$ (0.75 mL, 5.98 mmol) was added $\text{Al}(\text{tBu})_3$ (1.5 mL,

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5.98 mmol) at -78°C . The solution turned pale yellow immediately. After warming to room temperature the solution was stirred overnight. The volatiles were removed under vacuum to give a white solid (Yield: 1.2 g). Crystals for X-ray diffraction were obtained by crystallization from hexane.

Crystal data

Orthorhombic, 298 K, $M_r = 319.5$, space group Cmca , $a = 13.282(9)$, $b = 25.01(1)$, $c = 13.210(9)$ Å, $V = 4388(10)$ Å³, $Z = 4$, $D_x = 0.937$ g cm⁻³, $\text{Mo-K}\alpha$ radiation, $\lambda = 0.71073$ Å. Standard experimental details are given elsewhere.⁵ Crystals ($0.32 \times 0.38 \times 0.50$ mm) were obtained by crystallization of from hexane. Unit-cell dimensions from reflections with $10^{\circ} < \theta < 30^{\circ}$. Intensity data for 2105 reflections (up to $\theta = 40^{\circ}$), 1091 unique reflections, 532 observed reflections ($F > 5.0\sigma(F)$). The structure was solved by direct methods with least squares refinement. Refinement was performed with anisotropic thermal parameters for all non-hydrogen atoms: shift/error less than 0.001. The elongated thermal ellipsoids for N(1) and C(1), and chemically unrealistic bond lengths and angles suggested the possibility of disorder. Although the difference Fourier maps did not readily reveal two alternative positions for the amines nitrogen [N(1)] and α -carbon [C(1)] displacement of the atoms from the crystallographic mirror plane resulted in a significant decrease (ca. 6%) in the R factor. Despite the successful refinement of the disordered Al–N–C–C chain, large thermal parameters were observed for the *tert*-butyl groups and the *para*-carbon of the phenyl ring. Attempts to refine these as disordered moieties were unsuccessful. Final difference Fourier peaks less than 0.29 eÅ⁻³. $R = 0.0957$, $R_w = 0.0957$ for 117 variables.

Programs used were P3,⁶ and SHELXTL PLUS.⁷ Atomic parameters (with esd's) are given in Table 1 and selected bond lengths and angles are displayed in Table 2.

Results and discussion

The molecular structure of **1** is shown in Fig. 1; selected bond length angles are given in Table 2. The structure consists of a discrete monomeric $\text{Al}(\text{tBu})_3(\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph})$ units. As is commonly observed for four-coordinate Lewis acid–base complexes of alumi-

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å² $\times 10^3$).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq) ^a
Al(1)	5000	6599(2)	4014(3)	96(3)
N(1)	5405(12)	6205(5)	2689(13)	70(9)
C(1)	4692(23)	6221(8)	1807(13)	151(23)
C(2)	5000	5854(6)	991(12)	110(11)
C(3)	5000	5280(8)	1302(14)	92(14)
C(4)	4160(15)	5000(7)	1477(10)	132(10)
C(5)	4198(28)	4481(8)	1796(19)	200(19)
C(6)	5000	4203(20)	1974(39)	268(37)
C(11)	3783(17)	6333(6)	4667(10)	132(8)
C(12)	2846(16)	6486(11)	4109(14)	281(19)
C(13)	3737(19)	5723(6)	4778(17)	301(19)
C(14)	3644(14)	6558(6)	5713(10)	177(11)
C(21)	5000	7380(7)	3648(13)	156(16)
C(22)	5000	7709(6)	4591(13)	263(24)
C(23)	4082(14)	7536(5)	3015(12)	209(12)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

num^{8,9} the geometry around each aluminum is distorted from tetrahedral, with the angles associated with the amine ligand being the most acute. The similarity in aluminum coordination geometries in **1** and the chloride complex in $[\text{PPN}][\text{AlCl}(\text{tBu})_3]$ ¹⁰ is illustrated by comparing the sums of inter-ligand angles associated with the *tert*-butyl ligands: $342(1)^{\circ}$ in **1** and $341.5(3)^{\circ}$ in the $[\text{AlCl}(\text{tBu})_3]^-$ anion. This resemblance is perhaps unsurprising since we have previously observed that the geometry around aluminum is primarily dependent on the steric bulk of substituent ligands,¹¹ and in the case of these compounds, the coordination geometry is dominated by the sterically bulky *tert*-butyl ligands. Despite the severe disorder observed for the amine ligand, see below, the Al(1)–N(1) bond distance [$2.00(1)$ Å] is within the range previously observed for aluminum–nitrogen distances.¹² All other bond lengths

Table 2. Selected bond lengths (Å) and angles ($^{\circ}$).

Al(1)–N(1)	2.08(1)	Al(1)–C(11)	1.94(2)
Al(1)–C(21)	2.01(1)	Al(1)–N(1A)	2.08(1)
Al(1)–C(11A)	1.94(2)	N(1)–C(1)	1.50(2)
C(1)–C(2)	1.47(2)	C(2)–C(3)	1.49(2)
N(1)–Al(1)–C(11)	115.2(6)	N(1)–Al(1)–C(21)	105.0(6)
N(1)–Al(1)–C(11A)	89.8(6)	C(11)–Al(1)–C(21)	116.0(5)
C(11)–Al(1)–N(1A)	89.8(6)	C(11)–Al(1)–C(11A)	112.0(10)
C(21)–Al(1)–N(1A)	105.0(6)	C(21)–Al(1)–C(11A)	116.0(5)
N(1A)–Al(1)–C(11A)	115.2(6)	Al(1)–N(1)–C(1)	118.5(13)
N(1)–C(1)–C(2)	112.1(19)	C(1)–C(2)–C(3)	113.4(14)

