1494 J. Am. Chem. Soc. 1988, 110, 1494-1497

Synthesis and Molecular Structure of $[Al(CH_3)_3][12]aneS_4$: A Novel Example of an Axially Stabilized Trigonal Bipyramidal Coordination of Aluminum

Gregory H. Robinson* and Samuel A. Sangokoya

Contribution from the Department of Chemistry, Clemson University, Clemson, South Carolina 29634-1905. *Received June 1, 1987*

Abstract: Reaction of trimethylaluminum with the thiacrown ether $[12]aneS_4$ affords the crystalline complex $[Al(CH_3)_3][12]aneS_4$. The title compound crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters as follows: $a = 9.791$ (4) Å, $b = 8.441$ (9) Å, $c = 21.416$ (8) Å, $\beta = 102.36°$, $V = 1728$ Å^3, and $D_{calcd} = 1.33$ g cm^{-3} for $Z = 4$. Least-squares refinement based on 1486 observed reflections with intensities $I \geq 3\sigma(I)$ in the range $2.0° \leq 2\theta \leq 45.0°$ converged at $R = 0.069$, $R_w = 0.103$. The Al–S distance is 2.718 (3) Å. All four sulfur atoms are coplanar as are the aluminum and carbon atoms in the $Al(CH_3)_3$ unit. An examination of the unit cell reveals the aluminum atom of the neutral complex to be in a unique trigonal bipyramidal environment axially stabilized by two $[12]aneS_4$ moieties. The X-ray crystal structure of the uncomplexed sulfur macrocycle $[12]aneS_4$ was also determined. The sulfur atoms in $[12]aneS_4$ resides around the macrocyclic perimeter thus resulting in an exodentate conformation. The macrocycle crystallizes in the monoclinic space group Cc with unit cell parameters as follows: $a = 13.012$ (3) Å, $b = 12.860$ (2) Å, $c = 14.454$ (2) Å, $\beta = 108.14$ (2)°, $V = 2298$ Å^3, and $D_{calcd} = 1.39$ g cm^{-3} for $Z = 8$. Full-matrix least-squares refinement based on 2040 observed reflections converged at $R = 0.025$, $R_w = 0.035$.

The reaction of aluminum alkyls with macrocyclic ligands has been of interest to us for some time. Initially, the interaction of oxygen-based macrocyclic polyethers, crown ethers (CE), with AlR_3 was examined. These reactions were shown to result in $[AlR_3]_n[CE]$ complexes. We have reported several such complexes.[1-3] Importantly, in the presence of alkali metal salts, these complexes serve as precursors to a class of nonstoichiometric organoaluminum-based liquid inclusion compounds known as liquid clathrates.[4] Recently, we initiated an investigation of the organoaluminum chemistry of macrocyclic polyethers having nitrogen[5,6] or sulfur[7] atoms as the donor species instead of oxygen. As it is well documented that sulfur-based crown ethers (thiacrown ethers) such as $[12]aneS_4$ and $[14]aneS_4$ (Figure 1) form stable complexes with such transition-metal ions as Ni(II),[8,9] Cu(II),[10,11] Hg(II),[12] Co(III),[13] and Rh(III),[13] we are interested in the preparation of $[AlR_3]_n[CE]$ complexes employing such sulfur-based macrocyclic ligands. It is anticipated that such organoaluminum–thiacrown ether complexes will facilitate the preparation of organoaluminum inclusion compounds employing transition-metal ions such as those cited above. Herein, we report the synthesis and structure of $[Al(CH_3)_3][12]aneS_4$. Aside from representing only the fourth organoaluminum compound containing an Al–S bond that has been characterized by X-ray diffraction techniques, the title compound is unique in that the aluminum atom is five-coordinate in a trigonal bipyramidal environment. Additionally, we report the initial X-ray crystal structural determination of the uncomplexed sulfur macrocycle $[12]aneS_4$.

