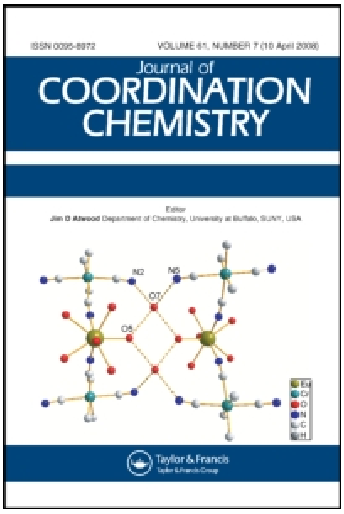

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS AND MOLECULAR STRUCTURE OF $[Al(CH_3)]_2[15]aneN_4[A](CH_3)_3]_2$: AN ALUMINUM-NITROGEN MACROCYCLIC CAGE

Gregory H. Robinson[a]; E. Suzanne Appel[a]; Samuel A. Sangokoya[a]; Hongming Zhang[b]; Jerry L. Atwood[b]
[a] Department of Chemistry, Clemson University, Clemson, South Carolina, U.S.A. [b] Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama, U.S.A.

To cite this Article Robinson, Gregory H. , Appel, E. Suzanne , Sangokoya, Samuel A. , Zhang, Hongming and Atwood, Jerry L.(1988) 'SYNTHESIS AND MOLECULAR STRUCTURE OF $[Al(CH_3)]_2[15]aneN_4[A](CH_3)_3]_2$: AN ALUMINUM-NITROGEN MACROCYCLIC CAGE', Journal of Coordination Chemistry, 17: 4, 373 — 379

To link to this Article: DOI: 10.1080/00958978808073931

URL: http://dx.doi.org/10.1080/00958978808073931

J. Coord. Chem. 1988, Vol. 17. pp. 373–379
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SYNTHESIS AND MOLECULAR STRUCTURE OF $[Al(CH_3)]_2[15]aneN_4[Al(CH_3)_3]_2$: AN ALUMINUM–NITROGEN MACROCYCLIC CAGE

GREGORY H. ROBINSON*, E. SUZANNE APPEL,
SAMUEL A. SANGOKOYA

Department of Chemistry, Clemson University, Clemson, South Carolina 29634-1905 U.S.A.

HONGMING ZHANG and JERRY L. ATWOOD

Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35487 U.S.A.

(Received September 21, 1987; in final form November 16, 1987)

The organoaluminum complex $[Al(CH_3)]_2[15]aneN_4[Al(CH_3)_3]_2$ was prepared by reaction of an excess of trimethylaluminum with the macrocyclic tetradentate secondary amine $[15]aneN_4$ in toluene. Isolated as large, colourless, extremely air-sensitive, prismatic crystals, $[Al(CH_3)]_2[15]aneN_4[Al(CH_3)_3]_2$ was characterized by single crystal X-ray diffraction: the title compound crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters $a = 10.826(2)$Å, $b = 18.221(5)$ Å, $c = 13.825(4)$Å, $\beta = 102.23(2)°$, $V = 2665.3$Å^3 and $D_c = 1.09\,\mathrm{g\,cm^{-3}}$ for $Z = 4$. Least-squares refinement based on 2064 observed reflections converged at $R = 0.056$, $R_w = 0.065$. The distortion displayed by the macrocycle is quite extensive. A planar four-membered Al_2N_2 ring occupies the central cavity of the macrocycle. The mean Al–N distance in the Al_2N_2 fragment is 1.958(5)Å while the mean Al–N–Al angle is 90.6(2)°. The Al $\cdots$ Al contact is 2.785(3)Å.

Keywords: Aluminum alkyl, macrocycle, X-ray, structure, synthesis

INTRODUCTION

Although the first nitrogen-based macrocyclic ligand[1] was reported some thirty years prior to Pedersen's fortuitous discovery of oxygen-based crown ethers,[2,3] the development of the chemistry of nitrogen macrocycles has not paralleled that of their oxygen analogues. Particularly noteworthy is the scarcity of data concerning the structural organometallic chemistry of nitrogen macrocycles. Nonetheless, the importance of nitrogen macrocycles is illustrated by their ability to form stable complexes with an ensemble of transition metal ions.[4–14] The majority of fundamental studies on nitrogen macrocycles has concerned tetradentate macrocyclic amines such as $[12]aneN_4$, $[14]aneN_4$, and $(CH_3)_4[14]aneN_4$. Quite surprisingly, few X-ray structural reports have involved the larger $[15]aneN_4$ macrocycle[15] (Figure 1).

