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Structural survey of the organoaluminum coordination chemistry of oxygen and sulfur (thia) crown ethers

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CONTENTS

A. INTRODUCTION

The emergence of main group chemistry has proven to be quite significant in the continued development of inorganic chemistry. This renaissance in main group chemistry is appropriately underscored by a substantial increase in research activity of the chemistry of the Group 13 elements. The activity in the organometallic chemistry of Group 13 is due, arguably in large measure, to the potential utility of some compounds of these elements as single-source molecular precursors to advanced materials. As evidenced by J.M. Lehn, D.J. Cram, and C.J. Pedersen receiving the 1987 Nobel Prize in chemistry, the last decade has also witnessed the maturation of the inorganic coordination chemistry of macrocyclic ligands. Crown ethers are particularly attractive in this regard due to their unique ability to form stable complexes with a variety of metal ions. Although oxygen-based crown ethers were initially brought to the forefront of inorganic chemistry by the seminal contributions of Pedersen [1], sulfur-based crown ethers, thiacrown ethers, have also been shown to be effective complexing agents for transition metal ions [2]. It is noteworthy that the Group 13 chemistry of oxygen- and thia-crown ethers originated in the realm of host–guest chemistry. This contribution will review the coordination chemistry of aluminum with regard to oxygen and thia crown ethers. The crown ethers of interest are given in Fig. 1. Although the organoaluminum chemistry of nitrogen-based crown

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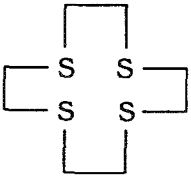

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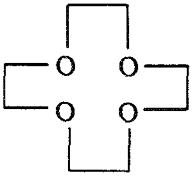

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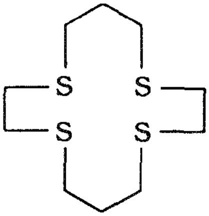

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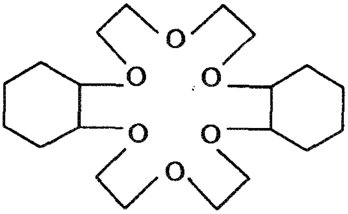

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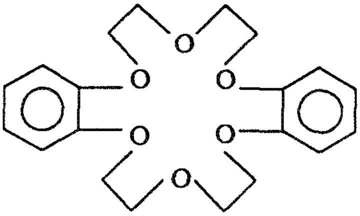

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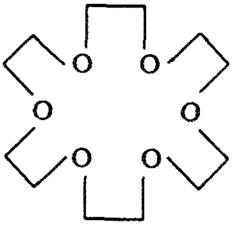

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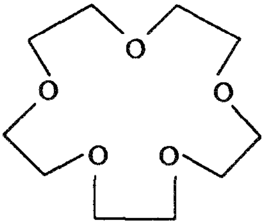

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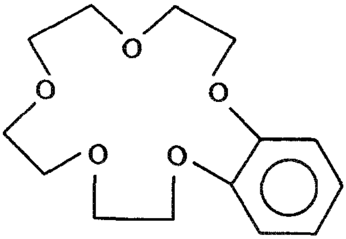


benzo-15-crown-5

Fig. 1. Oxygen and sulfur crown ethers.

ethers has been the subject of numerous recent studies, this area will not be addressed in this contribution.

B. ORGANOALUMINUM HOST–GUEST CHEMISTRY

(i) Liquid clathrates

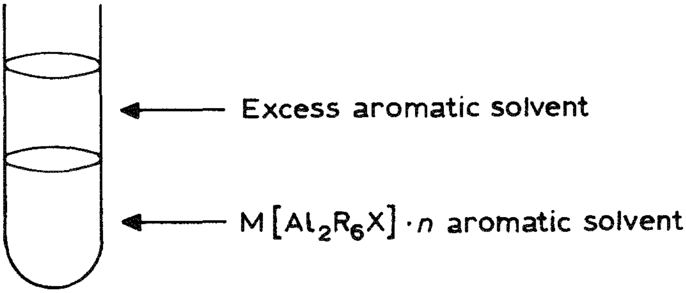
The origins of the interactions of aluminum species with crown ethers may be traced to organoaluminum host–guest chemistry. The essential experiments, performed by Ziegler in 1960 [3], concerned the reactions of neat R_3Al with MX (M = alkali-metal ion or tetraalkylammonium ion; X = halide or pseudohalide ion). These reactions were shown to result in 1:1 (eqn. (1)) or 1:2 (eqn. (2)) compounds which were isolated as white, extremely air-sensitive solids.

$$MX + R_3Al \rightarrow M[AlR_3X] \qquad (1)$$

$$MX + 2R_3Al \rightarrow M[Al_2R_6X] \qquad (2)$$

These reactions were studied by Atwood and coworkers more than a decade later. However, instead of performing the reactions in neat aluminum alkyls, aromatic solvents were employed as reaction solvents. The addition of toluene as the solvent to the $M[Al_2R_6X]$ complex (eqn. (2)) resulted in a visually dramatic event: the formation of two immiscible liquid layers [4]. ^1H NMR studies revealed that the lower, denser layer was composed of the aromatic solvent "complexed" with the $M[Al_2R_6X]$ moiety. The upper layer was shown to consist of only the aromatic solvent. The number of aromatic molecules associated with each $M[Al_2R_6X]$ moiety could be determined from integration of the aromatic protons relative to the aluminum alkyl protons in the ^1H NMR spectra. This ratio was termed the "aromatic to anion ratio" [5]. Importantly, upon cooling to $-78°$ C, the $M[Al_2R_6X]$ species was shown to crystallize, thereby surrendering the aromatic molecules. These $M[Al_2R_6X] \cdot n$ aromatic compounds thus had the characteristics of a unique type of host–guest system. The similarity of the solution behavior of these non-stoichiometric liquid host–guest compounds to classical solid-state clathrate systems was so pronounced that these compounds became known as "liquid clathrates." The term liquid clathrates, therefore, denotes a class of liquid non-stoichiometric inclusion compounds which form upon the interaction of aromatic molecules (guests) with certain $M[Al_2R_6X]$ moieties (hosts). A schematic representation of the liquid clathrate phenomena is illustrated below.