Table I. Crystal and Data Collection Parameters for $[Al(CH_3)_3][12]aneS_4$ (I) and $[12]aneS_4$ (II)

	I	II
empirical formula	$C_{11}H_{25}AlS_4$	$C_8H_{16}S_4$
color; habit	colorless prisms	colorless rectangles
size (mm)	0.25 × 0.20 × 0.20	1.00 × 0.50 × 0.60
space group	monoclinic, $P2_1/n$	monoclinic, Cc
unit cell dimens		
a, Å	9.791 (4)	13.012 (3)
b, Å	8.441 (9)	12.860 (2)
c, Å	21.416 (8)	14.454 (2)
β, deg	102.36 (3)	108.14 (2)
V, Å^3	1728 (2)	2298 (2)
molecules/cell	4	8
mol wt	312.55	240.47
D_{calcd}, g/cm^3	1.40	1.39
diffractometer	Nicolet R3m/V	Enraf-Nonius CAD-4
radiatn	Mo Kα (λ = 0.71073 Å)	
temp, °C	26	
2θ range, deg	2.0–45.0	2.0–50.0
reflctns collected	2618	4441
reflctns obsd	1486	2040
GOF	1.17	1.43
data/parameter	10.2	9.50
R	0.0697	0.025
R_w	0.103	0.035

Experimental Section

General Comments. The extreme air and water sensitivity of reactants and products warranted concerted effort to exclude oxygen and moisture from the synthesis and subsequent manipulations. Thus, standard Schlenk technique was employed in conjunction with an inert atmosphere drybox (Vacuum Atmosphere HE-43 Dri-Lab). Toluene was distilled under prepurified nitrogen from sodium/benzophenone immediately prior to use. ^1H NMR data were collected on a JOEL FX-90Q NMR spectrometer. X-ray data for $[Al(CH_3)_3][12]aneS_4$ were collected on a Nicolet R3m/V diffractometer while X-ray data for $[12]aneS_4$ were collected on an Enraf-Nonius CAD-4 diffractometer.

Preparation and Characterization of $[Al(CH_3)_3][12]aneS_4$. A 150-mL reaction vessel was charged with $[12]aneS_4$ (4.15 mmol) and taken inside the drybox where toluene (25 mL) and trimethylaluminum (16.6 mmol) were added via syringe. The reaction tube was removed from the drybox and heated in an oil bath (60 °C) for several hours. The reaction mixture was transferred to a 100-mL Schlenk flask (via cannula); solvent was reduced in vacuo. Upon cooling, a multitude of small, colorless, rectangular, extremely air-sensitive, X-ray quality crystals resulted in

---

(1) Robinson, G. H.; Hunter, W. E.; Bott, S. G.; Atwood, J. L. *J. Organomet. Chem.* **1987**, *326*, 9–16.

(2) Robinson, G. H.; Bott, S. G.; Elgamal, H.; Hunter, W. E.; Atwood, J. L. *J. Incl. Phenom.* **1985**, *3*, 65–69.

(3) Atwood, J. L.; Elgamal, H.; Robinson, G. H.; Bott, S. G.; Weeks, J. A.; Hunter, W. E. *J. Incl. Phenom.* **1984**, *2*, 367–376.

(4) Atwood, J. L. *Inclusion Compounds*"; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic: London, 1984; Vol. 1, pp 375–405.

(5) Robinson, G. H.; Rae, A. D.; Campana, C. F.; Byram, S. K. *Organometallics* **1987**, *6*, 1227–1230.

(6) Robinson, G. H.; Zhang, H.; Atwood, J. L. *J. Organomet. Chem.* **1987**, *331*, 153–160.

(7) Robinson, G. H.; Zhang, H.; Atwood, J. L. *Organometallics* **1987**, *6*, 887–889.

(8) Davis, P. H.; White, L. K.; Belford, R. L. *Inorg. Chem.* **1975**, *14*, 1753–1757.

(9) Rosen, W.; Busch, D. H. *J. Am. Chem. Soc.* **1969**, *91*, 4694–4697.

(10) Glick, M. D.; Gavel, D. P.; Diaddario, L. L.; Rorabacher, D. B. *Inorg. Chem.* **1976**, *15*, 1190–1193.

(11) Pett, V. B.; Diaddario, L. L., Jr.; Dockal, E. R.; Corfield, P. W.; Ceccarelli, C.; Glick, M. D.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1983**, *22*, 3661–3670.

(12) Alcock, N. W.; Herron, N.; Moore, P. *J. Chem. Soc., Dalton Trans.* **1978**, 394–399.

(13) Travis, K.; Busch, D. H. *Inorg. Chem.* **1974**, *13*, 2591–2598.

0002-7863/88/1510-1494$01.50/0

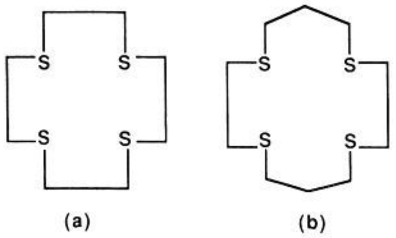

Figure 1. Thia crown ethers: (a) [12]aneS$_4$ and (b) [14]aneS$_4$.