Interest in macrocyclic ligands in this laboratory stems from the fact that they have been shown to react with aluminum alkyls resulting in organoaluminum–macrocyclic complexes. We have previously investigated the reaction of oxygen-based crown ethers with aluminum alkyls.[16–18] These substances were found to be precursors to non-stoichiometric organoaluminum inclusion compounds.[19] Currently, we are interested in the reaction of organoaluminum groups with macrocyclic ligands having sulfur or nitrogen as the donor species (instead of oxygen). We have reported

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* Author for correspondence.

organoaluminum complexes with the sulfur crown ethers [14]aneS_4[20] and [12]aneS_4[21] and with the nitrogen macrocycles $(CH_3)_4$[14]aneN_4[22] and [14]aneN_4.[23] Herein, we wish to report the synthesis and structure of $[Al(CH_3)]_2$[15]ane-$N_4$$[Al(CH_3)_3]_2$. The impetus for this study is two-fold. Since [15]aneN_4 is the largest nitrogen macrocycle of interest to this work, an evaluation of the effects of macrocyclic ring size in this organoaluminum chemistry would be quite valuable. In addition, there is a paucity of structural data concerning [15]aneN_4. Indeed, this report represents the first X-ray structural investigation into the organometallic chemistry of [15]aneN_4.

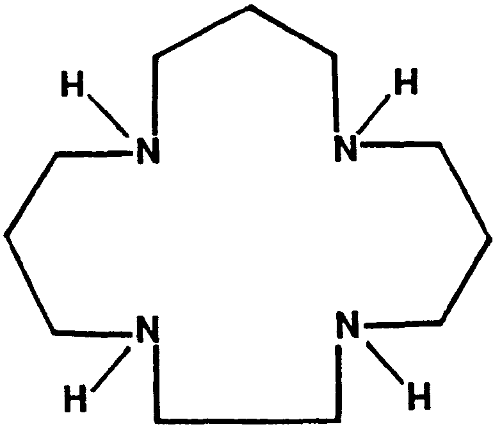

FIGURE 1 [15]aneN_4.

EXPERIMENTAL

General

Standard Schlenk technique[24] was employed in conjunction with an inert atmosphere dry box (Vacuum Atmospheres HE-43 Dri-Lab). Toluene was distilled from sodium/benzophenone under an atmosphere of N_2 immediately prior to use. The nitrogen macrocycle [15]aneN_4 and trimethylaluminum, both purchased from Aldrich Chemical Co., were used as received. Single crystal X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer. ^1H NMR data were recorded on a JOEL-FX90 NMR spectrometer.

Syntheses of $[Al(CH_3)]_2$*[15]ane*$N_4$$[Al(CH_3)_3]_2$

A reaction vessel was charged with [15]aneN_4 (1.95 mmol) and taken inside the dry box where toluene (25 cm^3) and $Al(CH_3)_3$ (15.6 mmol) were added *via* syringe. Reaction was immediate and exothermic. A substantial amount of amorphous fibrous material was initially formed in the reaction vessel. The reaction vessel was removed from the dry box and heated in an oil bath (24 hr at 120°C). A homogeneous solution resulted. Upon cooling to room temperature a multitude of large, colourless, extremely air-sensitive, prismatic crystals were obtained in quantitative yield (based on [15]aneN$_4$). ^{1}H NMR (C_6D_6): δ -0.439 (s, 9H, Al(CH$_3$)$_3$), -0.393 (s, 9 H, Al(CH$_3$)$_3$, -0.377 (s, 3 H, Al(CH$_3$)), -0.311 (s, 3 H, Al(CH$_3$)); 1.76–3.0 (m, 22 H, [15]aneN$_4$).

Structural solution and refinement

Single crystals of the title compound were sealed under an inert atmosphere of nitrogen in thin-walled glass capillaries. Data were collected by the θ–2θ scan technique as described previously.[25] Calculations were carried out using the SHELX system of computer programs.[26] Neutral atom scattering factors for Al were taken from Cromer and Waber,[27] 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 tables of Cromer and Liberman.[28] Final lattice parameters as determined from the least-squares refinement of $(\sin\theta/\lambda)^2$ values for 25 reflections ($2\theta \geq 40°$) accurately centered on an Enraf-Nonius CAD-4 diffractometer are given in Table I. Intensities were corrected for Lorentz, polarization, and absorption effects.

