

Invited review

Group 13 organometallic chalcogen derivatives: their structures and behavior in solution

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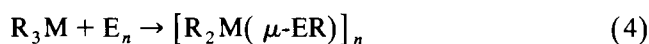
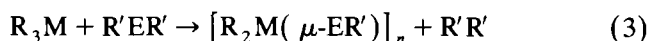
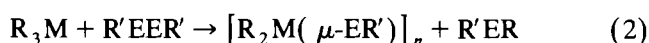
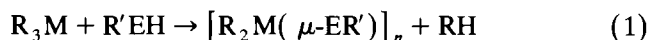
Abstract

The syntheses, structures and equilibria which occur for 13–16 organometallic compounds are reviewed. The organoaluminum thiolates form dimers, trimers, and tetramers with central (AlS)₂, (AlS)₃, and (AlS)₄ rings in the solid state. The structures of the gallium and indium thiolates are dominated by dimers, but a tetramer has been observed for gallium and a trimer for indium. Only dimeric derivatives have been reported for the selenium and tellurium derivatives. In hydrocarbon solutions, the aluminium thiolates establish equilibria between different aggregates and conformations with dimers and trimers most common. In the dimeric derivatives, [Me₂Al(μ-SMe)]₂ and [Me₂Al(μ-SeMe)]₂, *syn* and *anti* conformations are observed in solution at low temperature by NMR spectroscopy. In the trimeric derivatives, the chair conformation is observed in the solid state. In solution, a chair to chair inversion occurs with the rate dependent on the substituents bound to the sulfur.

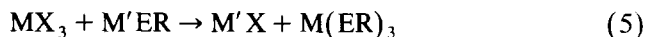
Keywords: Group 13; Aluminium; Indium; Gallium; Chalcogens; Fluxionality

The chemistry of organometallic compounds of the elements of Groups 13–16 has been studied for many years. A number of early reports described the synthesis and the chemical and physical properties of these compounds [1–4]. These reports provided details on several methods for the synthesis of such compounds and some studies on the chemical reactivity, but little information on their structures or behavior in solution. To rectify this, we started a systematic study of their properties and, specifically, to obtain information about the solid-state structures and the aggregation states of these derivatives in solution.

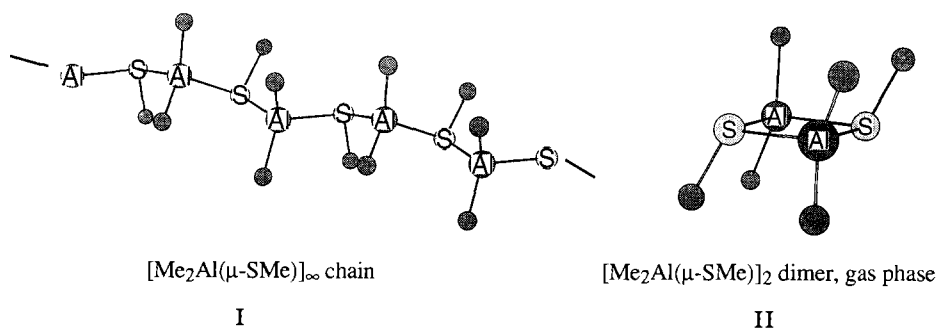
We have found that most of the compounds of interest may be obtained by one or more of the following reactions:



All of these methods were described earlier in the literature cited above. We have extended the use of these reactions to a wide variety of R and R' moieties to prepare the [R₂M(μ-ER)]_n derivatives. Alternative routes, such as salt elimination, shown in Eq. (5), have been used by others, especially for the synthesis of the M(ER)₃ derivatives [5], but the reactions shown in Eqs. (1)–(4) are generally applicable and give high yields under most circumstances, making them the methods of choice.

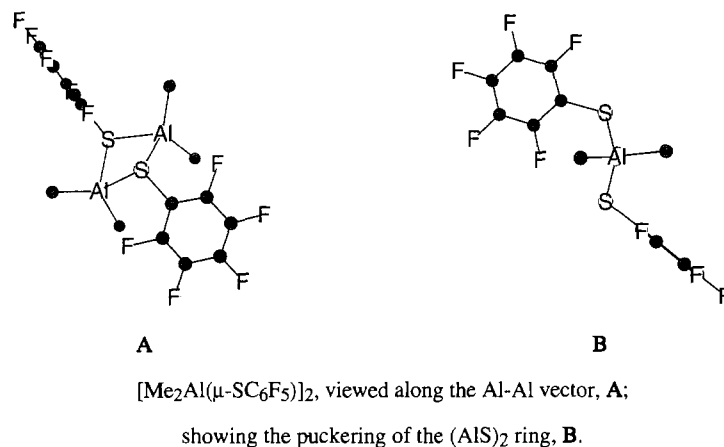


The first structural studies reported were those of Brauer and Stucky [6] and of Haaland et al. [7], who determined the structure of [Me₂Al(μ-SMe)]₂ in the solid state and in the gas phase. In the solid state, a chain with alternating Me₂Al and SMe units was observed, while in the gas phase a dimer with a central (AlS)₂ ring was observed. The chain structure is shown as