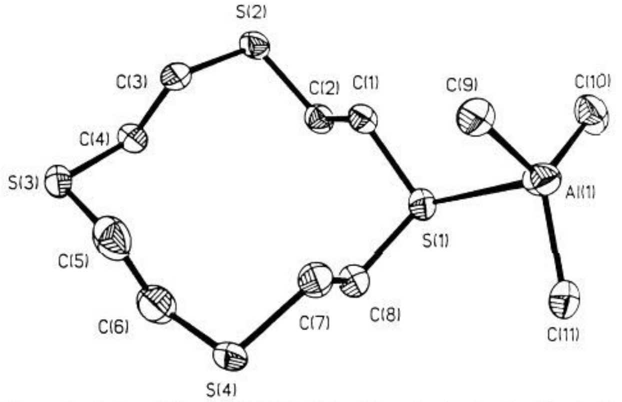

Figure 2. A view of the [Al(CH$_3$)$_3$][12]aneS$_4$ molecule showing the atom labeling scheme. Thermal ellipsoids show 50% probability levels; hydrogen atoms have been omitted.

quantitative yield (based on [12]aneS$_4$): ^{1}H NMR (C$_6$D$_6$) δ −0.240 (s, 9 H, Al-(C*H*$_3$)$_3$), 0.190–0.430 (m, 8 H, (S-C*H*$_2$C*H*$_2$-S)$_2$), 2.73 (s, 8 H, (S-C*H*$_2$C*H*$_2$-S)$_2$).

Crystallographic Structure Determinations. Structure Solution and Refinement for [Al(CH$_3$)$_3$][12]aneS$_4$. Single crystals of the title compound were obtained from the mother liquid and sealed under an atmosphere of nitrogen in thin-walled glass capillaries. X-ray intensity data were collected on a Nicolet R3m/V diffractometer by using an ω-scan technique with Mo Kα radiation (λ = 0.71073 Å) at 26 °C. The compound crystallizes in the monoclinic space group $P2_1/n$ with a = 9.791 (4) Å, b = 8.441 (9) Å, c = 21.416 (8) Å, β = 102.36°, V = 1728 Å^3, and D_{calcd} = 1.33 g cm^{-3} for Z = 4. The structure was solved by direct methods and refined, based on 1486 observed reflections with intensities $I \geq 3\sigma(I)$, by using SHELXTL.[14] Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms, located from difference Fourier maps, were placed in idealized positions with fixed isotropic temperature factors. Difference maps revealed atoms C(5) and C(6) to be slightly disordered. The disorder involves rotation of these two atoms about a twofold axis. Partial occupancy factors showed the disorder to be in the ratio of 5.67:1. The predominant model of the title compound is presented herein. Refinement converged at R = 0.069, R_w = 0.103. Relevant crystallographic data are given in Table I. The structure of the title compound is shown in Figure 2. Final fractional coordinates are given in Table II. Selected bond distances and angles are given in Table III.

Structure Solution and Refinement for [12]aneS$_4$. A colorless parallelopiped crystal of [12]aneS$_4$ was mounted in a glass capillary in a random orientation. Preliminary examination and data collection were performed on an Enraf-Nonius CAD4 diffractometer. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement by using 25 reflection in the range 11° < θ < 20°. The macrocycle crystallizes in the monoclinic space group Cc with unit cell parameters a = 13.012 (3) Å, b = 12.860 (2) Å, c = 14.454 (2) Å, β = 108.14 (2)°, V = 2298 Å^3, and D_{calcd} = 1.39 g cm^{-3} for Z = 8. Data were collected by using the ω-θ scan technique. The intensities were corrected for Lorentz, polarization, and absorption effects. Neutral atom scattering factors were taken from Cromer and Waber.[15] The scattering for all atoms was corrected for the real and imaginary components of anomalous dispersion by using the table of Cromer.[16] Anisotropic thermal parameters were used for all non-hydrogen atoms. The structure was solved by direct methods and refined based on 2040 observed reflections. Hydrogen atoms were located and added to the structure factor calculations, but their positions and thermal parameters were not refined. Full-matrix least-squares refinement converged at R = 0.025, R_w = 0.035. All calculations were performed on a MicroVAX II computer by using SDPVAX.[17] Crystal data is given in Table I. There are two crystallographically independent molecules in the asymmetric unit (Space group

