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Reaction of trimethylaluminum with a macrocyclic tetradentate tertiary amine. Synthesis and molecular structure of $[Al(CH_3)_3]_4[N\text{-tetramethylcyclam}]$

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Abstract

Reaction of the macrocyclic tetradentate tertiary amine *N*-tetramethylcyclam with trimethylaluminum produced the crystalline product $[Al(CH_3)_3]_4[N$-tetramethylcyclam]. The compound crystallizes in the orthorhombic space group *Pbca* with unit cell parameters *a* 13.928(5), *b* 18.522(6), *c* 1.4538(6) Å, and D_{calc} 0.96 g cm^{-3} for $Z = 4$. Least-squares refinement based on 1432 observed reflections led to a final R factor of 0.034, $R_w = 0.037$. The molecule resides on a crystallographic center of symmetry. The four nitrogen atoms are coplanar. The macrocyclic ligand is greatly distorted as the four $Al(CH_3)_3$ units have essentially turned it "inside-out" by forcing the nitrogen atoms from the interior cavity to the macrocyclic perimeter. The independent Al–N distances of 2.093(3) and 2.102(3) Å are among the longest reported.

Introduction

Reaction of Group IA (1) [1 *] metal salts with aluminum alkyls in aromatic solvents results in the non-stoichiometric organoaluminum based liquid inclusion compounds known as liquid clathrates [2]. These compounds have been studied in our laboratories for some time. Initially, simple salts, such as KN_3, were used. Recently, however, we have greatly extended the range of salts exhibiting liquid clathrate behavior by taking advantage of the metal ion coordinating ability of macrocyclic ligands such as crown ethers. We have subsequently found that crown

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* Reference number with asterisk indicates a note in the list of references.

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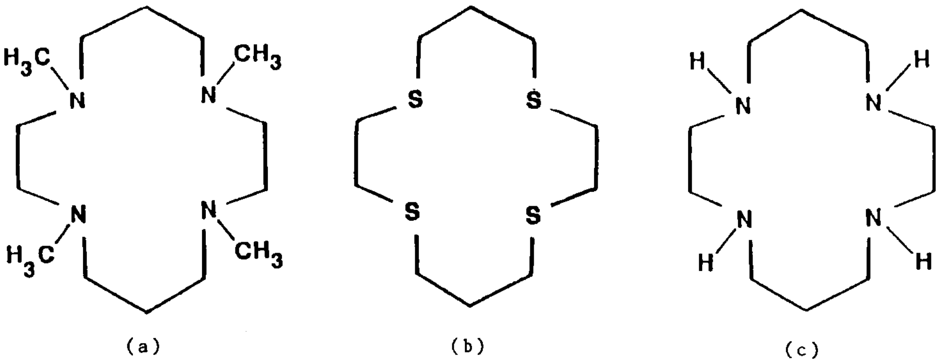


Fig. 1. Nitrogen and sulfur macrocyclic ligands: (a) *N*-tetramethylcyclam; (b) [14]aneS_4; (c) cyclam.

ethers first form stable complexes with aluminum alkyls [3–8]. When exposed to appropriate salts these organoaluminum-macrocyclic complexes dissociate to yield the desired liquid inclusion compounds [5].

In order to extend the range of salts exhibiting liquid clathrate behavior to include salts of transition metal ions, our attention has shifted from oxygen-based crown ethers to macrocycles that have shown transition metal specificity. Currently under investigation are the fourteen-membered sulfur- and nitrogen-based crown ethers shown in Fig. 1. The macrocyclic tetradentate tertiary amine 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, (Fig. 1 (a)) hereafter referred to as *N*-tetramethylcyclam, is of interest due to the fact that it has been shown to form stable complexes with a variety of transition metal ions [9–11]. Herein, we report the synthesis and X-ray crystal structure of $[Al(CH_3)_3]_4$[*N*-tetramethylcyclam] isolated from the reaction of trimethylaluminum with *N*-tetramethylcyclam.