Although M was initially restricted to alkali metal ions, as the field advanced M was shown to encompass such ions as Me_2Tl^{3+} [6], $(C_6H_6)_2Cr^{4+}$, or $(C_5H_5)_2Co^{4+}$ [7]. Similarly, the range of X was subsequently extended beyond the initial restriction of halides or pseudohalides to include such ions as NO_3^- [8], O_2^- [9] or CH_3COO^- [10].



(ii) Application of liquid clathrates

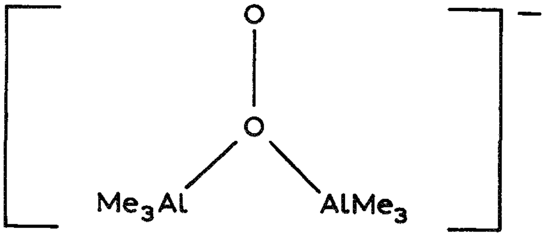
A variety of potential guest moieties have been examined relative to liquid clathrates. As liquid clathrates only form in the presence of aromatic solvents (as guests), one of the first applications of these compounds was the separation of aromatic molecules. If the M[Al_2R_6X] compound is exposed to two (or more) aromatic solvents of significantly different sizes, the organoaluminum inclusion compound will proportionally interact with more of the smaller aromatic at the expense of the larger. One may thus envisage a multi-step process wherein a pure aromatic fraction may be obtained. Liquid clathrates have also shown promise in the area of coal liquefaction where these compounds have effectively extracted significant amounts of coal material [11]. A third area where liquid clathrates have shown promise is optical resolution. A class of optically active liquid clathrates based on the optically active quaternary ammonium salt (S)-(−)-α-[(Ph)CHMeN(Me)$_3$I] has been reported [12].

C. REACTION OF R_3Al WITH OXYGEN-BASED CROWN ETHERS

The lattice energy, as reported by Atwood and Cummings [13], was a major consideration in the choice of MX. These workers pointed out that, in order for liquid clathrate formation to occur, the lattice energy of MX had to be sufficiently low such that it could be overcome at such a temperature that both MX and the ensuing M[Al_2R_6X] compound were stable. As a result of this limitation, many interesting MX species were initially excluded from examination. In an effort to further extend the range of MX species capable of demonstrating liquid clathrate behavior, Atwood and coworkers endeavored to employ the metal ion complexing ability of macrocyclic polyethers, oxygen-based crown ethers. Atwood and coworkers [14] reported the first synthesis of an M[Al_2R_6X] species that employed a crown ether in 1981. The synthesis concerned the preparation of a potassium superoxide-based liquid clathrate

$$KO_2 + 2Me_3Al + \text{dibenzo-18-crown-6} \rightarrow [K\cdot\text{dibenzo-18-crown-6}][Al_2Me_6O_2] \quad (3)$$

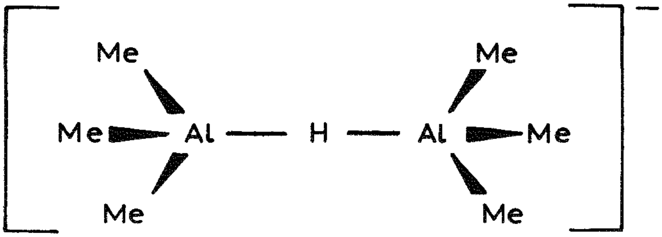
As the crown ether was shown simply to complex the potassium ion, the major point of interest was the structure of the anion. Initially, due to charge balance, the authors regarded the dioxygen moiety in the $[Al_2Me_6O_2]^-$ anion as a superoxide species. Single crystal X-ray diffraction studies of the anion revealed that it exhibited an unusual coordination mode for a metal dioxygen species. The X-ray crystal structure of the $[Al_2Me_6O_2]^-$ anion revealed that the two R_3Al moieties were bridged in the fashion



As the non-bridging oxygen atom in $[Al_2Me_6O_2]^-$ experienced considerable thermal motion in the solid state, the O–O bond distance could not be determined with great accuracy. The O–O bond distance was found to approach 1.47(2) Å. The rather long O–O bond was also supported by the IR spectrum (Nujol mull) in which the ν_{O-O} stretch was observed at 851 cm^{-1}. In support, the authors cited the resonance Raman spectrum of oxy emerythrin, performed by Shriver and coworkers [15] in which the O–O stretch was observed at 844 cm^{-1}. The Al–O bond distances were found to be 1.852(9) and 1.868(9) Å. The fact that the Al–O–Al bond angle of 128.3(7)° in $[Al_2Me_6O_2]^-$ was found to be comparable with the corresponding Al–N–Al bond angle in $K[Al_2Me_6N_3]$ (where two aluminum atoms are bridged by a terminal nitrogen atom of the azide ion) (129.0(3)°) [16] added support to the argument of the authors.

Subsequent to the superoxide study, Atwood and coworkers reported that reaction of sodium hydride with trimethylaluminum and 15-crown-5 in toluene afforded $Na[Me_3Al(H)AlMe_3]$ [17]. The structure of the $[Me_3Al(H)AlMe_3]^-$ anion was most striking as it was found to consist of a linear (180°) Al–H–Al linkage. The structure of the $[Me_3Al(H)AlMe_3)^-$ anion is shown below.