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for [Al(CH$_3$)$_3$][12]aneS$_4$

atom	x	y	z	U(eq)
Al(1)	2409 (3)	3227 (3)	−144 (1)	62 (1)
S(1)	90 (2)	3035 (2)	−1070 (1)	54 (1)
S(2)	−1200 (2)	−1244 (2)	−2233 (1)	57 (1)
S(3)	−262 (2)	1098 (3)	−3949 (1)	57 (1)
S(4)	1292 (2)	5289 (2)	−2753 (1)	56 (1)
C(1)	116 (7)	1049 (8)	−1405 (3)	48 (3)
C(2)	−1257 (7)	629 (9)	−1818 (3)	53 (3)
C(3)	−319 (8)	−643 (9)	−2859 (3)	56 (3)
C(4)	−1239 (8)	314 (9)	−3387 (3)	56 (3)
C(5)	887 (10)	2598 (12)	−3475 (5)	85 (4)
C(6)	157 (10)	3980 (11)	−3323 (5)	79 (4)
C(7)	1405 (8)	4190 (10)	−1995 (4)	59 (3)
C(8)	88 (8)	4294 (9)	−1758 (4)	59 (3)
C(9)	3693 (9)	2029 (10)	−516 (4)	65 (3)
C(10)	1418 (9)	2044 (12)	430 (4)	75 (4)
C(11)	2321 (8)	5537 (9)	−150 (3)	60 (3)

Table III. Selected Bond Distances (Å) and Angles (deg) for [Al(CH$_3$)$_3$][12]aneS$_4$

atoms	distance	atoms	distance
Al(1)–S(1)	2.718 (3)	Al(1)–S(3′)	3.052 (3)
Al(1)–C(9)	1.952 (8)	Al(1)–C(10)	1.943 (8)
Al(1)–C(11)	1.953 (8)	S(1)–C(1)	1.825 (7)
S(1)–C(8)	1.817 (8)	S(2)–C(2)	1.821 (8)
S(2)–C(3)	1.1815 (7)	S(3)–C(4)	1.816 (7)
S(3)–C(5)	1.846 (11)	S(4)–C(6)	1.834 (10)
S(4)–C(7)	1.853 (8)	C(1)–C(2)	1.485 (10)
C(3)–C(4)	1.518 (10)	C(5)–C(6)	1.442 (12)
C(7)–C(8)	1.486 (10)		
atoms	**angle**	**atoms**	**angle**
C(10)–Al(1)–C(9)	116.7 (4)	C(11)–Al(1)–C(10)	120.9 (4)
C(11)–Al(1)–C(9)	121.8 (3)	C(9)–Al(1)–S(1)	98.6 (3)
C(10)–Al(1)–S(1)	88.7 (3)	C(11)–Al(1)–S(1)	90.4 (4)
C(8)–S(1)–C(1)	102.5 (4)	C(3)–S(2)–C(2)	100.8 (3)
C(5)–S(3)–C(4)	103.4 (4)	C(7)–S(4)–C(6)	101.3 (4)

Table IV. Selected Bond Distances (Å) and Angles (deg) for [12]aneS$_4$

atoms	distance	atoms	distance
S(1)–C(1)	1.811 (3)	S(1)–C(2)	1.818 (3)
S(2)–C(3)	1.814 (3)	S(2)–C(4)	1.824 (3)
S(3)–C(5)	1.806 (3)	S(3)–C(6)	1.806 (3)
S(4)–C(7)	1.825 (3)	S(4)–C(8)	1.817 (3)
C(1)–C(8)	1.515 (4)	C(2)–C(3)	1.517 (4)
C(4)–C(5)	1.508 (4)	C(6)–C(7)	1.518 (4)
S(5)–C(9)	1.817 (3)	S(5)–C(10)	1.819 (4)
S(6)–C(11)	1.825 (3)	S(6)–C(12)	1.818 (3)
S(7)–C(13)	1.815 (3)	S(7)–C(14)	1.809 (3)
S(8)–C(15)	1.825 (3)	S(8)–C(16)	1.816 (3)
C(9)–C(16)	1.507 (4)	C(10)–C(11)	1.510 (4)
C(12)–C(13)	1.516 (4)	C(14)–C(15)	1.518 (4)
atoms	**angle**	**atoms**	**angle**
C(1)–S(1)–C(2)	101.0 (1)	C(3)–S(2)–C(4)	100.7 (1)
C(5)–S(3)–C(6)	101.5 (1)	C(7)–S(4)–C(8)	101.5 (1)
C(9)–S(5)–C(10)	101.9 (1)	C(11)–S(6)–C(12)	101.2 (1)
C(13)–S(7)–C(14)	100.8 (1)	C(15)–S(8)–C(16)	101.1 (1)

---

(14) Sheldrick, G. M. SHELXTL, Crystallographic Computing System, Revision 5.1, Nicolet Instruments Division, Madison, WI, 1986.