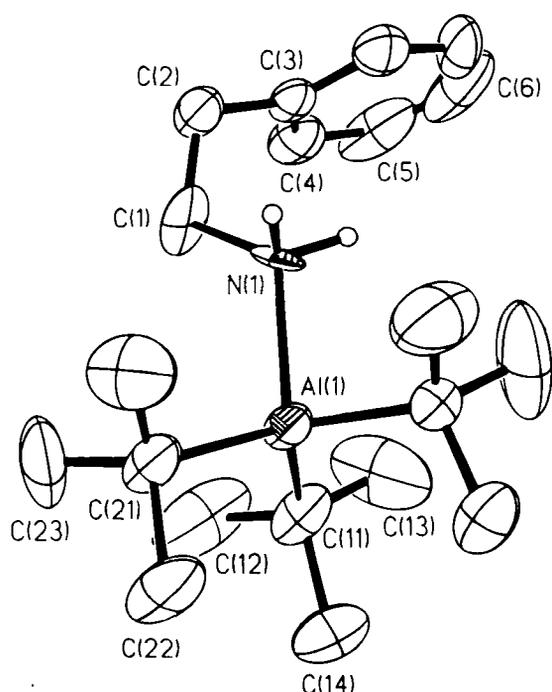


Fig. 1. Molecular structure of $\text{Al}(\text{tBu})_3(\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph})$. Thermal ellipsoids are shown at the 20% level. All hydrogens, except those bonded to N(1), are omitted for clarity.

are within the ranges previously reported for analogous species.¹⁰

The crystal packing arrangement of $\text{Al}(\text{tBu})_3(\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph})$ is interesting (see Fig. 2). Each molecule of $\text{Al}(\text{tBu})_3(\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph})$ is situated such that

the CH_2Ph unit is directly opposite an equivalent unit on the adjacent molecule. Thus, the molecular structure appears to be determined by the crystal packing of the phenyl rings and the pseudo-spherical $\text{Al}(\text{tBu})_3$ units. The crystal lattice may thus be viewed as a layered structure consisting of double sheets of phenyl rings intercalated by the $\text{Al}(\text{tBu})_3$ units. It is the packing of these subunits that define the overall geometry of the molecule and result in the phenyl ring being bent back over the aluminum *tert*-butyl groups in an unfavorable arrangement.

Given the near rigid placement of the $\text{Al}(\text{tBu})_3$ and phenyl molecular subunits in the crystal lattice it is unsurprising that the $\text{Al}(1)\text{--N}(1)\text{--C}(1)\text{--C}(2)$ linkage shows severe disorder (Fig. 3), such that N(1) and C(1) are positioned on opposite sides of the crystallographic mirror plane. Thus, the ligand makes a Z-shape between Al(1) and C(2). Despite this disorder the bond lengths and angles are similar to these observed previously for amines complexed to aluminum.^{10,12}

The structure of $\text{Al}(\text{tBu})_3(\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph})$ can be likened to a molecular "slinky," in which the rigid ends are fixed in space by molecular packing forces, leaving the interior link to adopt multiple orientations. In the present case these are energetically degenerate. However, the presence of substituents on the phenyl ring (i.e., an *ortho* or *meta*-methyl group) would differentiate the two orientations. In theory such species can be thought of as molecular switches with the low energy of activation being controlled by conforma-

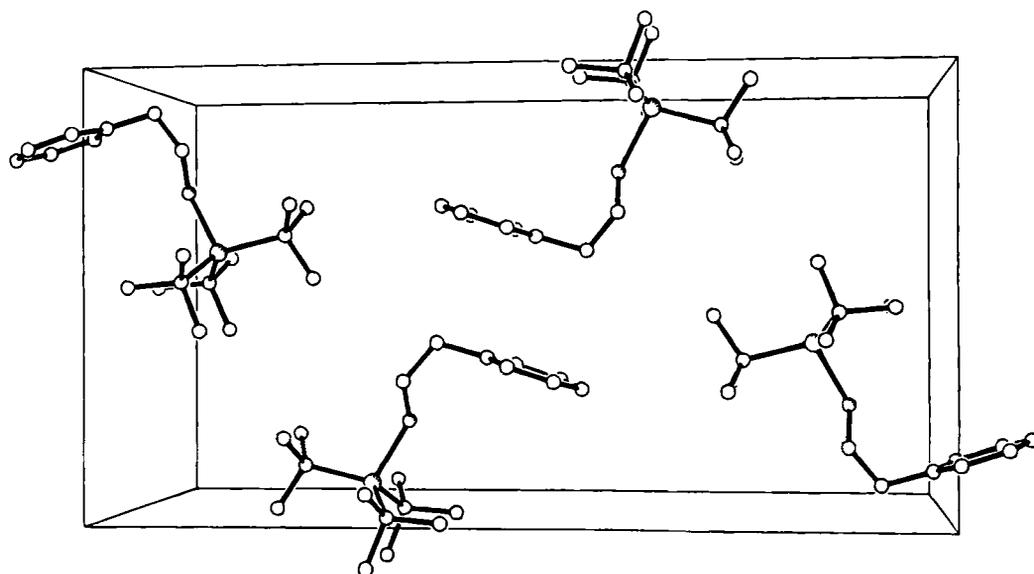


Fig. 2. Crystal packing diagram of $\text{Al}(\text{tBu})_3(\text{NH}_2\text{CH}_2\text{CH}_2\text{Ph})$ showing the stacking of the phenyl rings.

