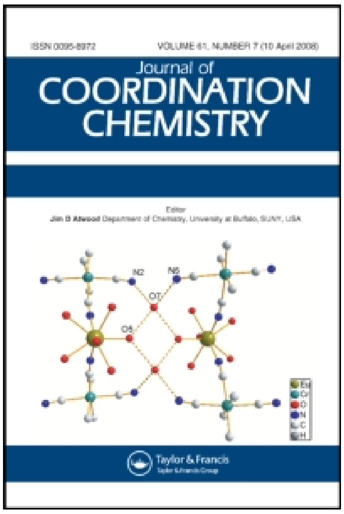

Journal of Coordination Chemistry

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

Organoaluminum-Thiacrown Ether Chemistry. Synthesis and Molecular Structure of $[Al(CH_3)_3]_4[12]aneS_4$: An Unusual Example of an Endodentate Conformation of $[12]aneS_4$

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To cite this Article Sangokoya, Samuel A. , Lee, Baosheng , Pennington, William T. and Robinson, Gregory H.(1989) 'Organoaluminum-Thiacrown Ether Chemistry. Synthesis and Molecular Structure of $[Al(CH_3)_3]_4[12]aneS_4$: An Unusual Example of an Endodentate Conformation of $[12]aneS_4$', Journal of Coordination Chemistry, 19: 4, 331 — 338

To link to this Article: DOI: 10.1080/00958978909408836

URL: http://dx.doi.org/10.1080/00958978909408836

J. Coord. Chem. 1989, Vol. 19. pp. 331-338
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ORGANOALUMINUM-THIACROWN ETHER CHEMISTRY. SYNTHESIS AND MOLECULAR STRUCTURE OF $[Al(CH_3)_3]_4[12]aneS_4$: AN UNUSUAL EXAMPLE OF AN ENDODENTATE CONFORMATION OF $[12]aneS_4$

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(Received May 30, 1988)

The crystalline organoaluminum macrocyclic ligand complex $[Al(CH_3)_3]_4[12]aneS_4$ was prepared by reaction of the sulfur-based crown ether with trimethylaluminum in toluene. The title compound crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 8.548(2)$, $b = 9.949(3)$, $c = 11.225(3)$ Å, $\alpha = 64.08(2)$, $\beta = 78.55(2)$, $\gamma = 86.96(3)°$, $V = 840$ Å^3, and $D_c = 1.04$ g cm^{-3} for $Z = 1$. Least-squares refinement based on 1761 observed reflections ($I \geq 3\sigma(I)$) in the range $3.50° < 2\theta < 45.0°$ converged at $R = 0.034$, $R_w = 0.044$. The molecule is situated about a crystallographic centre of symmetry with the four sulfur atoms constituting a plane. As evidenced by the independent distances of 2.530(1) Å and 2.500(1) Å, the Al-S interactions in the organoaluminum complex are rather substantial. Particularly significant is the fact that the conformation of the macrocycle in the title compound is endodentate as the four sulfur atoms are directed towards the interior of the macrocyclic cavity even as it accommodates four trimethylaluminum units.

Keywords: Aluminum alkyl, sulfur macrocycle, X-ray structure, conformation, stereochemistry

INTRODUCTION

Although the first sulfur-based macrocyclic ligand, 1,4,7,10,13,16-hexathiacyclooctadecane ($[18]aneS_6$),[1] was reported decades prior to Pedersen's discovery of dibenzo-18-crown-6,[2,3] the chemistry of thiacrown ethers has not developed in parallel with that of their oxygen analogues. However, the last few years has witnessed a plethora of fundamental studies on these interesting ligands.[4-11] The current resurgence of thiacrown ether chemistry may chiefly be ascribed to: (a) the discovery of thiaether coordination of copper in the blue protein plastocyanin;[12] (b) continuing interest in oxygen- and nitrogen-based macrocyclic ligands; and (c) vastly improved synthetic methods affording the facile preparation of thiacrown ethers in high yield.[13-16]

This laboratory has long been interested in the interactions of organoaluminum species with macrocyclic ligands. While initially concerned with the reaction of aluminum alkyls with oxygen-based macrocyclic ligands, crown ethers, our attention recently shifted to the corresponding chemistry of sulfur-based ligands, thiacrown ethers. Herein, we report the synthesis and molecular structure of $[Al(CH_3)_3]_4[12]aneS_4$ isolated from reaction of trimethylaluminum with $[12]aneS_4$

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(Figure 1). The title compound is unique in that the macrocycle is in an unusual endodentate conformation even as it accommodates four trimethylaluminum units.