The Al–H bond distance of 1.65 Å was cited as being comparable with that found in the electron-deficient bridge for the dimethylaluminum hydride dimer, $[(CH_3)_2AlH]_2$ [18]. An examination of B–H–B fragments underscores the significance of the linear Al–H–Al linkage in $Na[Me_3Al(H)AlMe_3]$. The literature reveals



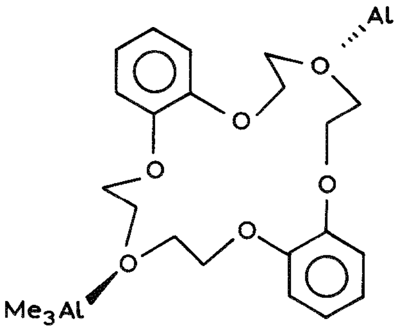
only one other crystal structure of a hydrogen atom bridging two Group 13 elements, $K[(C_4H_8)_2B_2H_3]$ [19]. The B–H–B bond angle in $[(C_4H_8)_2B_2H_3]^-$ was determined to be non-linear at 140°.

The absence of the 15-crown-5 crown ether in the $Na[Me_3Al–H–AlMe_3]$ reaction product was curious. Reaction was reportedly immediate, resulting in liquid clathrate formation. Crystals of $Na[Me_3Al–H–AlMe_3]$ reportedly began forming at this stage along the walls of the reaction vessel. In terms of a reaction mechanism accounting for the absence of 15-crown-5 in the reaction product, the following sequence of events was cited: (a) the initial formation of 1 mmol of [Na·15-crown-5]$[Me_3Al(H)AlMe_3]$ followed by the dissolution of NaH, which in turn reacted with the available Me_3Al; (b) the crown-ether-free $Na[Me_3Al–H–AlMe_3]$, being of lower solubility than the crown-ether-containing analogue, was able to crystallize out of solution.

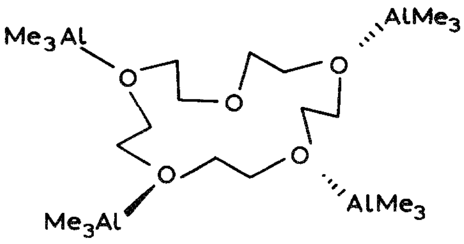
Aside from the synthesis and structure of $Na[Me_3Al(H)AlMe_3]$, this study had added significance as it was here that these workers first suggested that the crown ethers in these systems, in addition to complexing the cations of MX and thus increasing the solubility of MX in aromatic solvents, may play a less obvious, more subtle role. In 1982, Atwood and coworkers confirmed their suspicions of their oversimplification of the crown ether–MX interactions by reporting the synthesis and structures of two neutral organoaluminum-crown ether complexes: [dibenzo-18-crown-6]$[Me_3Al]_2$ and [15-crown-5]$[Me_3Al]_4$ [20]. The preparation of the aluminum alkyl–crown ether complexes entailed reaction of stoichiometric quantities of the two crown ethers with trimethylaluminum in toluene. While liquid clathrate formation was reported to occur upon introduction of the aluminum alkyl–crown ether complex, $CE[R_3Al]_n$, to the appropriate MX species, the aluminum alkyl–crown ether complexes proved to be stable, discrete molecular complexes in the absence of MX. The preparation of $CE[R_3Al]_n$ and subsequent formation of the organoaluminum-based liquid inclusion compounds is given by the equation

$$CE + nR_3Al \rightarrow CE[R_3Al]_n\text{–}MX \rightarrow [M\cdot CE][Al_2R_6X]\cdot n\ \text{aromatic} \qquad (4)$$

The structures of [dibenzo-18-crown-6]$[Me_3Al]_2$ (a) and [15-crown-5]$[Me_3Al]_4$ (b) are



(a)



(b)

Several points are worthy of note regarding structure and bonding in these two compounds. The six oxygen atoms of the crown ether in the dibenzo-18-crown-6 compound assumed a chair configuration so as to accommodate better the two Me_3Al units. The four oxygen atoms of the two catechol units of the crown were coplanar. With ratios as high as 5:1 (Me_3Al:dibenzo-18-crown-6), only the 2:1 compound was isolated. It was postulated that the benzo rings imparted sufficient steric demands on the remaining four oxygen atoms so as to prevent the formation of a third Me_3Al adduct. However, the crown ether demonstrated efficacious flexibility so as to allow substantial Al–O interaction resulting in short Al–O bonds. The Al–O bond distance was determined to be 1.967(3) Å. The magnitude of this Al–O bond may best be appreciated when one considers that the Al–O bond distance in [*p*-dioxan][Me_3Al]$_2$ was 2.02(2) Å [21]. The 15-crown-5 compound proved interesting in that the four Me_3Al units effectively turned the crown ether "inside out." In the process, the fifth oxygen atom of 15-crown-5 was forced towards the inner cavity, thereby preventing the formation of a fifth Me_3Al adduct. It was argued that the steric constraints were greater in the 15-crown-5 compound than in the dibenzo-18-crown-6 compound as the independent Al–O bond distance in the former was determined to be 2.005(6) Å. In a following study, Atwood and coworkers reported the synthesis and structure of [18-crown-6][Me_3Al]$_4$ and [dibenzo-18-crown-6][Me_3Al]$_3$ [22]. These two compounds were structurally very similar to the first two organoaluminum-crown ether compounds discussed. Table 1 provides a list of R_3Al–oxygen crown ether compounds.

The isolation of CE[R_3Al]$_n$ compounds underscored three important points: (1) In the absence of MX, CE[R_3Al]$_n$ compounds are stable discrete molecular complexes; (2) upon introduction of the appropriate MX species, the crown ether serves as a means of transport of R_3Al to the X^- species while the crown ether then returns to its traditional role of complexing the M^+ ion, resulting in [M·CE][Al_2R_6X]; (3) owing to the great Al–O bond strength and the relative flexibility of the crown ethers, aluminum alkyls demonstrated the ability essentially to turn the crown ether inside out.