I [6], and the dimeric structure is depicted as **II** [7]. These examples provide an excellent starting point for discussion of the structures of derivatives of the type, $[R_2M(\mu-ER')]_n$, where M is a Group 13 metal and E a chalcogen. The most important feature of these structures shown is the $-(R_2)Al-S(R)-$ sequence which forms the backbone of the chain in **I** and the central ring in **II**.

With this information available, we started a systematic investigation of the structure of aluminum thiolates as a function of the substituent attached to the aluminum and/or to the sulfur, and have extended these studies to all of the chalcogens and to the heavier Group 13 metals. Our initial studies led to the characterization of the dimer shown as

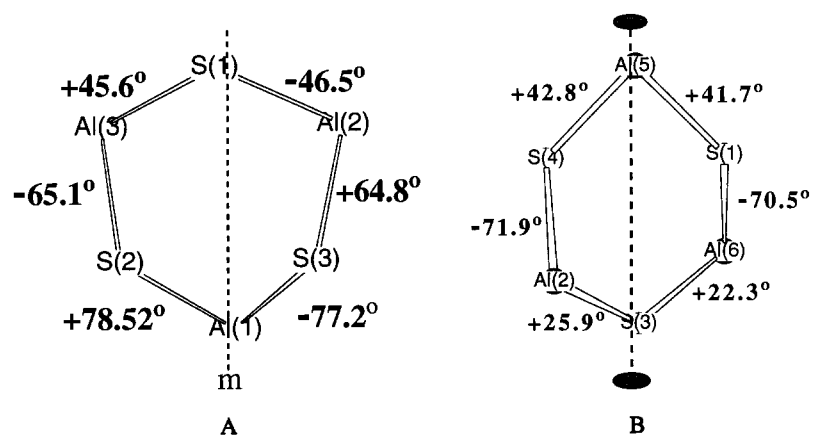
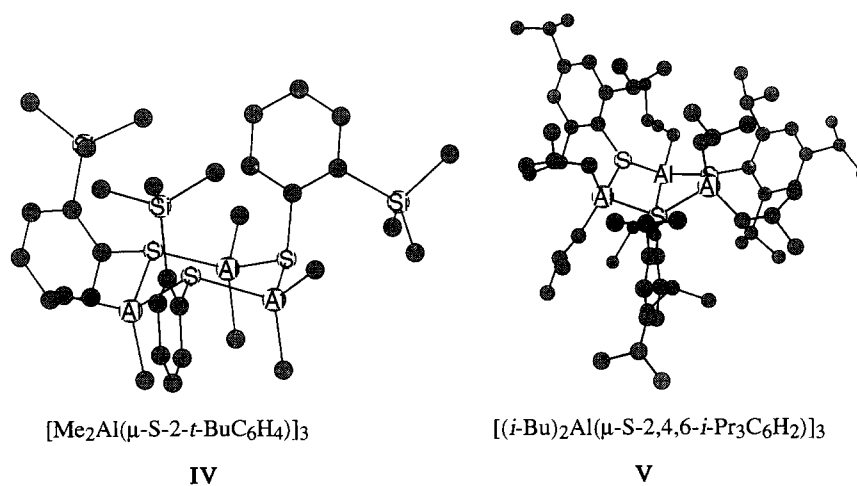


III [8], and then to a number of other dimeric species, including $[Mes_2Al(\mu-SBz)]_2$ (Mes = 2,4,5-Me₃C₆H₂), $[Me_2Al(\mu-SSiPh_3)]_2$, and $[Mes_2Al(\mu-SPh)]_2$ [9].

As the steric and electronic properties of the substituents were altered, we found that the structures of the thiolates could be considerably more complex, with the observation of trimers and tetramers. The structures of the dimers are similar to that of $[Me_2Al(\mu-SMe)]_2$, with the added feature that in all of the solid-state structures the organic substituent bound to the sulfur atom was observed only in the anti conformation. Fur-

ther, while the geometry around sulfur was pyramidal, the $(AlS)_2$ ring was not always planar as observed for the oxygen derivatives, but could be puckered (**IIIB**). The known dimeric structures are listed in Table 1 along with the relevant average bond distances and angles.