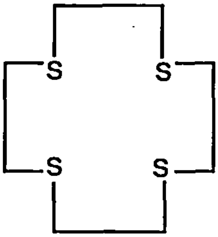

FIGURE 1 [12]aneS_4.

EXPERIMENTAL

General

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 drybox (Vacuum Atmospheres HE-43 Dri-Lab). Toluene was distilled from sodium/benzophenone under an atmosphere of argon immediately prior to use. Trimethylaluminum and [12]aneS_4, both purchased from Aldrich Chemical Co., were used as received

Synthesis of $[Al(CH_3)_3]_4[12]aneS_4$

A 150 cm^3 reaction vessel was charged with [12]aneS_4 (1.25 mmol) and taken inside the drybox where toluene (25 cm^3) and trimethylaluminum (25 mmol) were added *via* syringe. The reaction tube was removed from the drybox and heated in an oil bath (120°C) for several hours. The reaction mixture was transferred to a 100 cm^3 Schlenk flask (*via* cannula); solvent was reduced *in vacuo*. Upon cooling, a multitude of large, colourless, rectangular, extremely air-sensitive, X-ray quality crystals resulted in quantitative yield (based on [12]aneS_4). ^{1}H NMR ($CDCl_3$): δ −0.586 (s, 36H, 4 $Al(CH_3)_3$), 2.960 (s, 16H, S-CH_2-CH_2-S).

Structural Solution and Refinement

A single crystal of the title compound was sealed under an atmosphere of argon in a thin-walled glass capillary. X-ray intensity data were collected on a Nicolet R3m/V diffractometer by using an $\omega/2\theta$-scan technique with MoKα radiation (λ = 0.71073 Å) at 21°C. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement of the setting angles of 41 carefully centred reflections in the range $15.17 < 2\theta < 29.91°$, corresponded to a triclinic crystal system of space group $P\bar{1}$ with $a = 8.548(2)$, $b = 9.949(3)$, $c = 11.225(3)$ Å, $\alpha = 64.08(2)$, $\beta = 78.55(2)$, $\gamma = 86.96(3)°$, $V = 840$ Å^3, and $D_{calc} = 1.04$ g cm^{-3} for $Z = 1$. Least-squares refinement, based on 1761 observed reflections with intensities ($I \geqslant 3\sigma(I)$), using SHELXTL[17] refinement converged at $R = 0.034$, $R_W = 0.044$. Non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were located by standard difference Fourier techniques; methylene hydrogen atoms of the macrocyclic carbon atoms were refined using isotropic thermal parameters while those of the aluminum methyl groups were included in the structure factor calculations in idealized positions ($d_{C-H} = 0.95$ Å). Relevant crystallographic data are given in Table I. The structure of the title compound is shown in Figure 2. Final atomic coordinates are given in Table II while selected bond distances and angles are provided in Table III.

TABLE I
Summary of crystallographic data for $[Al(CH_3)_3]_4[12]aneS_4$.

Empirical formula	$C_{20}H_{52}Al_4S_4$
Molecular weight	528.88
Colour; habit	Colourless prisms
Size	0.90 mm × 0.30 mm × 0.15 mm
Space group	Triclinic, $P\bar{1}$
a, Å	8.548(2)
b, Å	9.949(3)
c, Å	11.225(3)
α, deg	64.08(2)
β, deg	78.55(2)
γ, deg	86.96(3)
Cell volume, Å^3	840
Z	1
D_c/g cm^{-3}	1.04
Diffractometer	Nicolet R3m/V
Radiation	MoKα ($\lambda = 0.71073$ Å)
Temperature	21°C
2θ Range	3.50 to 45.0°
Reflections collected	2634
Reflections observed	1452
GOF	1.28
R	0.034
R_w	0.044