TABLE 1

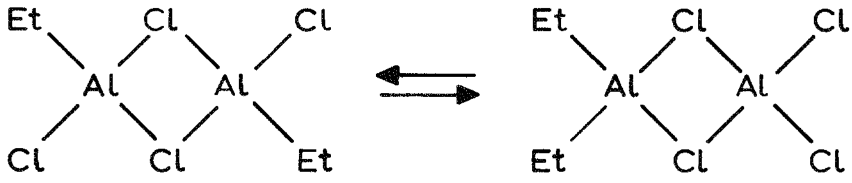
$[R_3Al]_n[CE]$ complexes

Compound	Al–O distance (Å)	Ref.
$[Me_3Al]_2$[dibenzo-18-crown-6]	1.967(3)	20
$[Me_3Al]_3$[dibenzo-18-crown-6]	1.982(5) 2.024(5) 1.972(5)	22
$[Me_3Al]_4$[18-crown-6]	1.985(6)	22
$[Me_3Al]_4$[15-crown-5]	2.005(6)	20
$[Me_3Al]_2$[12-crown-4]	1.977(3)	23
$[Et_3Al]_2$[dibenzo-18-crown-6]	1.978(7)	24
$[Et_3Al]_4$[18-crown-6]	2.00(1)	24
$[Me_3Al]_2$[dicyclohexyl-18-crown-6]	1.960(8) 1.936(8)	25

D. REACTION OF ALKYLALUMINUM HALIDES WITH OXYGEN-BASED CROWN ETHERS

The organoaluminum host–guest chemistry proved particularly fruitful. However, as this field advanced, considerably more attention was placed on the organoaluminum chemistry of crown ethers and less on organoaluminum host–guest chemistry. In an effort to explore the former further, Atwood and coworkers endeavored to investigate the chemistry of alkylaluminum halides, R_nAlX_{3-n}, with crown ethers.

The initial study in this regard concerned reaction of 12-crown-4 and 18-crown-6 with ethylaluminum dichloride in toluene. Formation of the liquid clathrate effect was observed after a short period of time. Slow cooling of the respective solutions to 5° C afforded colorless, air-sensitive crystals of the respective compounds. The reaction products, as determined from single crystal diffraction, were shown to be [12-crown-4·$AlCl_2$][Cl_3AlEt] and [18-crown-6·$AlCl_2$][Cl_3AlEt], respectively [26]. The structures of the [12-crown-4·$AlCl_2]^+$ and [18-crown-6·$AlCl_2]^+$ cations of the two products are shown in Figs. 2 and 3, respectively. Moreover, the octahedral coordination of the two aluminum atoms in the cations of the two products was unforeseen. The generation of the Cl_2Al^+ cation was traced to the nature of alkylaluminum halides. Although ethylaluminum dichloride is generally taken to exist as a symmetric dimeric species, the authors suggested that an interconversion process may occur which is similar to



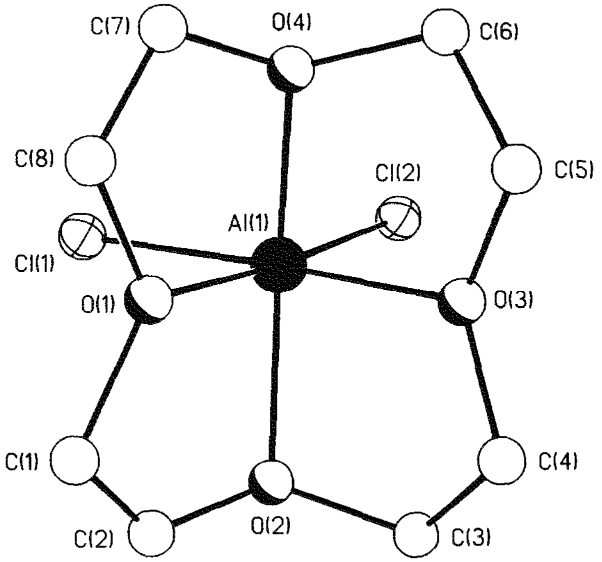


Fig. 2. View of the [12-crown-4·$AlCl_2$]$^+$ cation. Selected bond distances (Å) and angles (deg): Al(1)–P(1), 1.97(1); Al(1)–O(2), 1.97(1); Al(1)–O(3), 1.99(1); Al(1)–O(4), 1.92(1); Al(1)–Cl(1), 2.202(5); Al(1)–Cl(2), 2.200(8); Cl(2)–Al(1)–Cl(1), 92.2(3); Cl(1)–Al(1)–O(1), 88.0(3); Cl(2)–Al(1)–O(1), 176.0(4); Cl(1)–Al(1)–O(2), 97.9(4); Cl(2)–Al(1)–O(2), 107.4(5); Cl(1)–Al(1)–O(3), 172.3(4); Cl(2)–Al(1)–O(3), 95.5(4); Cl(1)–Al(1)–O(4), 99.5(4); Cl(2)–Al(1)–O(4), 99.2(4); O(1)–Al(1)–O(2), 76.5(5); O(1)–Al(1)–O(3), 84.3(4); O(1)–Al(1)–O(4), 76.8(4); O(2)–Al(1)–O(3), 79.6(5); O(2)–Al(1)–O(4), 147.5(5); O(3)–Al(1)–O(4), 79.5(5).

It was suggested that asymmetric cleavage of the asymmetric dimer could afford the Cl_2Al^+ cation as well as $Cl_2AlEt_2^-$ anions. Lastly, the authors indicated that the isolation of the [Cl_3AlEt]$^-$ anion in the reaction products was a matter of solubility.

The Al–Cl bonds in [12-crown-4·$AlCl_2$]$^+$ were found to be rather long with values of 2.200(8) and 2.202(5) Å. The mean Al–Cl bond distance in the [Cl_3AlEt]$^-$ anion was 2.12(1) Å. The mean Al–O bond distance of 1.96(2) Å is within the expected range of normal donor–acceptor complexes of aluminum. The ramifications of the larger crown ether in [18-crown-6·$AlCl_2$]$^+$ were most obvious in the wide range of bond distances observed. The Al–Cl bond distances were found to be 2.148(3) and 2.210(2) Å. The Al–O bond distances were also found to fall within a wide range, 1.946(5)–2.065(4) Å.