(15) Cromer, D. T.; Waber, J. T. "International *Tables for X-ray Crystallography*"; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(16) Cromer, D. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(17) Frenz, B. A. "The Enraf-Nonius CAD-4. A Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Determination", *Computing in Crystallography*"; Schlenk, H., Olthof-Hazelkamp, R., van-Konigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64–71.

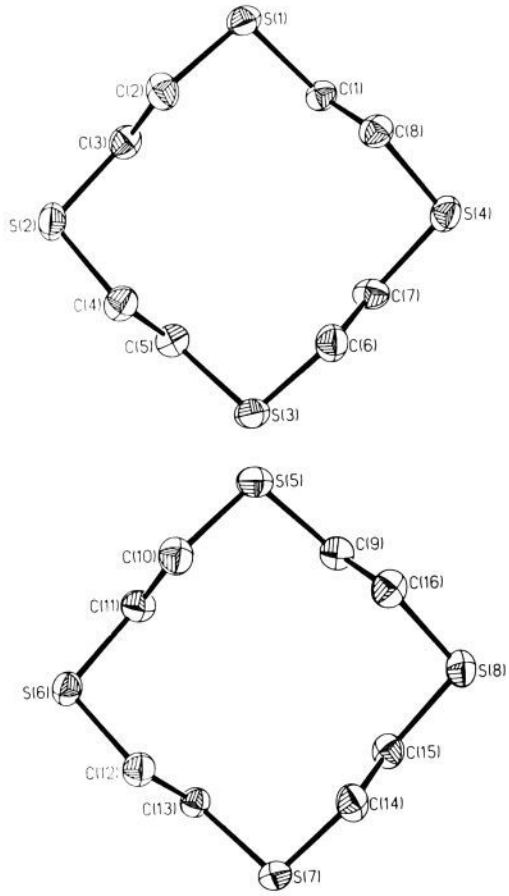

Figure 3. A view of the two crystallographically independent [12]aneS_4 molecules showing the atom labeling scheme. Thermal ellipsoids show 35% probability levels; hydrogen atoms have been omitted.

Table V. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for [12]aneS_4

atoms	*x*	*y*	*z*	*U*(eq)
S(1)	7220 (1)	2190 (1)	1920 (1)	44 (1)
S(2)	5458 (1)	87 (1)	3361 (1)	47 (1)
S(3)	8197 (1)	335 (1)	6097 (1)	46 (1)
S(4)	9999 (7)	2395 (1)	4654 (1)	46 (1)
S(5)	1057 (1)	1130 (1)	1813 (1)	45 (1)
S(6)	3649 (1)	3365 (1)	3342 (1)	43 (1)
S(7)	4309 (1)	1417 (1)	6011 (1)	42 (1)
S(8)	1618 (1)	−779 (1)	4485 (1)	49 (1)
C(1)	8505 (2)	1937 (2)	2833 (2)	38 (1)
C(2)	6286 (3)	1722 (3)	2543 (3)	45 (1)
C(3)	6277 (3)	546 (3)	2633 (2)	44 (1)
C(4)	6286 (3)	493 (3)	4574 (2)	43 (1)
C(5)	7295 (3)	−156 (2)	4963 (2)	43 (1)
C(6)	8746 (3)	1474 (3)	5690 (2)	47 (7)
C(7)	9566 (3)	1241 (3)	5167 (2)	45 (1)
C(8)	8784 (3)	2710 (2)	3665 (2)	41 (1)
C(9)	937 (3)	571 (3)	2929 (2)	44 (1)
C(10)	2357 (3)	1789 (3)	2248 (2)	47 (1)
C(11)	2319 (3)	2780 (3)	2797 (2)	44 (1)
C(12)	4260 (3)	2445 (2)	4213 (2)	41 (1)
C(13)	3765 (3)	2444 (2)	5133 (2)	36 (1)
C(14)	3617 (3)	296 (2)	5349 (3)	45 (1)
C(15)	2422 (3)	274 (3)	5256 (2)	44 (1)
C(16)	1687 (3)	−377 (3)	3292 (2)	45 (1)

*C*2/*c* was examined, but refinement proved unsuccessful.). As can be seen in Figure 3, the two molecules are virtually identical. Bond distances and angles are given in Table IV while final fractional coordinates are given in Table V.