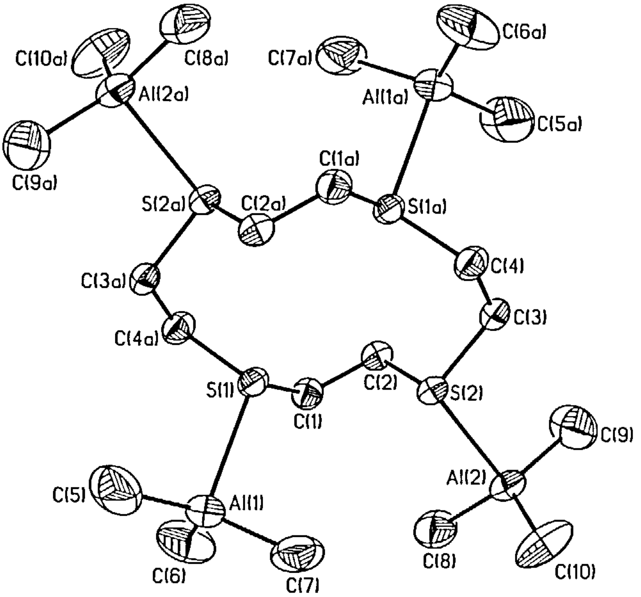

FIGURE 2 Structure of $[Al(CH_3)_3]_4[12]aneS_4$. Thermal ellipsoids are contoured at the 35% probability level.

TABLE II

Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters* ($Å^2 \times 10^3$) for $[Al(CH_3)_3]_4[12]aneS_4$.

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
S(1)	5531(1)	7157(1)	3671(1)	48(1)
S(2)	6957(1)	5428(1)	6439(1)	49(1)
Al(1)	7597(1)	9094(1)	1993(1)	65(1)
Al(2)	8447(1)	6536(1)	7555(1)	65(1)
C(1)	5086(5)	7643(4)	5082(3)	55(2)
C(2)	5029(4)	6291(4)	6412(3)	50(2)
C(3)	6490(4)	3487(3)	7640(3)	53(2)
C(4)	6303(4)	2484(4)	6989(4)	57(2)
C(5)	7426(7)	8903(6)	375(5)	148(4)
C(6)	6828(6)	10917(5)	2098(6)	130(3)
C(7)	9401(5)	8219(5)	2867(5)	113(3)
C(8)	7937(5)	8640(4)	6659(5)	97(2)
C(9)	7450(7)	5439(6)	9443(4)	129(3)
C(10)	10603(5)	6051(6)	6950(6)	128(4)

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

TABLE III

Bond distances (Å) and angles (deg) for $[Al(CH_3)_3]_4[12]aneS_4$.

Atoms	Distance	Atoms	Distance
S(1)–Al(1)	2.500(1)	S(1)–C(1)	1.815(3)
S(1)–C(4a)	1.818(3)	S(2)–Al(2)	2.530(1)
S(2)–C(2)	1.817(3)	S(2)–C(3)	1.816(3)
Al(1)–C(5)	1.941(5)	Al(1)–C(6)	1.940(4)
Al(1)–C(7)	1.951(4)	Al(2)–C(8)	1.954(4)
Al(2)–C(9)	1.941(5)	Al(2)–C(10)	1.945(4)
C(1)–C(2)	1.504(4)	C(3)–C(4)	1.502(5)

Atoms	Angle	Atoms	Angle
C(1)–S(1)–Al(1)	103.8(1)	C(4a)–S(1)–Al(1)	108.0(1)
C(1)–S(1)–C(4a)	104.0(2)	C(2)–S(2)–Al(2)	105.0(1)
C(3)–S(2)–Al(2)	106.0(1)	C(3)–S(2)–C(2)	104.0(2)
C(5)–Al(1)–S(1)	99.6(2)	C(6)–Al(1)–S(1)	103.2(2)
C(6)–Al(1)–C(5)	116.6(3)	C(7)–Al(1)–S(1)	96.9(1)
C(7)–Al(1)–C(5)	118.8(3)	C(7)–Al(1)–C(6)	116.0(2)
C(8)–Al(2)–S(2)	100.6(1)	C(9)–Al(2)–S(2)	101.6(2)
C(9)–Al(2)–C(8)	116.8(2)	C(10)–Al(2)–S(2)	98.6(1)
C(10)–Al(2)–C(8)	115.5(2)	C(10)–Al(2)–C(9)	118.5(3)
C(2)–C(1)–S(1)	111.8(2)	C(1)–C(2)–S(2)	109.5(2)
C(4)–C(3)–S(2)	113.5(3)	C(3)–C(4)–S(1a)	111.0(3)