TABLE I
Summary of the crystallographic data for [Al(CH$_3$)]$_2$[15]aneN$_4$[Al(CH$_3$)$_3$]$_2$.

Empirical formula	$C_{19}H_{46}Al_4N_4$
Molecular weight	437.92
Colour; habit	Colourless prisms
Size	0.20 mm × 0.25mm × 0.20 mm
Space group	Monoclinic, $P2_1/n$
a, Å	10.826(2)
b, Å	18.221(5)
c, Å	13.825(4)
β, deg	102.23(2)
Cell volume, Å^3	2665.30
Z	4
D_c, g cm^{-3}	1.09
Diffractometer	Enraf-Nonius CAD-4
Radiation	MoK_α (λ = 0.71073Å)
Temperature	26°C
2θ Range	2.0 to 40.0°
Reflections collected	2753
Reflections observed	2064
GOF	0.67
R	0.056
R_w	0.065

Structure solution was accomplished by means of the direct methods program MULTAN,[29] which afforded 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 refinement using fixed thermal parameters. Refinement converged at $R = 0.056$ and $R_w = 0.065$.

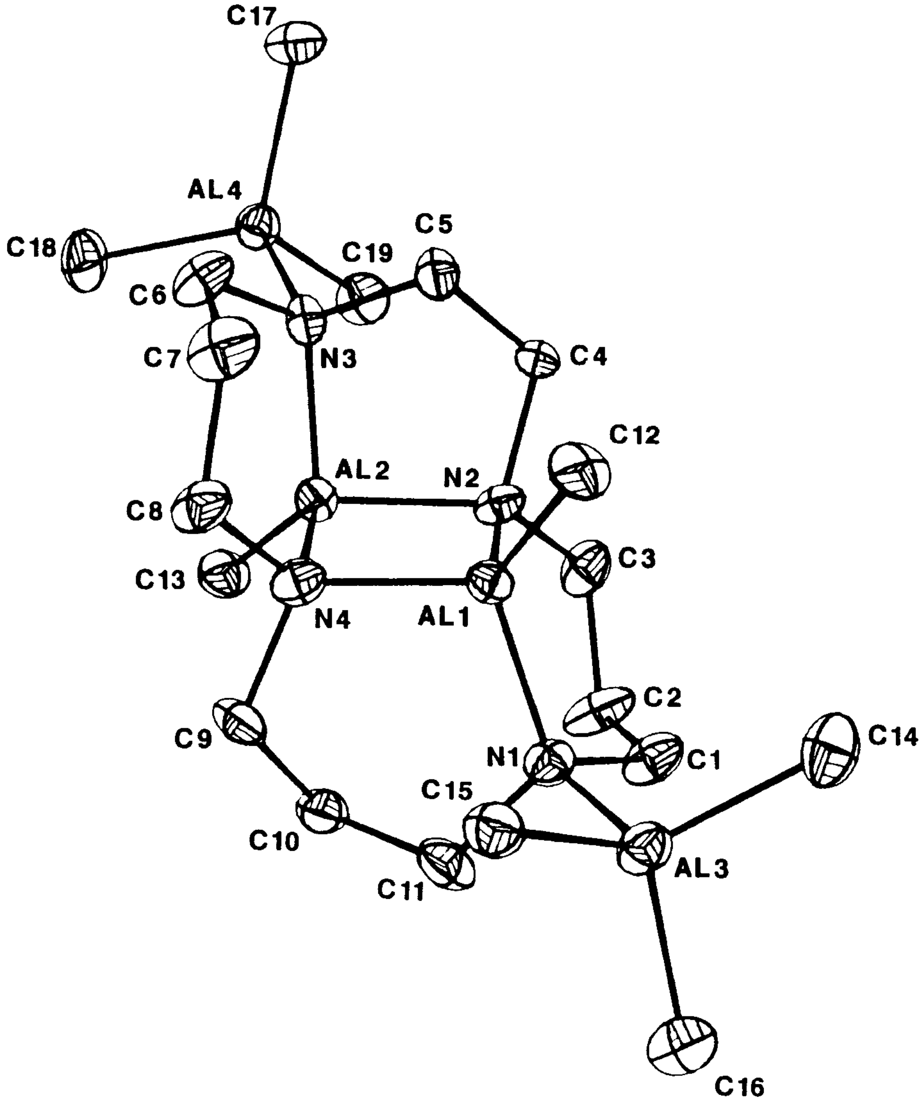

FIGURE 2 Structure of $[Al(CH_3)]_2[15]aneN_4[Al(CH_3)_3]_2$.