The size of the crown ether proved to be critical in determining the nature of the reaction product. For example, reaction of ethylaluminum dichloride with benzo-15-crown-5 in toluene initially results in the liquid clathrate effect [27]. Upon standing undisturbed, crystals formed in the lower layer of the system. The reaction product was determined to be [benzo-15-crown-5·$AlCl_2$][Cl_3AlEt]. Unlike the reaction products resulting from reaction of ethylaluminum dichloride with 12-crown-4 or 18-crown-6, where the aluminum atom of the cation was found to be six-coordinate, the aluminum atom in the [benzo-15-crown-5·$AlCl_2$]$^+$ cation was found to be

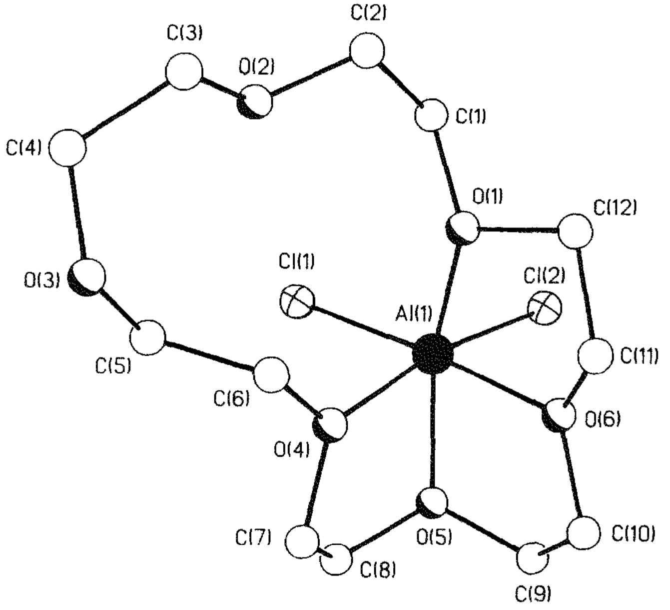
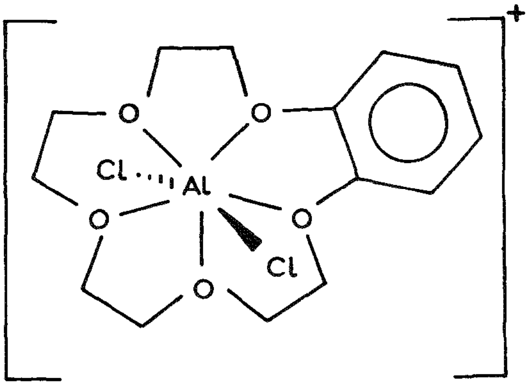


Fig. 3. View of the [18-crown-6·$AlCl_2$]$^+$ cation. Selected bond distances (Å) and angles (deg): Al(1)–Cl(1), 2.148(3); Al(1)–Cl(2), 2.210(2); Al(1)–O(1), 1.946(5); Al(1)–O(4), 2.065(4); Al(1)–O(5), 1.961(6); Al(1)–O(6), 1.976(4); Cl(1)–Al(1)–Cl(2), 96.8(1); Cl(1)–Al(1)–O(1), 101.4(2); Cl(2)–Al(1)–O(1), 96.1(1); Cl(1)–Al(1)–O(4), 89.4(1); Cl(2)–Al(1)–O(4), 171.5(2); O(1)–Al(1)–O(4), 88.3(2); Cl(1)–Al(1)–O(5), 100.1(2); Cl(2)–Al(1)–O(5), 94.6(2); O(4)–Al(1)–O(5), 78.5(2); Cl(1)–Al(1)–O(6), 173.4(2); Cl(2)–Al(1)–O(6), 89.78(1); O(1)–Al(1)–O(6), 78.7(2); O(4)–Al(1)–O(6), 84.0(2); O(5)–Al(1)–O(6), 78.5(2).

seven-coordinate. As the aluminum atom was found to be coplanar with the five oxygen atoms of the crown ether while the two chlorine atoms were found to reside in axial positions, the coordination of the aluminum atom was described as pentagonal bipyramidal. Two Al–O bonds adjacent to the benzo ring were reported to be a bit longer than the other three Al–O bonds (2.28(1), 2.30(1), 2.03(1), 2.06(1), and 2.08(1) Å, respectively). The [benzo-15-crown-5·$AlCl_2$]$^+$ cation represented a rare structurally characterized seven-coordinate aluminum complex. The Al–Cl bond distances of 2.200(3) Å compared with 2.143(6) Å in the anion. The driving force given by the authors to account for the fact that the aluminum atom in the [benzo-15-crown-5·$AlCl_2$]$^+$ cation is seven-coordinate while the aluminum atoms in [12-crown-4·$AlCl_2$]$^+$ and [18-crown-6·$AlCl_2$]$^+$ are six-coordinate is the relative ratio of the Al^{3+} ion to the crown ether cavity.

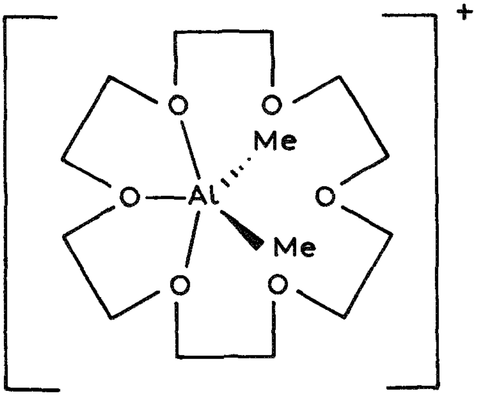
To this point in the development of this chemistry, the organoaluminum moiety was always associated with the anionic species. In an effort to facilitate interaction of the organoaluminum species with the cationic species as well as explore the role of cationic organoaluminum moieties relative to Ziegler–Natta aluminoxane systems, Atwood and coworkers allowed Cp_2TiCl_2 to react with Me_3Al and 18-crown-6 in



toluene [28]. The balanced equation of this reaction is

$$Cp_2TiCl_2 + 2Me_3Al + 18\text{-crown-6} \rightarrow [18\text{-crown-6} \cdot AlMe_2][Me_2AlCl_2] + Cp_2TiMe_2 \qquad (5)$$

The most striking feature of the compound is the structure of the [18-crown-6·AlMe$_2$]$^+$ cation



The coordination of the aluminum atom was described as five-coordinate residing in a distorted trigonal bipyramidal environment. The Al–O bond distances were found to be 1.929(5), 2.181(5), and 2.435(5) Å. The authors conceded that, while the last of these Al–O interactions is very long, it may still be considered a formal bond. The Al–C bonds in the cation, were cited as rather short at 1.915(6) and 1.939(7) Å, while those in the anion were reported as 2.005(7) and 2.053(6) Å.

