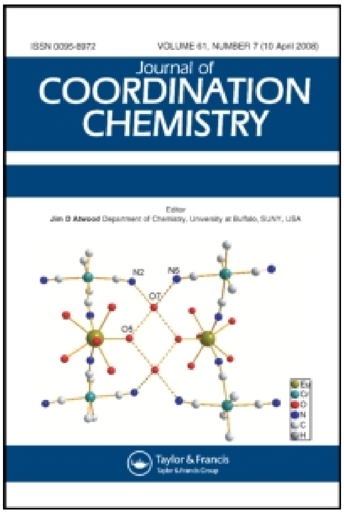

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MULTIPLE INSERTION OF ACETONITRILE INTO A NOVEL ALUMINUM-AMIDE COMPLEX. SYNTHESIS AND MOLECULAR STRUCTURE OF (tren)Al[$(CH_3)CN(CH_3)CN]_3$

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Reaction of trimethylaluminum with tris(2-aminoethyl)amine (tren) in acetonitrile affords the crystalline product (tren)Al[$(CH_3)CN(CH_3CN]_3$. The title compound crystallizes in the rhombohedral space group $R\bar{3}$ (No. 148) with unit cell parameters $a = 11.631(4)$, $c = 26.440(9)$ Å, $V = 3097(2)$ Å^3 and $\rho = 1.34$ g cm^{-3} for Z = 6. Least-squares refinement based on 551 observed reflections with intensities $I > 3\sigma(I)$ in the range $3.50 > 2\theta > 45.0°$ converged at $R = 0.070$, $R_w = 0.088$. Acetonitrile was observed to undergo an interesting oligomerization in this system; each primary amine linkage of tren, $CH_2CH_2NH_2$, was extended by the coupling of two acetonitrile fragments. The core aluminum atom in (tren)Al$(CH_3CN)_6$ resides in an octahedral environment as the terminal nitrogen atoms of tren occupy three coordination sites while the three remaining coordination sites are occupied by terminal nitrogen atoms of the coupled acetonitrile units. The title compound resides about a crystallographic three-fold axis which contains the core aluminum atom and the tertiary nitrogen atom of tren.

Keywords: Aluminum alkyl, amine, X-ray structure

INTRODUCTION

Recent work in this laboratory has concerned the organoaluminum chemistry of macrocyclic[1–2] and multidentate open-chain amines.[4,5] Reactions of organoaluminum species with multidentate open-chain amines containing N–H fragments are characterized by alkane elimination and products possessing Al_2N_2 fragments with extensive Al–N association. In particular, the predominant coordination mode of aluminum, four-coordinate tetrahedral, was readily exceeded in these studies often resulting in five- and six-coordinate aluminum species. To assess the possible effects of solvent on the stabilization of higher coordination numbers of aluminum, acetonitrile was allowed to interact with an organoaluminum/open-chain amine system. Herein, we report the synthesis and molecular structure of (tren)-Al[$(CH_3)CN(CH_3)Cn]_3$, isolated from reaction of trimethylaluminum, tris(2-aminoethyl)amine (tren), and acetonitrile. The title compound contains a six-coordinate aluminum atom in an octahedral environment. In addition, acetonitrile was observed to undergo an interesting insertion as each primary amine linkage of tren,-$NCH_2CH_2NH_2$, was extended by the coupling of two acetonitrile fragments. Figure 1 shows schematic illustrations of the tren amine and the title compound while the X-ray crystal structure of the title compound is shown in Figure 2.

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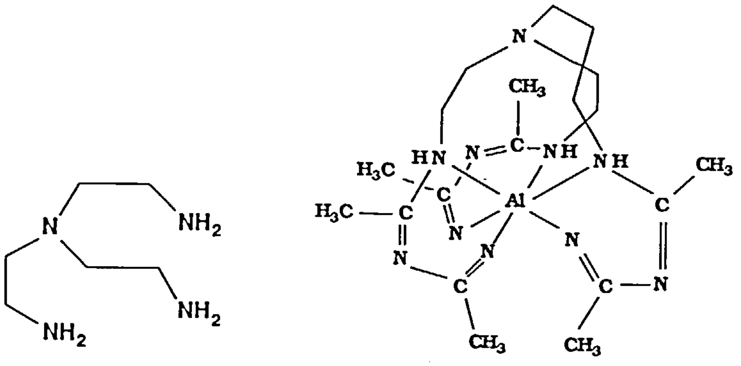

(a) (b)

FIGURE 1 (a): A schematic view of the amine tren; (b): the (tren)Al(CH_3CN)$_6$ complex.