RESULTS AND DISCUSSION

The origin of the liquid clathrate effect[19] may be traced to the reaction of AlR_3 with MX salts (M = alkali-metal ion or tetraalkylammonium ion; X = halide or pseudohalide ion).[30] Many MX species, however, did not react in a facile manner with AlR_3 as expected. The metal ion coordinating ability of oxygen-based crown ethers (CE) was thus employed as a means to facilitate reaction. Reaction of MX with CE yields [M·CE]X complexes. Subsequent reaction of AlR_3 with [M·CE]X produces the desired $[M{\cdot}CE][Al_2R_6X]$ compounds. Alternatively, the inclusion compounds may be prepared by reaction of AlR_3 with CE yielding $[AlR_3]_n[CE]$ complexes (*1*). These organoaluminum macrocyclic complexes are then allowed to react with MX to produce the inclusion compound (*2*). In effect, the organoaluminum macrocyclic complexes, $[AlR_3]_n[CE]$, often function as precursors to liquid clathrates by serving as a means of transport of AlR_3 to X^-.[31] Crown ethers thus afforded a vast extension of MX species exhibiting liquid clathrate behavior.

$$n\ AlR_3 + CE \rightarrow [AlR_3]_n[CE] \qquad (1)$$

$$[AlR_3]_n[CE] + MX \rightarrow [M{\cdot}CE][Al_2R_6X] \qquad (2)$$

The examination of macrocyclic ligands capable of forming complexes with transition metal ions represents an important extension of this work. To this end, nitrogen-based macrocyclic ligands are of interest as they have been shown to form stable complexes with a plethora of transition metal ions. The macrocyclic tetradentate secondary amine $[15]aneN_4$ was examined with regard to (*1*); $[Al(CH_3)]_2$-$[15]aneN_4[Al(CH_3)_3]_2$ was the only product isolated.

TABLE II
Final fractional atomic coordinates for $[Al(CH_3)]_2[15]aneN_4[Al(CH_3)_3]_2$.

Atom	*x/a*	*y/b*	*z/c*
Al(1)	0.2535(2)	0.1047(1)	0.1091(1)
Al(2)	0.2412(2)	0.1546(1)	0.2972(1)
Al(3)	0.2829(2)	0.1463(1)	−0.1154(2)
Al(4)	0.2455(2)	0.0684(1)	0.5048(2)
N(1)	0.3238(5)	0.1717(3)	0.0315(4)
N(2)	0.3687(5)	0.1051(3)	0.2404(4)
N(3)	0.1934(5)	0.0677(3)	0.3550(4)
N(4)	0.1286(5)	0.1569(3)	0.1660(4)
C(1)	0.4651(7)	0.1692(5)	0.0650(6)
C(2)	0.5147(8)	0.1903(5)	0.1716(6)
C(3)	0.4999(6)	0.1337(5)	0.2452(6)
C(4)	0.3828(7)	0.0317(4)	0.2932(5)
C(5)	0.2606(8)	0.0074(4)	0.3152(6)
C(6)	0.0516(7)	0.0554(5)	0.3283(6)
C(7)	−0.0047(8)	0.0553(5)	0.2184(7)
C(8)	0.0000(7)	0.1262(5)	0.1637(6)
C(9)	0.1055(8)	0.2336(4)	0.1265(6)
C(10)	0.2241(8)	0.2744(4)	0.1167(6)
C(11)	0.2793(8)	0.2504(4)	0.0322(6)
C(12)	0.210(1)	0.0079(5)	0.0527(7)
C(13)	0.2644(9)	0.2449(5)	0.3706(7)
C(14)	0.370(1)	0.0555(6)	−0.1390(7)
C(15)	0.0964(9)	0.1416(5)	−0.1448(7)
C(16)	0.3521(9)	0.2279(6)	−0.1812(7)
C(17)	0.2302(9)	−0.0341(5)	0.5475(7)
C(18)	0.130(1)	0.1357(6)	0.5521(7)
C(19)	0.4237(7)	0.1026(5)	0.5361(6)