RESULTS AND DISCUSSION

The interactions of aluminum species with macrocyclic ligands, crown ethers (CE), have proven to be a particularly fruitful area of organoaluminum chemistry. Our interest in this chemistry stems from the fact that reaction of aluminum alkyls with macrocyclic ligands, in the presence of alkali metal salts (MX), results in non-stoichiometric organoaluminum inclusion compounds known as liquid clathrates.[18] A typical preparation of these inclusion compounds is given in (*1*)

$$n\ AlR_3 + CE \rightarrow [AlR_3][CE]—MX \rightarrow [CE{\cdot}M][Al_2R_6X] \qquad (1)$$

While the primary function of the crown ether in the inclusion compound is to complex the alkali metal ion, it is important to note that in the absence of MX the crown ether has been shown to form stable molecular complexes with the aluminum alkyl units resulting in novel $[AlR_3]_n[CE]$ complexes. Indeed, the $[AlR_3]_n[CE]$ complexes serve as precursors to the inclusion compounds by essentially serving as a means of transport of AlR_3 to X^-.[19] We have reported several such $[AlR_3]_n[CE]$ complexes.[20-22]

The preparation of organoaluminum inclusion compounds utilizing transition metal species as the MX group represents an important extension of this work. Macrocyclic ligands possessing nitrogen, phosphorus, or sulfur atoms as donor species are well documented in the literature as being good complexing agents for transition metal ions. To this end, we recently initiated an investigation into the interactions of organoaluminum species with these macrocycles. Moreover, we have recently reported a series of corresponding $[AlR_3]_n[CE]$ organoaluminum-aza[23-29] and -thia[30,31] macrocyclic ligand complexes. Additionally, we have examined multidentate phosphorus ligands in this regard.[32,33] The twelve-membered sulfur-based macrocycle $[12]aneS_4$ is of interest to us as it has been shown to form stable complexes with such transition metal ions as Cu(II).[8] This macrocycle was allowed to react with a five-fold excess of trimethylaluminum; $[Al(CH_3)_3]_4[12]aneS_4$ was the only product isolated. However, $[Al(CH_3)_3][12]aneS_4$[30] was produced when stoichiometric amounts of $Al(CH_3)_3$ and $[12]aneS_4$ were allowed to react.

TABLE IV
Organoaluminum compounds containing Al–S bonds.

Compound	Distance (Å)	Ref.
$[(CH_3)_2AlS(CH_3)_n$	2.328(2)	35
$K[Al_2(CH_3)_6SCN]$	2.489(2)	36
$[Al(CH_3)_3]_4[12]aneS_4$	2.515(1)	this study
$[Al(CH_3)_3]_4[14]aneS_4$	2.522(2)	33
$[Al(CH_3)_3][12]aneS_4$	2.718(3)	32

Several points are worthy of note regarding structure and bonding in $[Al(CH_3)_3]_4[12]aneS_4$. As can be seen from Figure 2, the title compound is situated about a crystallographic centre of symmetry. The four sulfur atoms, as well as the four aluminum atoms, each constitute a plane. The literature reveals a paucity of structural data for compounds containing Al–S bonds which have been characterized by X-ray diffraction techniques. When compared to other organoaluminum compounds containing Al–S bonds (Table IV) the independent Al–S distances of

2.530(1) Å and 2.500(1) Å for $[Al(CH_3)_3]_4[12]aneS_4$ (Table III) must be considered to constitute quite a substantial Al–S interaction. Interestingly, the Al–S distances found in the title compound are comparable to those found in the related (but larger) organoaluminum complex $[Al(CH_3)_3]_4[14]aneS_4$ (Table IV). Thus, the smaller thiacrown ether $[12]aneS_4$ is sufficiently flexible so as to facilitate strong Al–S interactions. These Al–S distances are placed in further perspective when one considers that the Al–S bond distance in the recently reported 1:1 (ligand:AlR_3)$[Al(CH_3)_3][12]aneS_4$[30] complex was determined to be 2.718(3) Å.