In the same study, the authors also reported the corresponding 15-crown-5 product according to eqn. (5), [15-crown-6·AlMe$_2$][Me$_2$AlCl$_2$]. While the crown ether was found to experience substantial crystallographic disorder, the authors were able to determine that the aluminum atom of the cation could be regarded as seven-coordinate in a pentagonal bipyramidal geometry. Indeed, the overall structure of $[15\text{-crown-6}\cdot AlMe_2]^+$ is very similar to the $[\text{benzo-15-crown-5}\cdot AlCl_2]^+$ cation previously discussed.

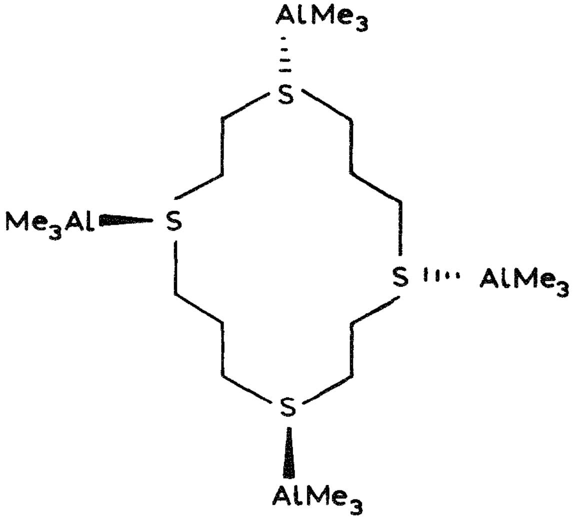
E. REACTION OF R_3Al WITH SULFUR-BASED (THIA) CROWN ETHERS

The organoaluminum chemistry of sulfur-based crown ethers, thiacrown ethers, represented a natural extension of the work with oxygen crown ethers. The organoaluminum chemistry of non-cyclic sulfur-based ligands, however, has not been developed to a significant extent. Indeed, the literature reveals a paucity of aluminum–sulfur compounds characterized by single crystal X-ray diffraction techniques.

The initial study in the organoaluminum chemistry of thiacrown ethers, performed by Robinson et al., concerned the reaction of excess Me_3Al with $[14]aneS_4$ in toluene [29]. A quantitative yield of the crystalline reaction product $[14]aneS_4[Me_3Al]_4$ was isolated according to the equation

$$[14]aneS_4 + 4Me_3Al \rightarrow [14]aneS_4[Me_3Al]_4 \qquad (6)$$

The product was isolated as colorless, extremely air-sensitive crystals. A single crystal X-ray study of $[14]aneS_4[Me_3Al]_4$ confirmed a structure similar to



This compound represented the first reported Group 13-thiacrown ether complex. The compound was found to reside about a crystallographic center of symmetry. All four sulfur atoms were observed to be coplanar. The non-bonding distances between the sulfur atoms ranged from 4.287 to 6.260 Å. The mean S–C distance was 1.816 Å.

The independent Al–S bond distances were found to be 2.512(2) and 2.531(2) Å. As the literature revealed only two other organometallic compounds containing Al–S bonds that had been characterized by X-ray diffraction methods, namely $[Me_2AlSCH_3]_n$ (Al–S = 2.348 Å) [30] and $K[Al_2Me_6SCN]$ (Al–S = 2.489(2) Å) [31], it was difficult to place the Al–S distances observed in $[14]aneS_4[Me_3Al]_4$ in a meaningful perspective.

The $[14]aneS_4$ thiacrown proved interesting as its conformation with transition metal ions was shown to vary widely. For example, with $Hg(ClO_4)_2 \cdot xH_2O$, $[14]aneS_4$ was observed to assume an endodentate conformation (the four sulfur atoms being directed towards the central cavity of the crown). However, the exodentate conformation was observed with $[14]aneS_4$ when it was introduced to an excess of $HgCl_2$ [32] and $NbCl_5$ in $[14]aneS_4[NbCl_5]_2$ [33]. The thiacrown assumed the exodentate conformation in $[14]aneS_4[Me_3Al]_4$. It is important to note that the uncomplexed $[14]aneS_4$ thiacrown was found to exist in both *endo* and *exo* conformations in the solid state [34]. This behavior is in stark contrast to that of oxygen crown ethers where the uncomplexed crown ethers are endodentate exclusively.

The organoaluminum chemistry of the smaller $[12]aneS_4$ thiacrown ether was also examined. In spite of reaction of a four-fold excess of Me_3Al with $[12]aneS_4$ in toluene, only the 1:1 crystalline complex $[12]aneS_4[Me_3Al]$ was isolated [35]. All four sulfur atoms were found to be coplanar. A view of the $[12]aneS_4[Me_3Al]$ molecule is given in Fig. 4. The Al–S distance of 2.718(3) Å in $[12]aneS_4[Me_3Al]$ was regarded as exceedingly long. For comparative purposes, the authors cited the