The X-ray crystal structure of $[Al(CH_3)]_2[15]aneN_4[Al(CH_3)_3]_2$ is shown in Figure 2. Final fractional atomic coordinates are given in Table II while selected bond distances and angles are given in Table III. The organoaluminum macrocyclic compound essentially consists of "a ring inside a ring". Indeed, the structure of the title compound may be considered as an aluminum–nitrogen macrocyclic cage. Although not overtly isolated, it is evident that methane was released during the course of the reaction. The release of alkane from reaction of AlR_3 with simple primary amines and the subsequent formation of Al_2N_2 cage fragments has been previously reported by Smith.[32]

TABLE III
Selected bond distances (Å) and angles (deg) for $[Al(CH_3)]_2[15]aneN_4[Al(CH_3)_3]_2$.

Atoms	Distance	Atoms	Distance
Al(1)–N(1)	1.888(5)	Al(1)–N(2)	1.973(5)
Al(1)–N(4)	1.950(6)	Al(1)–C(12)	1.945(8)
Al(2)–N(2)	1.947(5)	Al(2)–N(3)	1.894(6)
Al(2)–N(4)	1.960(5)	Al(2)–C(13)	1.922(9)
Al(3)–N(1)	2.038(6)	Al(3)–C(14)	1.96(1)
Al(3)–C(15)	1.97(1)	Al(3)–C(16)	1.97(1)
Al(4)–N(3)	2.028(5)	Al(4)–C(17)	1.977(9)
Al(4)–C(18)	1.96(1)	Al(4)–C(19)	1.986(8)
N(1)–C(1)	1.503(9)	N(1)–C(11)	1.513(9)
N(2)–C(3)	1.501(8)	N(2)–C(4)	1.517(8)
N(3)–C(5)	1.486(9)	N(3)–C(6)	1.518(9)
N(4)–C(8)	1.495(9)	N(4)–C(9)	1.503(9)
C(1)–C(2)	1.51(1)	C(2)–C(3)	1.48(1)
C(4)–C(5)	1.49(1)	C(6)–C(7)	1.51(1)
C(7)–C(8)	1.50(1)	C(9)–C(10)	1.51(1)
C(10)–C(11)	1.49(1)	Al(1) · · · Al(2)	2.785(3)

Atoms	Angle	Atoms	Angle
Al(1)–N(1)–Al(3)	113.0(3)	Al(1)–N(2)–Al(2)	90.5(2)
Al(2)–N(3)–Al(4)	112.5(3)	Al(1)–N(4)–Al(2)	90.8(2)
N(1)–Al(1)–N(2)	105.6(2)	N(1)–Al(1)–C(12)	116.8(3)
N(2)–Al(1)–C(12)	115.1(3)	N(4)–Al(1)–C(12)	118.3(3)
N(1)–Al(1)–N(4)	108.1(2)	N(2)–Al(1)–N(4)	89.1(2)
N(2)–Al(2)–N(3)	93.7(2)	N(2)–Al(2)–N(4)	89.5(2)
N(3)–Al(2)–N(4)	103.7(2)	N(2)–Al(2)–C(13)	125.8(3)
N(3)–Al(2)–C(13)	120.6(3)	N(4)–Al(2)–C(13)	117.2(3)
N(1)–Al(3)–C(14)	110.3(3)	N(1)–Al(3)–C(15)	102.2(3)

A comparison of the title compound to the previously reported[23] $[14]aneN_4$ analogue is noteworthy. Quite expectedly, the mean Al–N distance in the Al_2N_2 fragment of the title compound (1.958(5)Å) is comparable to the corresponding fragment in the smaller macrocycle (1.936(4)Å). Furthermore, the Al · · · Al distance in the title compound (2.785(3)Å) is virtually identical to that determined for the smaller macrocycle (2.735(3)Å). The Al · · · Al contacts in these two compounds represent the shortest approach of two aluminum atoms in compounds having Al_2N_2 fragments.[33–35]

ACKNOWLEDGEMENT

G.H.R. (RII-8520554) and J.L.A. are grateful to the National Science Foundation for support of this work.

SUPPLEMENTARY MATERIAL AVAILABLE

Tables of bond distances and angles, final fractional coordinates, and thermal parameters (6 pages) and a listing of observed and calculated structure factors (13 pages) are available from the Editor.

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