The trimeric aggregates are formed with six-membered $(AlS)_3$ rings. The conformation of the ring is a function of the substituents on the metal and sulfur atoms. The conformations observed so far are the chair and twist-boat forms shown as

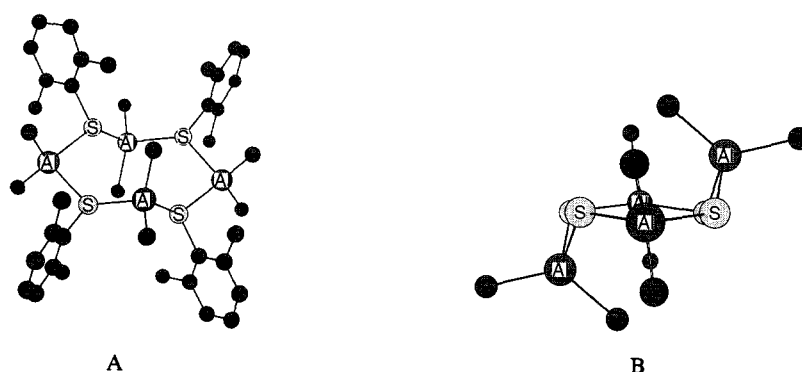


Torsion angles observed in $[\text{Me}_2\text{Al}(\mu\text{-2-}t\text{-BuC}_6\text{H}_5)]_3$ (chair conformation), **A**, and in $[(i\text{-Bu})_2\text{Al}(\mu\text{-2,4,6-}i\text{-Pr}_3\text{C}_6\text{H}_2)]_3$ (twist-boat conformation), **B**.

VI

IV and **V**. This is best illustrated by examining the torsion angles around the ring (**VIA** and **VIB**). We have found that changes in the substituent on the aluminum and/or on the sulfur can alter the structures of these

molecules substantially. A single tetrameric derivative has been observed, namely $[\text{Me}_2\text{Al}(\mu\text{-S-2,6-Me}_2\text{C}_6\text{-H}_3)]_4$, with eight-membered rings



A
 B
 $[\text{Me}_2\text{Al}(\mu\text{-S-2,6-Me}_2\text{C}_6\text{H}_3)]_4$ viewed from above the plane
 described by the four sulfur atoms, A, and parallel to this plane, B.

VII

(VII).

Examination of I–VII shows that in each case the critical portion of the structure is the initial unit, $(-\text{Al}-\text{S}-)$. The Al–S bond distances are all within a narrow range of 2.35 to 2.41 Å. The Al–S single-bond distance (2.185 Å) in the monomer, $\text{Al}(\text{SMes}^*)_3$ ($\text{Mes}^* = 2,4,6\text{-}t\text{-Bu}_3\text{C}_6\text{H}_2$) [10], is shorter than those distances, showing an increase in bond length upon bridge formation. This should also correspond to a decrease in bond energy, and be reflected in the ease with which these compounds can dissociate. The S–Al–S bond angles are constrained in the dimers, ranging from 85° to 90°. In the trimers and in the tetramer, there is considerably more flexibility, with the S–Al–S angles varying from

89° to 101°. The angles around the sulfur atom in the dimer are in the range 87–89.5°. In the trimers and tetramer, the angles are substantially larger, ranging from 115° to 132°. It might be noted that, in the polymer, the S–Al–S and Al–S–Al angles are 100.1° and 103° respectively.

There have been only a modest number of studies of the heavier chalcogen derivatives of aluminum (Table 1). The structures so far reported show that the heavier chalcogens form dimeric species with only minor modifications in the geometry around the aluminum and the chalcogen. This is illustrated for the derivatives, $[\text{Ph}_2\text{Al}(\mu\text{-SeMe})_2]$

Table 1
 Structural parameters for $[\text{R}_2\text{Al}(\mu\text{-ER})]_n$ thiolates, selenotates, tellurolates and related compounds