Experimental

General comments

Owing to the extreme air and water sensitivity of both trimethylaluminum and the title compound, the exclusion of oxygen and moisture from the synthesis and subsequent manipulations was essential. To this end, standard Schlenk technique was employed in conjunction with an inert atmosphere glove box (Vacuum Atmospheres HE-43 Dri-Lab). Toluene was distilled from sodium/benzophenone under an atmosphere of nitrogen immediately prior to use. Trimethylaluminum and *N*-tetramethylcyclam, both purchased from Alderich Chemical Co., were used as received.

Synthesis of $[Al(CH_3)_3]_4$[N-tetramethylcyclam]

A glass reaction tube was charged with *N*-tetramethylcyclam (1.95 mmol) and taken into the glove box where toluene (30 ml) was added. Trimethylaluminum (15.6 mmol) was slowly added. A substantial amount of amorphous material formed in the bottom of the tube. The reaction vessel was removed from the glove box and heated in an oil bath for several hours at 80 ° C. A homogeneous solution resulted.

Upon cooling to room temperature, small, colorless, rectangular, air-sensitive crystals were obtained in quantitative yield. ^{1}H NMR data were recorded on a JOEL-FX90 NMR spectrometer. ^{1}H NMR (C_6D_6): the trimethylaluminum resonance consisted of a sharp singlet at $\delta = -0.28$; the resonance for the *N*-methyl groups was centered at $\delta = 1.94$ while the rest of the ligand appeared as a complex multiplet at $\delta = 1.04–2.68$. The complex appears to lose trimethylaluminum on prolonged exposure to vacuum. Crystalline samples of the product were mounted in thin-walled glass capillaries (in the glove box) and subjected to X-ray diffraction analysis.

Structural solution and refinement

Final lattice parameters as determined from the least-squares refinement of $(\sin \Theta/\lambda)^2$ values for 25 reflections ($2\Theta \geq 44°$) accurately centered on an Enraf–Nonius CAD-4 diffractometer are given in Table 1. Data were collected by the $\Theta - 2\Theta$ scan technique as described previously [12]. Intensities were corrected for Lorentz, polarization, and absorption effects. Calculations were carried out using the SHELX system of computer programs [13]. Neutral atom scattering factors for Al were taken from Cromer and Waber [14], and those stored within the SHELX program were used for other atoms. The scattering for all atoms was corrected for the real and imaginary components of anomalous dispersion using the table of Cromer and Liberman [15].

Structure solution was accomplished by means of the direct methods program MULTAN [16], which afforded the location of the Al atoms. Difference Fourier maps phased on these atoms readily revealed the positions of the remaining non-hydrogen atoms. Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms, located from difference maps, were included in the

Table 1

Summary of the crystallographic data for $[Al(CH_3)_3]_4$[*N*-tetramethylcyclam]

Empirical formula	$C_{26}H_{68}N_4Al_4$
Color; habit	Colorless prisms
Size	0.30×0.20×0.30 mm
Space group	Orthorhombic, *Pbca*
Unit cell dimensions	*a* 13.928(5) Å
	b 18.522(6) Å
	c 14.538(6) Å
Volume	3850 Å^3
Molecules/cell	4
Molecular weight	544.18 g/mol
Density (calc.)	0.96 g/cm^3
Diffractometer	Enraf–Nonius CAD 4
Radiation	Mo-K_α (λ 0.71073 Å)
Temperature	26 ° C
2θ-range	2.0 to 44.0 °
Reflections collected	2634
Reflections observed	1452
GOF	0.50
R	0.034
R_w	0.037

Table 2

Final fractional atomic coordinates and isotropic thermal parameters for $[Al(CH_3)_3]_4[$*N*-tetramethylcyclam]