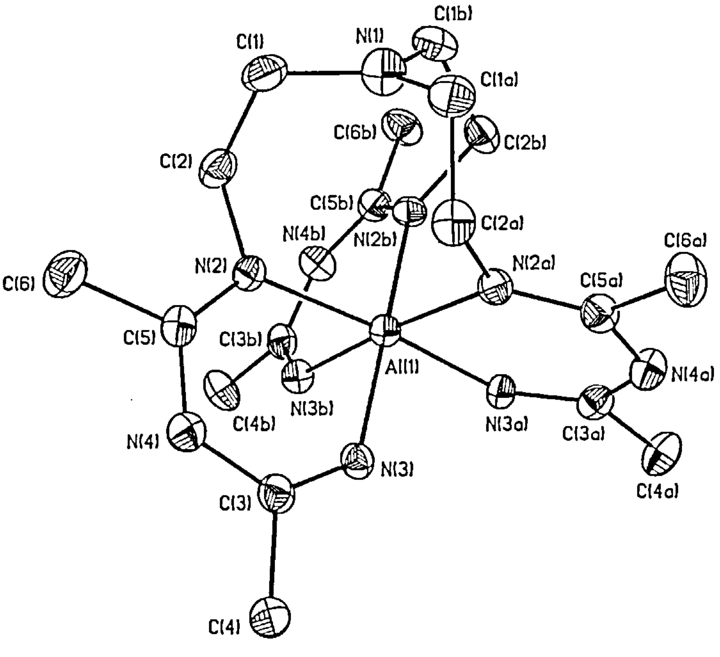

FIGURE 2 A view of the (tren)Al(CH_3CN)$_6$ molecule showing the atom-labelling scheme. Thermal ellipsoids show 35% probability levels. Hydrogen atoms have been omitted for clarity.

EXPERIMENTAL

General

Standard Schlenk technique was employed in conjunction with an inert atmosphere dry box (Vacuum Atmospheres HE-43 Dri-Lab). Tris(2-aminoethyl)amine and trimethylaluminum, purchased from Aldrich Chemical Co. and Alfa Products, respectively, were used as received. Single crystal X-ray data were collected on a Nicolet R3m/V diffractometer. ^1H NMR data were recorded on a Bruker AC-300-P NMR spectrometer.

Synthesis of (tren)Al[(CH$_3$)CN(CH$_3$)CN]$_3$

A 50 cm^3 reaction vessel was charged with tren (6.68 mmol) and trimethylaluminum (6.62 mmol) in 15 cm^3 of acetonitrile. Reaction was immediate and vigorous. The resulting light brown solution was heated overnight in an oil bath (90°C). The system was vented frequently. After cooling to room temperature, the solution was filtered *via cannula* to a 100 cm^3 Schlenk flask where the solution was concentrated. The resulting orange-light brown solution was allowed to stand undisturbed for several hours at room temperature. A multitude of small, colourless, extremely air-sensitive crystals was subsequently obtained in 84% yield. m.p. 208–210°C. ^1H NMR ($CDCl_3$): δ 1.25 [broad singlet, 3H, N*H*], 1.99, 2.01 [singlets, 18H, CH_3CN], 2.66–3.25 [complex multiplet, 12H, $N(CH_2)_2N$].

Structural solution and refinement

A single crystal of (tren)Al[(CH$_3$)CN(CH$_3$)CN]$_3$ was mounted in a thin-walled glass capillary under an inert atmosphere of argon in the dry box. The title compound crystallizes in the rhombohedral space group $R\bar{3}$ with unit cell parameters $a = 11.631(4)$, $c = 26.440(9)$ Å, $V = 3097(2)$ Å^3, and $\rho = 1.34$ g cm^{-3} for $Z = 6$. The structure was solved by direct methods and refined, based on 551 observed reflections, using SHELXTL.[6] Anisotropic thermal parameters were used for non-hydrogen atoms. Hydrogen atoms were located by standard difference Fourier techniques and were included in the structure factor calculation at optimized positions ($d_{C-H} = 0.96$ Å). Least-squares refinement converged at $R = 0.070$, $R_w = 0.088$. Relevant crystallographic data are given in Table I. Final atomic coordinates are given in Table II while selected bond distances and angles are provided in Table III.