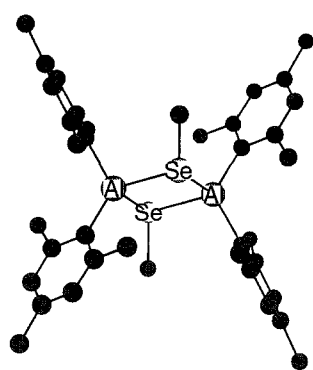
Compound	Al–E (Å)	E–Al–E (deg)	Al–E–Al (deg)	Sum of angles around E (deg)	Al–C (Å)	C–Al–C (deg)	Ref.
$[\text{Me}_2\text{Al}(\mu\text{-SMe})]_6$	2.348	100.1	103.0	310.3	1.944	122.0	[6]
$[\text{Me}_2\text{Al}(\mu\text{-SMe})]_2$	2.370	85.5	94.5	306.7	1.945	128.6	[7]
$[\text{Me}_2\text{Al}(\mu\text{-SC}_6\text{F}_5)]_2$	2.405	89.5	87.1	305.5	1.943	126.3	[8]
$[\text{Mes}_2\text{Al}(\mu\text{-SBz})]_2$	2.381	89.1	90.9	305.99	1.966	119.6	[9]
$[\text{Me}_2\text{Al}(\mu\text{-SSiPh}_3)]_2$	2.36	87.5	92.2	330.5	1.926	120.6	[9]
$[\text{Mes}_2\text{Al}(\mu\text{-SPh})]_2$	2.395	86.4	93.6	319.5	1.968	120.2	[9]
$\{\text{Me}_2\text{Al}[\mu\text{-S}(2\text{-}t\text{-BuC}_6\text{H}_4)]\}_3$	2.35	99.9 ^a	114.9 ^a	324.3 ^a	1.94	120.6	[9]
		88.8 ^b	123.2 ^b	338.5 ^b			
$\{\text{Me}_2\text{Al}[\mu\text{-S}(2\text{-Me}_3\text{SiC}_6\text{H}_4)]\}_3$	2.364	100.0 ^a	114.2 ^a	323.5 ^a	1.945	119.6	[9]
		89.4 ^b	120.1 ^b	335.7 ^b			
		90.2 ^b	122.5 ^b	337.1 ^b			
$\{\text{Me}_2\text{Al}[\mu\text{-S}(2\text{-}i\text{-PrC}_6\text{H}_4)]\}_3$	2.36	100.7 ^a	115.0 ^a	322.3 ^a	1.934	121.8	[9]
		90.2 ^b	122.5 ^b	337.1 ^b			
$\{(i\text{-Bu})_2\text{Al}[\mu\text{-S}(2,4,6\text{-}i\text{-Pr}_3\text{C}_6\text{H}_2)]\}_3$	2.37	92.8 ^c	128.6 ^c	357.9	1.96	129.7	[9]
$\{\text{Me}_2\text{Al}[\mu\text{-S}(2,6\text{-Me}_2\text{C}_6\text{H}_3)]\}_4$	2.36	99.5 ^d	128.8	345.6	1.943	126.0 ^d	[9]
						120.3	
$[\text{Mes}_2\text{Al}(\mu\text{-SeMe})]_2$	2.519	90.6	89.4	290.0	1.981	118.4	[11]
$[(t\text{-Bu})_2\text{Al}(\mu\text{-Te-}t\text{-Bu})]_2$	2.732	86.1	93.9	322.6	2.00	120.8	[12]

^a Atom located in the seat of the chair.

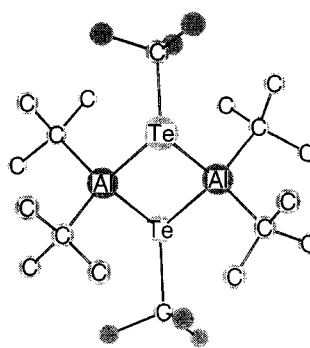
^b Atom located in the back of the chair.

^c Angles in the twist-boat conformation range from 89.1 to 96.10 for S–Al–S and from 126.8 to 131.5° for Al–S–Al.

^d Al atom located in the back of the chair.

 $[\text{Ph}_2\text{Al}(\mu\text{-SeMe})]_2$

VIII

 $[(t\text{-Bu})_2\text{Al}(\mu\text{-Te-}t\text{-Bu})]_2$

IX

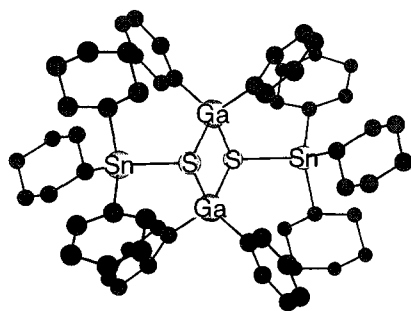
(VIII) [11] and $[(t\text{-Bu})_2\text{Al}(\mu\text{-Te-}t\text{-Bu})]_2$ (IX) [12]. These represent the only reported structures containing selenium and tellurium in simple organoaluminum derivatives. The tellurium structure is disordered over two positions, and the details have not yet been reported.