The most profound feature of $[Al(CH_3)_3]_4[12]aneS_4$, however, is the conformation of the macrocycle. Surprisingly, the conformation of $[12]aneS_4$ in the title compound is essentially endodentate. The conformational geometry of thiacrown ethers has been the subject of a recent study.[6] Unlike oxygen- and nitrogen-based crown ethers, whose donor atoms are directed towards the interior of the macrocyclic cavity (endodentate conformation), thiacrown ethers characteristically exhibit an exodentate conformation (the sulfur atoms directed towards the macrocyclic perimeter).[34] Even though $[12]aneS_4$ is depicted in Figure 1 in an endodentate conformation, X-ray crystal structure examinations of $[12]aneS_4$[6,30] have revealed the macrocycle to be in an exodentate conformation. The uncomplexed macrocycle resembles a "$(S–CH_2–CH_2–)_4$ square" with the four sulfur atoms at the corner positions. Cooper and co-workers[6] likened the structure of $[12]aneS_4$ to the fusion of two S–C–C–S–C–C–S "right triangle brackets". As evidenced by the non-bonded S–S contacts of 3.480(2) Å and 3.272(2) Å (for S(1)–S(2a) and S(1)–S(2), respectively) in $[Al(CH_3)_3]_4[12]aneS_4$ and the corresponding S–S contacts in the uncomplexed ligand of 4.458(4) Å and 6.242(3) Å, the macrocyclic cavity is substantially smaller in the title compound. Torsional angles for the title compound are given in Table V.

TABLE V
Torsional angles (deg) for $[Al(CH_3)_3]_4[12]aneS_4$.

Atoms				Angle
C1	S1	Al1	C5	−161.3
C1	S1	Al1	C6	−40.9
C1	S1	Al1	C7	77.8
C4a	S1	Al1	C5	−51.3
C4a	S1	Al1	C6	69.1
C4a	S1	Al1	C7	−172.1
C2	S2	Al2	C8	−43.7
C2	S2	Al2	C9	76.7
C2	S2	Al2	C10	−161.7
C3	S2	Al2	C8	−153.4
C3	S2	Al2	C9	−33.0
C3	S2	Al2	C10	88.6
Al1	S1	C1	C2	−134.6
C4a	S1	C1	C2	112.5
Al2	S2	C2	C1	94.2
C3	S2	C2	C1	−154.7
S1	C1	C2	S2	60.6
Al2	S2	C3	C4	−153.7
C2	S2	C3	C4	95.9
S2	C3	C4	S1A	−71.3

In the $[Al(CH_3)_3][12]aneS_4$ complex[30] the exodentate conformation of the macrocycle is essentially unperturbed. Importantly, while only one trimethylaluminum unit was accommodated by the macrocycle, the $Al(CH_3)_3$ unit was found to be planar and bridging two $[12]aneS_4$ macrocycles. The coordination geometry of the aluminum atom was thus described as trigonal bipyramidal.

The title compound represents the first example of an AlR_3 saturated $[AlR_3]_n[CE]$ complex where the macrocycle approaches an endodentate conformation. The associated steric strain in the ring coupled with slight changes in overall geometry serves to discourage the expected exodentate geometry. Additionally, crystal packing interactions of the molecule may also contribute to the observed conformation. If the ligand is flexible, the endodentate conformation could result in a more favourable packing of the macrocycle and the associated $Al(CH_3)_3$ units. The behaviour of thiacrown ethers in organoaluminum systems often yields unexpected results. Other studies are forthcoming.

ACKNOWLEDGEMENT

G.H.R. is grateful to the National Science Foundation for support of this work (RII-8520554).

SUPPLEMENTARY MATERIAL AVAILABLE

Summary of crystal data, tables of bond distances and angles, final fractional coordinates, and thermal parameters (13 pages) and a listing of observed and calculated structure factors (7 pages) are available from G.H.R.

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