Results and Discussion

The origin of the organoaluminum-based liquid inclusion compounds known as liquid clathrates may be traced to the reaction of aluminum alkyls with MX moieties (M = alkali metal or tetraalkylammonium ion; X = halide or pseudohalide ion).[18] These reactions were shown to result in 1:1 (eq 1) or 2:1 (eq 2)

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

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

complexes. Upon interaction with aromatic solvents the 2:1 complex affords the desired inclusion compound. Over the last several years we have employed the metal ion complexing ability of crown ethers to extend the range of MX species exhibiting liquid clathrate behavior beyond simple salts. As a natural progression of this work, we are interested in the preparation of organoaluminum-based inclusion compounds by using transition-metal ions. Sulfur- and nitrogen-based crown ethers are attractive ligands in this task as they have been shown to form stable complexes with a plethora of transition-metal ions. Thus, an important step in the preparation of organoaluminum inclusion compounds using transition-metal ions is the preparation of $[AlR_3]_n[CE']$ complexes (CE′ = thia- and azacrown ethers). To this end, an excess of trimethylaluminum was allowed to react with [12]aneS_4; $[AlCH_3)_3]$[12]aneS_4 was the only product isolated.

Table VI. Comparison of Mean Bond Distances (Å) in Organoaluminum Compounds Containing Al–S Bonds

compound	distance	ref
$[(CH_3)_2AlS(CH_3)]_n$	2.328 (2)	*a*
$K[Al_2(CH_3)_6SCN]$	2.489 (2)	*b*
$[Al(CH_3)_3]_4$[14]aneS_4	2.522 (2)	*c*
$[Al(CH_3)_3]$[12]aneS_4	2.718 (3)	this study

[a] Reference 19. [b] Reference 20. [c] Reference 7.

There is an obvious paucity of structural data concerning organoaluminum–sulfur compounds containing Al–S bonds which have been structurally characterized by X-ray diffraction methods. The literature reveals only three such organoaluminum–sulfur compounds. As can be seen from Table VI, the three compounds, $[(CH_3)_2AlS(CH_3)]_n$,[19] $K[Al_2(CH_3)_6SCN]$,[20] and $[Al(CH_3)_3]_4$-[14]aneS_4,[7] have mean Al–S distances of 2.328 (2), 2.289 (2), and 2.522 (2) Å, respectively. Thus, the Al(1)–S(1) bond distance of 2.718 (3) Å in $[Al(CH_3)_3]$[12]aneS_4 must be considered the longest such interaction reported. This distance may be placed in further perspective when one considers that, with use of radii values given by Pauling, an expected Al–S interaction would approach 2.34 Å.[21]

In that 12-crown-4 is the oxygen congener of [12]aneS_4, the previously reported organoaluminum oxygen-based crown ether complex $[Al(CH_3)_3]_2$[12-crown-4][3] affords convenient comparison with $[Al(CH_3)_3]$[12]aneS_4. The two $Al(CH_3)_3$ units in $[Al(CH_3)_3]_2$[12-crown-4] forced the endodentate macrocycle into a distorted chair conformation as the four oxygen atoms assumed an exodentate geometry. The sulfur atoms of $[Al(CH_3)_3]$[12]aneS_4 are also exodentate (Figure 2). However, contrary to the case with oxygen crown ethers, it is unreasonable to assume that the sole $Al(CH_3)_3$ unit effected the given orientation of the sulfur atoms in $[Al(CH_3)_3]$[12]aneS_4. Indeed, the exodentate geometry was also confirmed for the uncomplexed ligand by an independent X-ray crystal structure (as reported herein). The structure of [12]aneS_4 is shown in Figure 3. Surprisingly, the four sulfur atoms are coplanar both in the uncomplexed ligand and the title compound. Moreover, a comparison of the structure of [12]aneS_4 with that of $[Al(CH_3)_3]$[12]aneS_4 reveals that the overall geometry and conformation of the macrocycle is virtually unchanged. While exodentate donor atoms in uncomplexed thiacrown ethers represent the predominant conformation, [9]aneS_3,[22] [14]aneS_4,[23] and

---

(18) Ziegler, K.; Koster, R.; Lehmkugl, H.; Reinert, K. *Justus Liebigs Ann. Chem.* **1960**, *33*, 629.

(19) Brauer, D. J.; Stucky, G. D. *J. Am. Chem. Soc.* **1969**, *91*, 5462–5466.