RESULTS AND DISCUSSION

The seminal work of Smith *et al.*[7–12] concerned the organoaluminum chemistry of monodentate primary and secondary amines. Recent studies in our laboratory concerning the organoaluminum chemistry of macrocyclic and multidentate open-chain amines have revealed a rich and varied chemistry particularly with regard to coordination environments of the associated aluminum atoms. In an effort to determine the effect of solvent interaction with these systems, acetonitrile was employed in the reaction of trimethylaluminum with the multidentate amine tris(2-aminoethyl)amine, tren. The title compound (tren)Al[(CH$_3$)CN(CH$_3$)CN]$_3$ results

TABLE I

Summary of crystallographic data for $(tren)Al[(CH_3)CN(CH_3)CN]_3$.

Empirical formula	$C_{18}H_{33}N_{10}Al$
Molecular weight	416.59
Colour; habit	colourless; hexagonal plate
Space group	$R\bar{3}$
a Å	11.6314(4)
c, Å	26.4396(9)
Cell volume, Å3	3097(2)
Z	6
ρ, g cm^{-3}	1.34
Diffractometer	Nicolet R3m/V
Radiation	MoKα (λ = 0.71073 Å)
Temperature	21°C
2θ range, deg	3.50 to 45.0
Reflections collected	1017
Reflections observed	551
GOF	2.31
R	0.070
R_w	0.088

TABLE II

Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å $\times 10^3$) for $(tren)Al[(CH_3)CN(CH_3)CN]_3$.

Atom	x/a	y/b	z/c	U(eq)*
Al(1)	6667	3333	554(1)	26(1)
N(1)	6667	3333	1874(3)	47(3)
N(2)	5931(5)	4353(5)	949(2)	29(2)
N(3)	5077(5)	2705(5)	129(2)	28(2)
N(4)	4000(5)	3799(5)	452(2)	37(3)
C(1)	6446(8)	4456(7)	1881(2)	43(3)
C(2)	6743(7)	5189(6)	1373(2)	37(3)
C(3)	4131(6)	2976(6)	130(2)	32(3)
C(4)	3032(6)	2379(6)	−259(2)	43(3)
C(5)	4857(7)	4409(6)	835(2)	33(3)
C(6)	4459(7)	5275(7)	1135(2)	46(4)

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

from a unique reaction involving the cleavage of N–H and Al–CH_3 bonds (resulting in methane elimination) and the multiple insertion of acetonitrile bridging the aluminum centre and the open-chain amine, (*1*).

$$\text{tren} + Al(CH_3)_3 \xrightarrow{6CH_3CN} (\text{tren})Al[CH_3)CN(CH_3)CN]_3 + 3CH_4 \qquad (1)$$

While the mechanism leading to the title is not well understood, the unique cyclization of acetonitrile is due in large measure to the reduction of the carbon–nitrogen triple bond. The resulting diimine bridges are composed of alternating

TABLE III
Selected bond distances (Å) and angles (deg) for (tren)Al[$(CH_3)CN(CH_3)CN]_3$.

Atoms	Distance	Atoms	Distance
Al(1)–N(2)	2.060(6)	Al(1)–N(3)	1.964(5)
N(1)–C(1)	1.452(10)	N(2)–C(2)	1.477(7)
N(2)–C(5)	1.318(10)	N(3)–C(3)	1.287(11)
N(4)–C(3)	1.345(10)	N(4)–C(5)	1.347(7)
C(1)–C(2)	1.534(8)	C(3)–C(4)	1.512(8)
C(5)–C(6)	1.524(12)		

Atoms	Angle	Atoms	Angle
N(2)–Al(1)–N(3)	85.3(2)	N(2)–Al(1)–N(2A)	96.6(2)
N(3)–Al(1)–N(2A)	87.3(2)	N(3)–Al(1)–N(2B)	175.5(2)
N(3)–Al(1)–N(3A)	90.7(2)	N(2A)–Al(1)–N(3A)	85.3(2)
C(1)–N(1)–C(1A)	120.0(3)	Al(1)–N(2)–C(2)	116.8(5)
Al(1)–N(2)–C(5)	126.1(4)	C(2)–N(2)–C(5)	116.8(6)
Al(1)–N(3)–C(3)	132.0(4)	C(3)–N(4)–C(5)	122.2(7)
N(1)–C(1)–C(2)	113.4(7)	N(2)–C(2)–C(1)	114.0(4)
N(3)–C(3)–N(4)	126.2(5)	N(3)–C(3)–C(4)	121.1(6)
N(4)–C(3)–C(4)	112.7(7)	N(2)–C(5)–N(4)	107.3(3)
(N2)–C(5)–C(6)	121.5(5)	N(4)–C(5)–C(6)	110.5(7)

carbon–nitrogen double bonds with N(4), N(3), C(3) and C(5) being coplanar. The mean planar deviation is 0.0075 Å. Coordination of the nitrile to transition metals or other Lewis acids has been shown to promote reactions with amines leading to amidines.[13–16]