Atom	x/a	y/b	z/c	U_{eq}
Al(1)	0.85102(8)	0.51098(6)	−0.28280(8)	0.043
Al(2)	0.98664(9)	0.76060(6)	−0.07810(9)	0.052
N(1)	0.8330(2)	0.5329(1)	−0.1426(2)	0.034
N(2)	0.9664(2)	0.6715(1)	0.0094(2)	0.037
C(1)	0.9023(3)	0.5907(2)	−0.1168(3)	0.035
C(2)	0.8871(3)	0.6225(2)	−0.0212(3)	0.038
C(3)	1.0604(3)	0.6328(2)	0.0197(3)	0.039
C(4)	0.9378(3)	0.4297(2)	−0.0869(3)	0.047
C(5)	0.8415(3)	0.4669(2)	−0.0834(3)	0.039
C(6)	0.7320(3)	0.5600(3)	−0.1325(3)	0.050
C(7)	0.9349(4)	0.7020(2)	0.0999(3)	0.053
C(8)	0.9888(3)	0.4972(3)	−0.3038(3)	0.067
C(9)	0.7692(4)	0.4262(3)	−0.3028(4)	0.077
C(10)	0.8057(5)	0.5992(4)	−0.3439(4)	0.093
C(11)	1.0633(5)	0.8268(3)	−0.0026(4)	0.086
C(12)	1.0595(4)	0.7254(3)	−0.1848(4)	0.073
C(13)	0.8548(4)	0.7917(3)	−0.1041(4)	0.085

refinement using fixed thermal parameters. Refinement converged at $R = 0.034$ and $R_w = 0.037$. Final fractional coordinates are given in Table 2.

Results and discussion

The reaction of AlR_3 with alkali metal or tetraalkylammonium salts, MX, resulting in 1 : 1 (eq. 1) and 1 : 2 (eq. 2) compounds has been previously reported [17].

$$MX + AlR_3 \rightarrow M[AlR_3X] \qquad (1)$$

$$MX + 2\ AlR_3 \rightarrow M[Al_2R_6X] \qquad (2)$$

When prepared in the presence of aromatic solvents the 1 : 2 complexes (eq. 2) result in the liquid inclusion compounds known as liquid clathrates [2]. As the range of MX compounds was extended, it was observed that many MX moieties did not react according to eq. 2. The failure to isolate the desired compound was ascribed chiefly to two factors: the MX lattice energy and the insolubility of certain MX species. In an attempt to overcome this problem crown ethers were employed. It was soon discovered that in the absence of MX, crown ethers (CE) formed stable complexes with AlR_3 of the general formula $[AlR_3]_n[CE]$ (eq. 3). Several such organoaluminum-crown ether complexes have been reported [3–8]. If, however, an MX moiety is allowed to react with the $[AlR_3]_n[CE]$ complex, dissociation readily occurs yielding the desired compound (eq. 4). Thus, we have found that $[AlR_3]_n[CE]$ complexes often behave as precursors to liquid clathrates by essentially serving as a means of transport of AlR_3 to X^- [5].

$$n\ AlR_3 + CE \rightarrow [AlR_3]_n[CE] \qquad (3)$$

$$[AlR_3]_n[CE] + MX \rightarrow [CE \cdot M][Al_2R_6X] \qquad (4)$$

The preparation of liquid clathrates utilizing transition metal ions as the metallic species in the MX moiety (instead of alkali metal ions) represents an important extension of this work. Macrocyclic ligands with sulfur and nitrogen as donor species are well documented in the literature as being good complexing agents for transition metal ions. Perhaps the best known sulfur and nitrogen crown ethers are the fourteen-membered macrocycles shown in Fig. 1. Both the sulfur-based crown ether [14]aneS_4 [7] (Fig. 1 (b)) and the nitrogen-based crown ether cyclam [8] (Fig. 1 (c)) have been examined with respect to eq. 3.

The importance of the macrocyclic tetradentate tertiary amine *N*-tetramethylcyclam to this work is illustrated by the fact that it readily forms complexes with such transition metal ions as Ni^{II}, Cu^{II}, and Zn^{II} [9] as well as with Cd^{II}, Hg^{II} [10], and Ru^{IV} [11]. The macrocycle was examined with respect to eq. 3, $[Al(CH_3)_3]_4$[*N*-tetramethylcyclam] was the only product isolated.

The structure of $[Al(CH_3)_3]_4$[*N*-tetramethylcyclam] is shown in Fig. 2. Bond distances and angles are given in Table 3. The molecule resides on a crystallographic center of symmetry. The four nitrogen atoms are coplanar. It is somewhat surprising that Al(1) and Al(2) are both located on the same side of the nitrogen plane at displacements of 1.590 and 1.326 Å, respectively, while the tertiary methyl carbon atoms, C(6) and C(7), lie on the opposite side of the plane at displacements of 0.995 and 1.176 Å, respectively. The tertiary nitrogen atoms impart sufficient rigidity so as to force a rather weak Al–N interaction. As can be seen from Table 4, the independent Al–N bond distances of 2.093(3) and 2.102(3) Å for Al(1)–N(1) and Al(2)–N(2), respectively, are among the longest reported.