The principal differences observed on changing the chalcogen appear to be the increase in metal–chalcogen bond length and the tendency for the chalcogen to become more pyramidal. Both of these trends are shown by the data in Table 1. The Al–E bond lengths increase in the order Al–S (2.39 Å), Al–Se (2.52 Å), and Al–Te (2.73 Å). The sums of the angles around the chalcogen are 314° for the sulfur derivative, 290° for the selenium compound, and 323° for the tellurium derivative. The increase in the sum of the angles around tellurium is most likely associated with steric interactions between the *t*-butyl groups. It is probable that, as additional examples are studied, this will be confirmed, and that most tellurium derivatives will be found to have pyramidal structures with the sum of the angles around Te below 290° . This is supported by the observation that, for the gallium and indium derivatives described below,

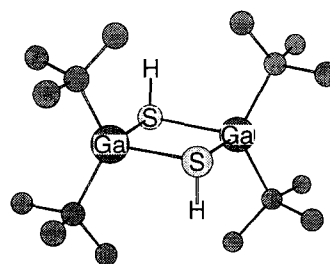
the geometry around the chalcogen becomes more pyramidal in the order $\text{S} < \text{Se} < \text{Te}$. When steric interactions are present — for example, in $[(t\text{-Bu})_2\text{Al}(\mu\text{-Te-}t\text{-Bu})]_2$ — the energy required for bending is small, and the sum of the angles around the chalcogen is easily increased.

The formation of higher aggregates for aluminum, gallium and indium thiolates has been established in solution by molecular weight measurements and NMR studies [13–17], but was not observed in the solid state until our recent work [9,18]. From the data available for the sulfur derivatives, it appears probable that use of less bulky groups on the aluminum atom will lead to such aggregates. There are already observations of trimeric and tetrameric fragments in the gas phase that may be interpreted in terms of a polymeric structure for $[\text{Me}_2\text{Al}(\mu\text{-SeMe})]_n$.

The structures that have been determined for the heavier Group 13 metal chalcogen derivatives show that the predominant form is the dimer with a planar, or nearly planar, four-membered ring serving as the central building unit.

 $[\text{Ph}_2\text{Ga}[\mu\text{-SSn}(\text{C}_6\text{H}_{11})_3]]_2$

X

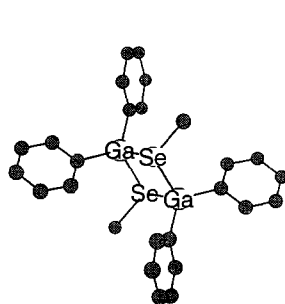
 $[(t\text{-Bu})_2\text{Ga}(\mu\text{-SH})]_2$

XI

X is a typical example of the gallium–sulfur derivatives. In this case an additional metal center has been added, which makes this species more interesting [19]. The SH derivative, $[(t\text{-Bu})_2\text{Ga}(\mu\text{-SH})]_2$ (**XI**) [20], was obtained by reaction of H_2S with $(t\text{-Bu})_3\text{Ga}$ under mild conditions. Warming this derivative leads to elimination of butane and formation of a cubane, which is discussed below. No trimers have been reported in the solid state, but the structure has been determined for the tetramer

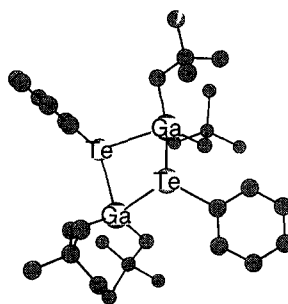
$[\text{Me}_2\text{Ga}(\mu\text{-S-2,6-Me}_2\text{C}_6\text{H}_3)]_4$ [9]. This observation and the solution studies reported by Hoffman [14,16,21,22] strongly support the view that trimers will be found in the solid state for the gallium derivatives once a systematic investigation is undertaken.

There are few examples of gallium derivatives with the heavier chalcogens, but a selenium and a tellurium derivative are shown as



$[\text{Ph}_2\text{Ga}(\mu\text{-SeMe})]_2$

XII

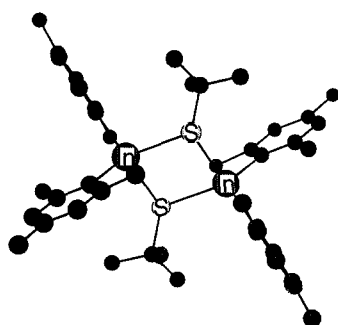


$[\text{Np}_2\text{Ga}(\mu\text{-TePh})]_2$

XIII

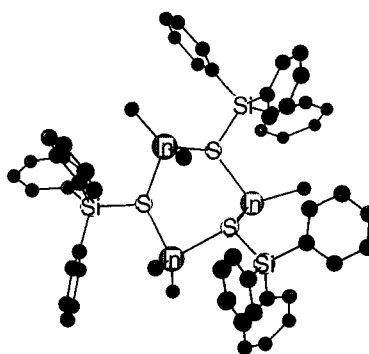
XII and **XIII**. All of the known structures of the simple diorganogallium thiolates, selenolates and tellurolates are listed in Table 2. The bond distances and angles are very similar to those in the aluminum derivatives, in keeping with the similar radii for aluminum and gallium.