Several points are worthy of note regarding structure and bonding in (tren)-Al[$CH_3)CN(CH_3)CN]_3$. The molecule resides about a three-fold axis coincident with the tertiary nitrogen atom of tren, N(1), and the central aluminum atom (Figure 2). Particularly significant is the fact that the central aluminum atom, Al(1), is six-coordinate, residing in an ideal octahedral environment and bonding to the three nitrogen atoms of the amine in addition to three nitrogen atoms from the bridging diimine moieties. The N(3)–Al(1)–N(2b) bond angle is 175.5(2)°. The Al(1)–N(2 bond distance of 2.060(6) Å compares to 1.964(5) Å for Al(1)–N(3). While the tertiary nitrogen atom of tren did not interact with the aluminum atom previous studies have shown that this nitrogen atom can be induced to interact with metal atoms.[17–19] It is reasonable that the intermolecular condensation of trimethylaluminum with the acidic protons of the primary amine nitrogen atoms of tren was a greater driving force than simple adduct formation with the tertiary nitrogen. The elevated reaction temperature was also crucial in obtaining the title compound. Room temperature reactions showed no evidence of aluminum–amide complex being formed. It is interesting that the literature reveals the trimethylaluminum–acetonitrile adduct $(CH_3)_3Al\cdot NCCH_3$ as the only other structurally characterized organo-aluminum-acetonitrile product. Surprisingly, this product was isolated from the reaction of tetraisocyanatogermanium with trimethylaluminum.[20]

An examination of the unit cell of the title compound (Figure 3) reveals six (tren)Al[$CH_3)CN(CH_3)CN]_3$ molecules arranged in a hexameric circle about the *z* axis. The dashed lines indicate weak hydrogen bonding occurring at the lone proton, H(1), on the N(3) atom with the N(4) atom of an adjacent tren–aluminum complex. The interatomic distance N(3)···N(4) is 3.313(7) Å while H(1)···N(4) distance is 2.26 Å. Each hexamer of molecules in a layer possesses $\bar{3}$ symmetry. These layers stack along the *c* axis.

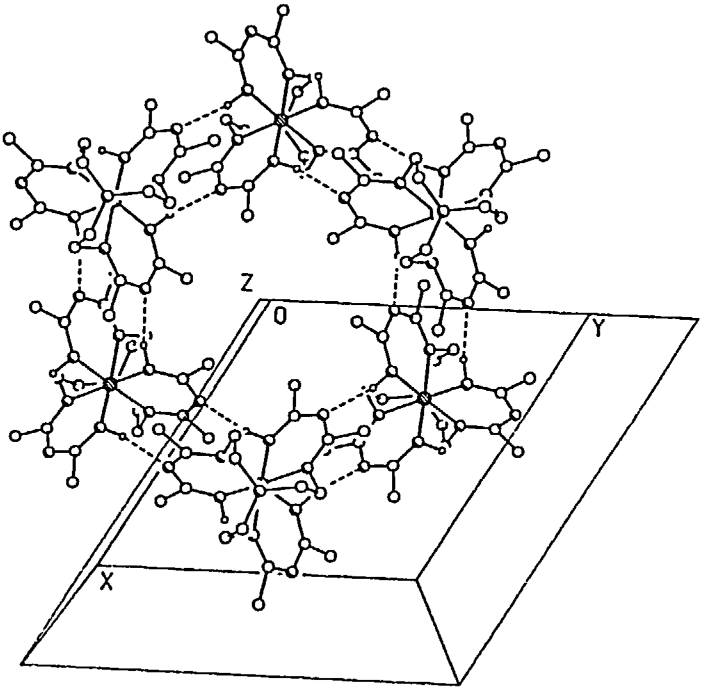

FIGURE 3 A view of the unit cell of (tren)Al$(CH_3CN)_6$ along *c*.

The isolation of this unusual, monomeric, octahedral aluminum complex has stimulated our interest in nitrile/open-chain amine systems. In future contributions we will continue to explore the role of nitrile solvents on the organoaluminum chemistry of multidentate open-chain amines.

ACKNOWLEDGEMENTS

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SUPPLEMENTARY MATERIAL

Summary of data collection and refinement, molecular plots, tables of bond distances and angles, final fractional coordinates, thermal parameters and listings of observed and calculated structure factors are available from G.H.R.

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