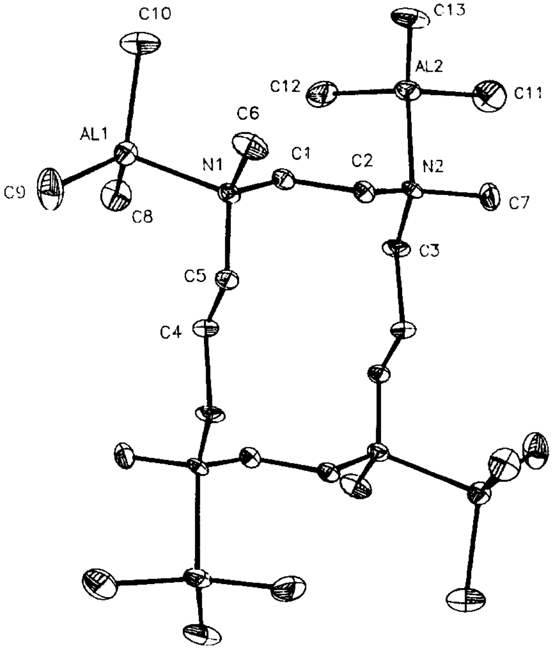


Fig. 2. Structure of $[Al(CH_3)_3]_4$[*N*-tetramethylcyclam].

Table 3

Selected bond distances (Å) and angles (deg) for $[Al(CH_3)_3]_4$[*N*-tetramethylcyclam]

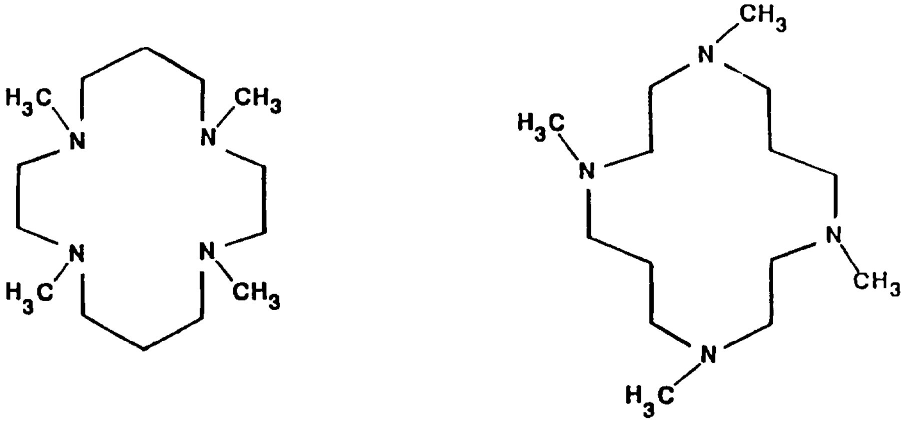
Al(1)-N(1)	2.093(3)	Al(2)-N(2)	2.102(3)
N(1)-C(6)	1.501(5)	N(2)-C(7)	1.498(5)
Al(1)-C(10)	1.964(6)	Al(2)-C(13)	1.962(6)
Al(1)-C(9)	1.962(5)	Al(2)-C(11)	1.962(6)
Al(1)-C(8)	1.960(5)	Al(2)-C(12)	1.966(6)
N(1)-C(1)	1.489(4)	N(2)-C(2)	1.497(4)
N(1)-C(5)	1.500(4)	N(2)-C(3)	1.500(5)
C(1)-C(2)	1.525(5)	C(4)-C(5)	1.509(6)
C(3)-C(4)′	1.516(6)		
Al(1)-N(1)-C(1)	107.9(2)	Al(2)-N(2)-C(2)	113.3(2)
Al(1)-N(1)-C(5)	113.0(2)	Al(2)-N(2)-C(3)	108.6(2)
Al(1)-N(1)-C(6)	105.8(2)	Al(2)-N(2)-C(7)	106.0(2)
N(1)-C(1)-C(2)	114.7(3)	N(2)-C(2)-C(1)	113.7(3)
N(1)-C(5)-C(4)	115.0(3)	N(2)-C(3)-C(4)′	116.3(3)
C(1)-N(1)-C(6)	110.0(3)	C(2)-N(2)-C(7)	105.8(3)
C(1)-N(1)-C(5)	113.0(3)	C(2)-N(2)-C(3)	112.6(3)
N(1)-Al(1)-C(8)	107.1(2)	N(2)-Al(2)-C(11)	103.0(2)
N(1)-Al(1)-C(9)	103.3(2)	N(2)-Al(2)-C(12)	106.6(2)
N(1)-Al(1)-C(10)	103.9(2)	N(2)-Al(2)-C(13)	102.8(2)