The structures of dialkylindium chalcogenides that have been reported are listed in Table 3. We have determined the structures of dimeric



$[\text{Mes}_2\text{In}(\mu\text{-S-}t\text{-Bu})]_2$

XIV



$[\text{Me}_2\text{In}(\mu\text{-SSiPh}_3)]_3$

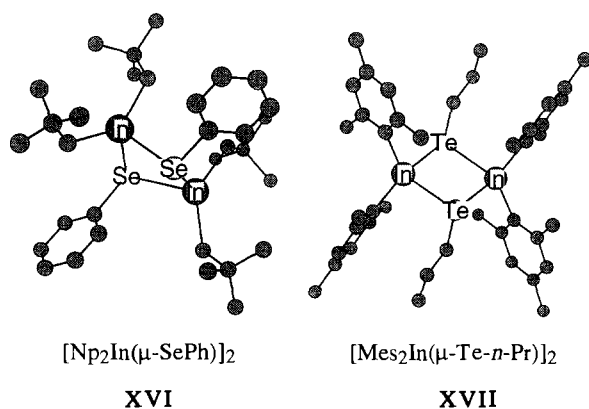
XV

Table 2
Structural parameters for gallium thiolates, selenolates, tellurolates and related compounds

Compound	Ga–E (Å)	E–Ga–E (deg)	Ga–E–Ga (deg)	Sum of angles around E (deg)	Ga–C (Å)	C–Ga–C (deg)	Ref.
[Ph ₂ Ga(μ-SEt)] ₂	2.379	93.6	86.4	294.9	1.964	121.2	[22]
[<i>t</i> -Bu ₂ Ga(μ-SH)] ₂	2.433	90.5	89.5	282.5	2.009	123.9	[20]
[Me ₂ Ga(μ-SC ₆ F ₅)] ₂	2.450	88.44	130.6	303.8	1.94	126.9	[29]
[Me ₂ Ga(μ-SC ₆ H ₃ Me ₂ -2,6)] ₄	2.398	93.1	128.0	343.4	1.935	126.9	[9]
[Me ₂ Ga(μ-S-c-C ₅ H ₉)] ₂	2.388	93.8	86.2	300.2	1.951	126.3	[30]
[Ph ₂ Ga(μ-S-c-C ₅ H ₉)] ₂	2.388	93.0	87.1	297.8	1.991	121.0	[30]
[Ph ₂ Ga(μ-SSiMe ₃)] ₂	2.383	90.8	89.0	313.4	1.966	118.2	[30]
{(<i>m</i> -Xy) ₂ Ga[μ-SSn(c-C ₆ H ₁₁)] ₃ }] ₂	2.380	91.4	88.6	322.1	1.967	124.6	[30]
{Ph ₂ Ga[μ-SSn(c-C ₆ H ₁₁)] ₃ }] ₂	2.342	93.5	86.5	309.7	1.958	114.5	[19]
[I ₂ Ga(μ-SMe)] ₂	2.379	94.5	85.5	292.6	–	–	[31]
[I ₂ Ga(μ-S- <i>i</i> -Pr)] ₂	2.329	89.1	84.7	296.9	–	–	[21]
[Ph ₂ Ga(μ-SeMe)] ₂	2.501	96.9	83.1	289.0	1.957	121.8	[11]
[Np ₂ Ga(μ-TePh)] ₂	2.755	92.0	83.8	289.9	1.976	130.1	[32]
[(Me ₃ Si) ₂ CH] ₂ GaTeSi(SiMe ₃) ₃	2.535	–	–	–	1.980	126.5	[33]

(XIV) and trimeric (XV) diorganoindium thiolates. These structures are closely related to those of aluminum and gallium derivatives, with the alkyl groups bound to the sulfur in the anti conformation, and the trimer in a twist-boat conformation [18].

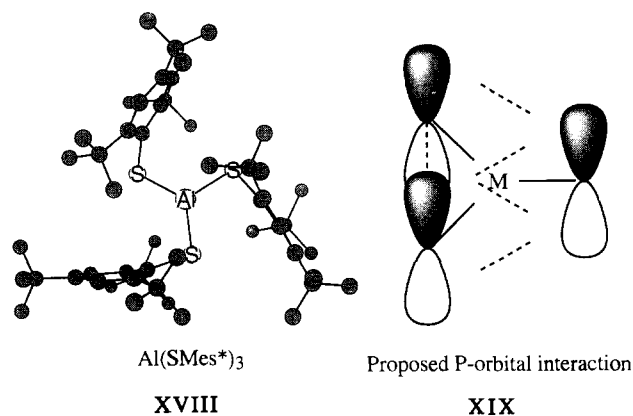
The only selenium and tellurium derivatives observed are dimeric, with two of the structures shown as



XVI and **XVII**. Once again, the structures are in the anti conformation; the angles around the chalcogen become more acute in the series S > Se > Te, and the sums of the angles around the chalcogen decrease from about 330° to about 270°.