(20) Shakir, R.; Zaworotko, M. J.; Atwood, J. L. *J. Organomet. Chem.* **1979**, *171*, 9–16.

(21) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960.

(22) Glass, R. S.; Wilson, G. S.; Setzer, W. N. *J. Am. Chem. Soc.* **1980**, *102*, 5068–5069.

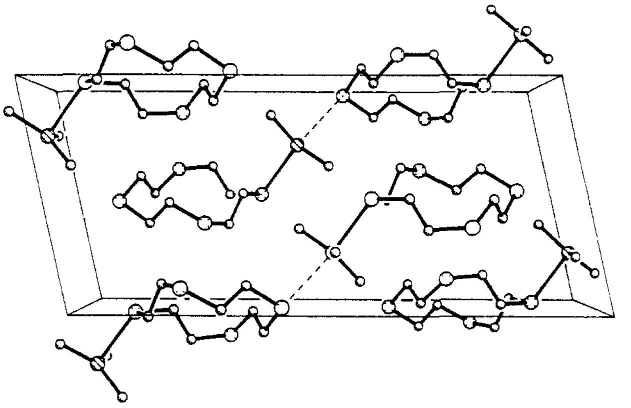

Figure 4. Crystal packing diagram of [Al(CH$_3$)$_3$][12]aneS$_4$ viewed along the *b* axis.

[18]aneS$_6$[24] have exhibited endodentate geometries. This provided further impetus to examine the structure of [12]aneS$_4$.

The structure of bis(trimethylaluminum) dioxanate, [Al(CH$_3$)$_3$]$_2$[C$_4$H$_8$O$_2$],[25] offers further insight into the comparison of Al–O and Al–S compounds. The geometry of the Al(CH$_3$)$_3$ units in [Al(CH$_3$)]$_2$[C$_4$H$_8$O$_2$] is similar to that observed in the title compound. Oxygen is a stronger Lewis base toward aluminum than sulfur. Thus, the Al–O bonding interactions would be more extensive than Al–S interactions resulting in longer Al–S bond distances. It may, therefore, be postulated that the longer Al–S bonds result in an increase in access to the fifth coordination site on the aluminum atom.

Size and flexibility of thiacrown ethers dramatically affects structure and bonding in organoaluminum–thiacrown ether complexes. Consider the recently reported [Al(CH$_3$)$_3$]$_4$[14]aneS$_4$[7] complex. The slightly larger and more flexible [14]aneS$_4$ macrocycle was able to accommodate four Al(CH$_3$)$_3$ units. The Al–S distances (2.522 (2) Å) are shorter than the Al–S distance determined for [Al(CH$_3$)$_3$][12]aneS$_4$. Larger macrocycles have less severe steric constraints than smaller macrocycles, thus facilitating more extensive Lewis acid–donor atom interaction.

Particularly significant about [Al(CH$_3$)$_3$][12]aneS$_4$ is the coordination of the aluminum atom. Notably, the aluminum and carbon atoms of the Al(CH$_3$)$_3$ unit are coplanar. A view of the unit cell, Figure 4, illustrates an Al–S interaction between the aluminum atom of the [Al(CH$_3$)$_3$][12]aneS$_4$ complex and a sulfur atom of a neighboring [Al(CH$_3$)$_3$][12]aneS$_4$ moiety. This Al–S interaction, indicated as a dotted line in Figure 4, at 3.052 (3) Å is only slightly longer than that determined for Al(1)–S(1). Indeed, this Al–S interaction plays an important role in the resulting Al(CH$_3$)$_3$ planar arrangement. In effect, the environment around the aluminum atom is quite novel in that it approaches that of a trigonal bipyramid as the planar Al(CH$_3$)$_3$ unit is stabilized by two axially positioned neutral [12]aneS$_4$ moieties. The S–Al–C bond angles with values of 98.6 (3)°, 88.7 (3)°, and 90.4 (3)° (for S(1)–Al(1)–C(9), S(1)–Al–C(10), and S(1)–Al(1)–C(11), respectively) are in support of such a geometry as are the C–Al–C bond angles in the planar Al(CH$_3$)$_3$ unit of 116.7 (4)°, 121.8 (3)°, and 120.9 (4)° (for C(9)–Al(1)–C(10), C(9)–Al(1)–C(11), and C(10)–Al(1)–C(11), respectively).