Another notable feature concerning the title compound is the great flexibility displayed by the macrocycle. As shown in Fig. 2, *N*-tetramethylcyclam has essentially been turned "inside out" as the four nitrogen atoms have been forced from the customary *endo* geometry by the four $Al(CH_3)_3$ units. The macrocycle has, in effect, assumed an *exo*-geometry with the nitrogen atoms occupying positions around the perimeter of the macrocyclic skeleton. The *exo*- and *endo*-conformations of *N*-tetramethylcyclam are illustrated in Fig. 3. To the best of our knowledge, this is the first report of *N*-tetramethylcyclam assuming such a conformation. It is not, however, the first fourteen-membered macrocyclic ligand to exhibit an ability to achieve this

Table 4

Comparison of Al–N bond distances

Compound	Al–N (Å)	Ref.
$Cl_2\overline{AlN(C_2H_5)C_2H_4N}(CH_3)_2$	1.770(2), 1.963(2)	21
$LiAl[N{=}C(C_4H_9)_2]_4$	1.78, 1.87	22
$Al[N\{Si(CH_3)_3\}_2]_3$	1.78(2)	23
$Al_4Cl_4\{N(CH_3)_2\}_4\{N(CH_3)\}_2$	1.79, 1.90, 1.94	24
$[ClAlNC_3H_7]_6$	1.898(3), 1.914(3), 1.955(3)	25
$\{(CH_3)_2Al[N(CH_3){=}C(CH_3)]_2\}_2$	1.923(1), 1.928(1)	26
$[(CH_3)_2AlN{=}C(CH_3)_2]_2$	1.925(2), 1.930(2)	27
$[(CH_3)_2AlN(CH_3)H]_3$	1.940(5) ave.	28
$K[Al_2(CH_3)_6SCN]$	1.951(5)	29
$[(CH_3)_2AlN(CH_3)_2]_2$	1.958(5) ave.	28
$(CH_3)_5Al_2[N(C_6H_5)_2]$	2.005(3)	30
$CH_3CNAl(CH_3)_3$	2.02(1)	31
$[Al(CH_3)]_2[C_{10}H_{20}N_4][Al(CH_3)_3]_2$	1.959(4), 1.886(4) 2.042(4)	8
$[Al(CH_3)_3]_4$[*N*-tetramethylcyclam]	2.093(3), 2.102(3)	This study



(a) (b)

Fig. 3. *Endo-* (a) and *exo-* (b) conformations of *N*-tetramethylcyclam.

geometry. The sulfur macrocycle [14]aneS_4 (Fig. 1 (b)) has been shown to assume the *exo*-geometry both as the uncomplexed ligand [18] and in organometallic complexes [7,19,20].

The ability of the macrocyclic tetradentate tertiary amine *N*-tetramethylcyclam to form complexes with various transition metal ions coupled with its capacity to form stable complexes with aluminum alkyls is a strong indication that liquid clathrates derived from transition metals are quite feasible. Studies are currently aimed at this goal.

Supplementary Material Available. Tables of bond distances and angles, thermal parameters, and observed and calculated structure factors are available from the authors.

Acknowledgment

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1 The periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated. Groups IA and IIA thus become groups 1 and 2. The *d*-transition elements comprise groups 3 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)
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