The observed structures include monomers, dimers, trimers, tetramers and infinite chains for the [R₂M(ER)]_n and the aluminum derivatives; monomers, dimers and tetramers for the gallium; monomers, dimers, trimers and polymers for the indium. The variation in structures for these species shows that there are very small differences in the energies associated with the different aggregates in the solid state, allowing structural changes that can be controlled by varying the substituents on the metal or on the chalcogen.

Introduction of a second or third ER group on the metal to form units of the type [RM(ER)₂]_n or [M(ER)₃]_n has received very little attention, but greatly expands the possible structures. Several studies have appeared on derivatives specifically prepared with very bulky R groups to prevent aggregate formation. An example is shown as



XVIII, and all have the same general structural feature; namely, a central three-coordinate metal with a planar or nearly planar ME₃ central core. The most interesting feature of these compounds is the M–E bond length, which may be shortened as a result of π-overlap, as illustrated by **XIX**. A tabulation of the M–E bond lengths for the known monomers is given in Table 4. These bond distances can be compared with those for the “ate” complexes, M(ER)₄[–], for the adducts, R₃M·ER₂, and for the bridged dimers, [R₂M(μ-ER)]₂. For the Al–S and Ga–S derivatives, typical distances are 2.25–2.30 Å for the “ate” derivatives, 2.35–2.41 Å for the bridge bonds, and 2.5–2.7 Å for the adducts.

When less sterically demanding ligands are present,

Table 3
Structural parameters for indium thiolates, selenolates, tellurolates and related compounds

Compound	In–E (Å)	E–In–E (deg)	In–E–In (deg)	Sum of angles around E (deg)	In–C (Å)	C–In–C (deg)	Ref.
$[\text{Ph}_2\text{In}(\mu\text{-SSn}(\text{C}_6\text{H}_{11})_3)_2]$	2.551	90.72	89.28	311.9	2.145	116.3	[19]
$[\text{Mes}_2\text{In}(\mu\text{-SSiPh}_3)_2]$	2.498	77.82	102.18	352.1	2.179	128.3	[18]
$[\text{Mes}_2\text{In}(\mu\text{-S-}i\text{-amyl})_2]$	2.592	84.2	95.9	324.0	2.23	111.8	[18]
$[\text{Me}_2\text{In}(\mu\text{-SSiPh}_3)_3]$	2.609	90.5 ^a	117.3 ^a	351.8	2.13	132.8	[18]
$[\text{Mes}_2\text{In}(\mu\text{-SePh})_2]$	2.732	90.24	89.75	292.48	2.168	121.5	[24]
$[\text{Mes}_2\text{In}(\mu\text{-SeMes})_2]$	2.715	90.5	88.7	292.3	2.183	119.5	[24]
$[\text{Np}_2\text{In}(\mu\text{-SePh})_2]$	2.743	89.6	86.1	295.2	2.157	133.6	[34]
$[\text{In}(\text{SePh})_3]_n$	2.776	88.7	98.5	301.8	2.154	–	[23]
$[\text{Me}(\text{PhSe})\text{In}(\mu\text{-SePh})_n]$	2.682 ^b 2.541 ^c	88.7 ^b	98.5 ^b	301.8 ^b	2.154	125.5 ^d	[24]
$\text{Np}_2\text{In}(\mu\text{-SePh})(\mu\text{-P-}i\text{-Bu}_2)\text{InNp}_2$	2.769 In–Se 2.653 In–P	84.3 P–In–Se	91.6 In–SeIn 96.4 In–P–In	305.5	2.190	120.9	[35]
$[\text{Mes}_2\text{In}(\mu\text{-TePh})_2]$	2.915	92.5	87.5	285.7	2.179	121.9	[36]
$[\text{Mes}_2\text{In}(\mu\text{-Te-}n\text{-Pr})_2]$	2.909	92.2	87.8	274.4	2.167	122.1	[36]

^a The In–S–In angles range from 109.4° to 123.7°.

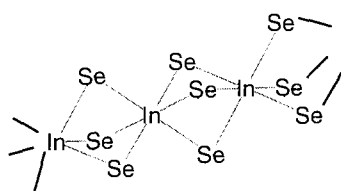
^b Bridging SeR groups.

^c Terminal SeR groups.

^d C–In–Se (terminal) angle.