Table VII. Organolauminum Complexes Containing Five-Coordinate Aluminum Atoms as Determined by X-ray Diffraction

compound	geometry of Al atom	ref
[AlH$_3$][N(CH$_3$)$_3$]$_2$	trigonal bipyramidal	*a*
[(CH$_3$)$_2$AlOC(C$_6$H$_5$)N(C$_6$H$_5$)]$_2$	trigonal bipyramidal	*b*
[Al(C$_{22}$H$_{22}$N$_4$)]	square pyramidal	*c*
[*i*-Bu$_2$AlOCH$_2$-2-C$_5$H$_4$N]$_2$	trigonal bipyramidal	*d*
[C$_{18}$H$_{12}$AlNO$_3$]$_2$	trigonal bipyramidal	*e*
[Al(CH$_3$)]$_2$[C$_8$H$_{20}$N$_6$][Al(CH$_3$)$_2$]$_2$	square pyramidal	*f*
[(CH$_3$)$_2$AlO(CH$_2$)$_2$O(CH$_3$)]$_2$	trigonal bipyramidal	*g*

[a] Reference 28. [b] Reference 29. [c] Reference 30. [d] Reference 31. [e] Reference 32. [f] Reference 34. [g] Reference 35.

Five-coordinate aluminum atoms in organometallic chemistry are quite rare. Historically, support for such complexes has been based upon stoichiometry and/or inconclusive NMR data as opposed to X-ray diffraction experiments.[26-28] The literature reveals, to the best of our knowledge, only seven organoaluminum complexes containing five-coordinate aluminum atoms that have been characterized by X-ray diffraction techniques.[29-35] These compounds, along with the coordination geometry about the aluminum atom(s), are given in Table VII.

Conclusions

The title compound [Al(CH$_3$)$_3$][12]aneS$_4$ is important, inter alia, in that it represents a very interesting trigonal bipyramidal coordination of an organoaluminum complex where a planar Al(CH$_3$)$_3$ unit is axially stabilized by two neutral sulfur macrocycles. The fact that the macrocycle does not experience a significant degree of distortion coupled with the extremely long Al–S bonds undoubtedly plays a significant role in the apparent tendency of [Al(CH$_3$)$_3$][12]aneS$_4$ to oligomerize. It is quite clear from this study that products resulting from reaction of aluminum alkyls with oxygen and sulfur macrocyclic ligands differ substantially in structure and bonding.

Acknowledgment. We are grateful to the National Science Foundation for support of this work to G.H.R. (RII-8520554). Additionally, we thank Dr. Ashfaq Syed of Enraf-Nonius (Bohemia, NY) for assistance in the structural solution of the sulfur crown ether.

Registry No. [12]aneS$_4$, 25423-56-7; [Al(CH$_3$)$_3$][12]aneS$_4$, 112440-15-0; Al(CH$_3$)$_3$, 75-24-1.

Supplementary Material Available: Tables of crystal data, bond distances and angles, final fractional coordinates, and thermal parameters for [12]aneS$_4$ and [Al(CH$_3$)$_3$][12]aneS$_4$ (11 pages); a listing of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

---

(23) DeSimone, R. E.; Glick, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 762–767.

(24) Hartman, J. A. R.; Wolf, R. E.; Foxman, B. M.; Cooper, S. R. *J. Am. Chem. Soc.* **1983**, *105*, 131–132.

(25) Atwood, J. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1967**, *89*, 5362–5366.

(26) Mole, T.; Jeffery, E. A. *Organoaluminum Compounds*; Elsevier: New York, 1972; p 115.

(27) Storr, A.; Thomas, B. S. *Can. J. Chem.* **1970**, *48*, 3667.

(28) Mole, T. *Chem. Ind. (London)* **1964**, 281.

(29) Heitsch, C. W.; Nordman, C. E.; Parry, R. W. *Inorg. Chem.* **1963**, *2*, 508–511.

(30) Kai, Y.; Yasuoka, N. Kasai, N. Kakudo, M. *Chem. Commun.* **1969**, 575–576.

(31) Goedken, V. L.; Ito, H.; Ito, T. *J. Chem. Soc., Chem. Commun.* **1984**, 1453–1454.

(32) van Vliet, M. R. P.; Buysingh, P.; van Koten, G.; Vrieze, K. *Organometallics* **1985**, *4*, 1701–1707.

(33) Müller, E.; Bügi, H. S. *Helv. Chim. Acta* **1987**, *70*, 520.

(34) Robinson, G. H.; Sangokoya, S. A. *J. Am. Chem. Soc.* **1987**, *109*, 6852–6853.

(35) Benn, R.; Rufinska, A.; Lehmkuhl, H.; Janseen, E.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 799–780.