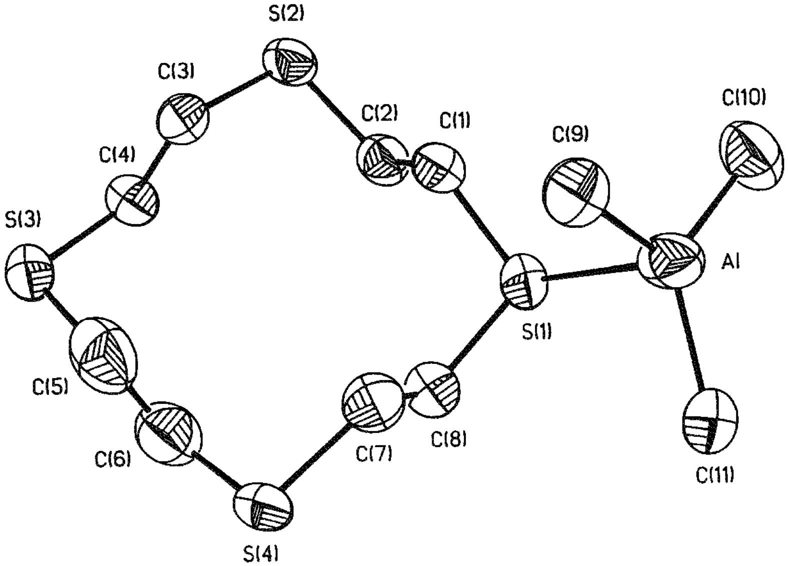


Fig. 4. View of the $[12]aneS_4[Me_3Al]$ complex.

predicted Al–S distance of 2.34 Å by Pauling [36]. It was particularly noteworthy that the aluminum atom and the three carbon atoms of the Me_3Al unit were found to be coplanar. The unusual character of the Me_3Al moiety prompted the workers to examine the cell packing diagram. The unit cell of [12]aneS_4[Me_3Al] (Fig. 5) proved very informative. A secondary Al–S interaction with a neighboring [12]aneS_4-[Me_3Al] complex was observed (broken line) at a distance of 3.052(3) Å. This secondary interaction, along with the shorter Al–S bond, was suggested as playing an important role in the planarity of the Me_3Al moiety. Essentially, the Me_3Al moiety approached planarity as the aluminum atom was approached on either side by a thiacrown ether. The environment about the aluminum atom was viewed as five-coordinate as the planar Me_3Al unit was stabilized by two [12]aneS_4 units in axial positions. The coordination was described as distorted trigonal bipyramidal. Indeed, considering the situation in the unit cell, the compound was regarded as a $\{[12]\text{aneS}_4 \cdot \text{AlMe}_3\}_n$ oligomer.

A subsequent study with [12]aneS_4 revealed some unexpected behavior. Reaction of [12]aneS_4 with a twelve-fold excess of Me_3Al in toluene afforded the [12]aneS_4[Me_3Al]$_4$ saturated product. The independent Al–S bond distances were found to be 2.530(1) and 2.500(1) Å. These Al–S bonds are comparable with those observed in the larger [14]aneS_4 thiacrown ether previously discussed. The most profound feature of [12]aneS_4[Me_3Al]$_4$ is the approximate endodentate conformation of the thiacrown.

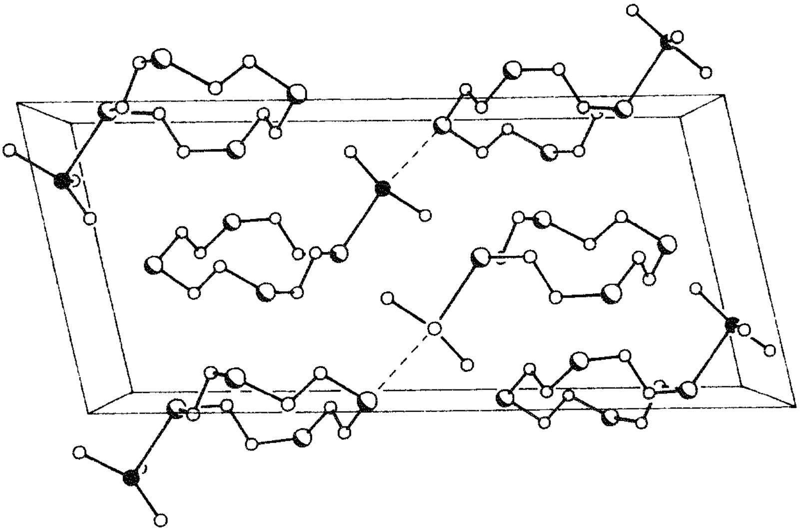
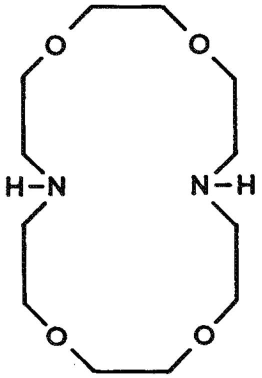


Fig. 5. Crystal packing diagram of [12]aneS_4[Me_3Al] viewed along the *b* axis. The broken line indicates a secondary interaction.

F. REACTION OF DIETHYLALUMINUM CHLORIDE WITH DIAZA-18-CROWN-6

Lewis acid–Lewis base adduct formation is a fundamental cornerstone of the chemistry of aluminum. While many of the compounds discussed thus far in this contribution may be regarded as quite novel from a coordination perspective, on a rudimentary level these compounds may be viewed as simple Al–O or Al–S Lewis acid–Lewis base adduct products. Although not the subject of this contribution, one of the most celebrated areas of the chemistry of aluminum is the interaction of aluminum species with various amines. Reactions of organoaluminum species with primary and secondary amines have long been known to eliminate alkane and afford products possessing extensive Al–N association [37]. Reactions of organoaluminum species with nitrogen-based crown ethers (azacrowns) containing N–H moieties have been examined. These systems eliminate alkane and often result in products containing aluminum in unusual coordination environments [38]. As the behavior of azacrown ethers is considerably different from that of oxygen or thiacrown ethers, Robinson and coworkers endeavoured to examine the organoaluminum chemistry of a crown ether which possessed both adduct formation capabilities as well as the potential for condensation. The oxygen–nitrogen mixed donor crown ether 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, diaza-18-crown-6 (below), offered a convenient probe as it contains both types of donor species.



Reaction of an excess of Et_2AlCl with diaza-18-crown-6 in toluene afforded the crystalline complex [diaza-18-crown-6·$(AlEt)_2$][$EtAlCl_3$]$_2$ in high yield [39]. A view of the [diaza-18-crown-6·$(AlEt)_2$]$^{2+}$ cation is provided in Fig. 6.

The most prominent feature of the [diaza-18-crown-6·$(AlEt)_2$]$^{2+}$ cation concerned the coordination of the aluminum atoms. The coordination sphere of each of the two aluminum atoms is composed of two oxygen and two nitrogen atoms of the crown. With these four atoms constituting a plane with the remaining ethyl group residing in an apical position, the coordination environment about each of the two aluminum atoms was described as square pyramidal. The cation was also found to

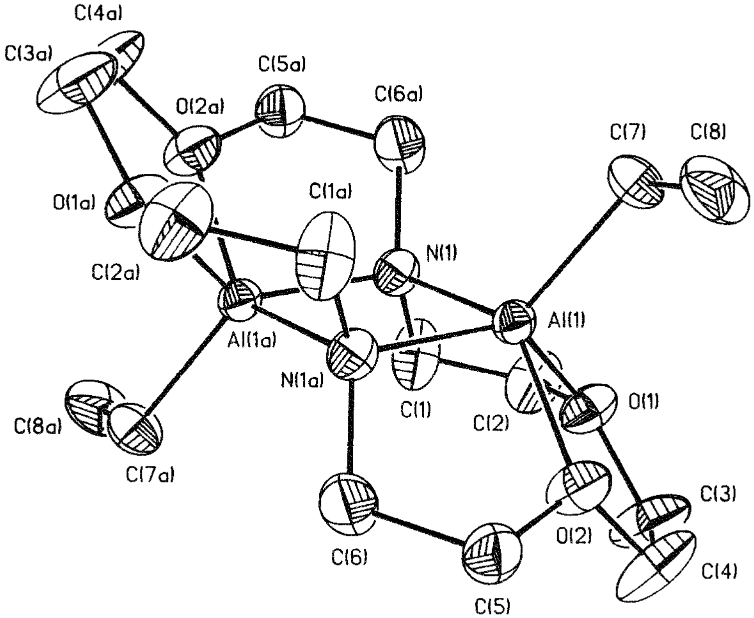
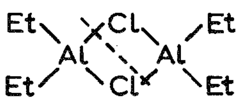


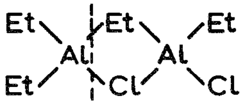
Fig. 6. View of the [diaza-18-crown-6$\cdot$(AlEt)$_2$]$^{2+}$ cation. Selected bond distances (Å) and angles (deg.): Al(1)–C(7): 1.944(5); Al(1)–O(1): 1.950(5); Al(1)–O(2): 1.959(5); Al(1)–N(1): 1.972(3); Al(1)–N(1a); 1.963(4); Al(1)–Al(1a): 2.902(3); C(7)–Al(1)–N(1): 114.5(2); C(7)–Al(1)–N(1a): 117.1(2); C(7)–Al(1)–O(1): 108.9(2); C(7)–Al(1)–O(2): 106.3(2); O(1)–Al(1)–N(1): 82.9(2); O(1)–Al(1)–O(2): 76.9(2); N(1)–Al(1)–N(1a): 85.0(2); O(2)–Al(1)–N(1a): 83.3(2); Al(1)–C(7)–C(8): 117.2(5).

reside about a crystallographic center of symmetry located about the center of the Al_2N_2 four-membered ring. The Al–N–Al bond angle of 95.0(2)° compared with 85.0(2)° for the N–Al–N bond angle. The Al(1)–C(7) bond distance of 1.944(5) Å compared well with other five- [40] and six-coordinate [41] organoaluminum species.

The authors suggested an interesting disproportionation of diethylaluminum chloride, wherein Et_2Al^+ and $EtAlCl_3^-$ were generated, as a plausible mechanism to account for the preparation of [diaza-18-crown-6$\cdot$(AlEt)$_2$][$EtAlCl_3$]$_2$. The central point in the mechanism was the nature of the dimeric organoaluminum species. The authors pointed out that, while the symmetric bridge cleavage of the dihalo-bridged dimers (**I**) is commonly accepted, asymmetric bridge cleavage of mixed halide–alkyl bridged dimers (**II**) is seldom encountered. However, asymmetric cleavage of (**II**) could easily afford Et_2Al^+ and $Et_2AlCl_2^-$. It was deemed reasonable that the Et_2Al^+ species could react with the crown ether to produce the [diaza-18-crown-6$\cdot$(AlEt)$_2$]$^{2+}$ cation. Symmetric cleavage of the same chloro-ethyl bridged diethylaluminum chloride dimer (**III**) would result in Et_3Al and $EtAlCl_2$. The authors reasoned that the $EtAlCl_3^-$ anion could result from reaction of $Et_2AlCl_2^-$ with $EtAlCl_2$. Indeed, similar disproportionations of alkylaluminum halides as a means to afford the stronger Lewis acid species was proposed by Ziegler more than 30 years ago [42].



(I)



(II)

(III)

G. CONCLUSIONS

Organoaluminum coordination chemistry has made great strides in the last decade. Once thought to be predictable and generally unremarkable, the coordination of aluminum has been shown to demonstrate great versatility. No longer is four-coordinate tetrahedral the chief mode of aluminum coordination. Five-coordinate trigonal bipyramidal and square pyramidal and even six-coordinate aluminum complexes are becoming almost commonplace. Furthermore, oxygen-based crown ethers demonstrate fundamentally different behavior towards organoaluminum species compared with sulfur-based crown ethers. Certainly it is clear that, under appropriate circumstances, the organometallic coordination chemistry of aluminum can be quite surprising. It is anticipated that the next decade will afford more discoveries in this area.

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