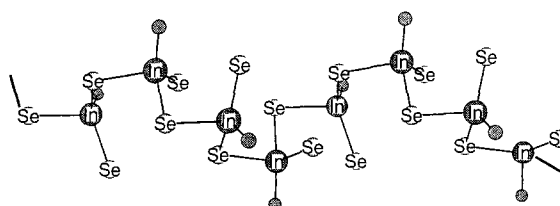
the derivatives, $[\text{RM}(\text{ER}')_2]$ and $\text{M}(\text{ER})_3$, may form chains or more complex two- or three-dimensional lattices. Two structures showing this behavior have been

determined, the first by Annan et al. [23], and the second by our group [24]. The contrast between these is in the coordination at indium. In



The InSe portion of the structure of $[\text{In}(\text{SePh})_3]_\infty$. Ph groups have been omitted so that the InSe_3 structure can be seen.

XX



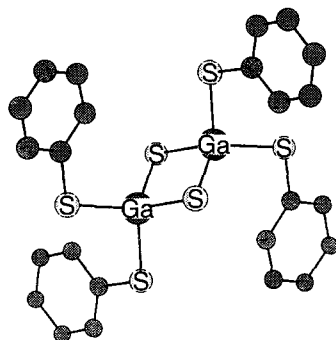
$[\text{MeIn}(\text{SePh})(\mu\text{-SePh})]_\infty$. Ph groups have been omitted so that the Se–In chain can be seen.

XXI

XX, the indium is six-coordinate, with each selenium atom serving as a bridge, whereas in **XXI** the two selenium groups differ, one serving as a bridge and the second remaining two-coordinate.

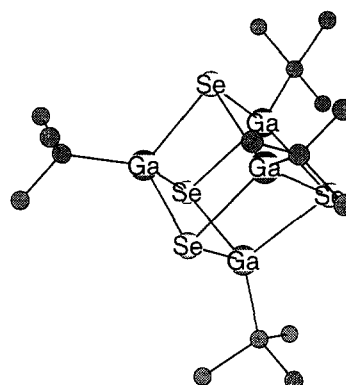
As noted earlier, chalcogenide derivatives may be obtained for the Group 13 metals. These derivatives

have been reported only for gallium and indium at this stage of development, but a variety of different structural types has already been observed. These include a simple dimeric sulfide di-anion, $[(\text{PhS})_2\text{Ga}(\mu\text{-S})_2\text{-Ga}(\text{SPh})_2]^{-2}$



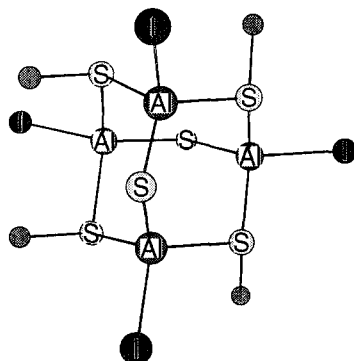
$$[(\text{PhS})_2\text{Ga}(\mu\text{-S})_2\text{Ga}(\text{SPh})_2]^{2-}$$

XXII



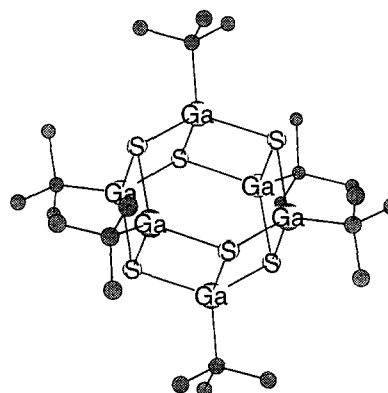
$$[(t\text{-Bu})\text{Ga}(\mu_3\text{-Se})_4]$$

XXIII



$$(\text{Al})_4(\mu\text{-S})_2(\mu\text{-SMe})_4$$

XXIV



$$[(t\text{-Bu})\text{Ga}(\mu_3\text{-S})_6]$$

XXV

(XXII) [25], several cubanes of the type shown as XXIII [26], and larger aggregates as shown by XXIV [27] and XXV [26]. The substituents bound to the gallium or indium may be alkyls or, in several cases, transition-metal moieties. In each of these molecules, the chalcogen serves to bridge three Group 13 metals, leading to a three-dimensional structure, with the cubic forms being the simplest species observed. Scattered reports have described the structures of aluminum, gallium, and indium derivatives. Similar structures have been observed for organoselenium derivatives and for tellurium derivatives with the tellurium bound to a transition metal moiety [28]. It seems highly likely that many more derivatives with cage or cluster structures will appear once groups begin systematic study of these species.

There have been numerous comments about the equilibria observed for Group 13 derivatives in solution, but

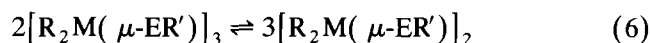
few studies have provided quantitative information. Hoffman [13–15] studied the equilibria of a few $[\text{R}_2\text{Al}(\mu\text{-SR})]_n$ and $[\text{R}_2\text{Ga}(\mu\text{-SR})]_n$ systems in solution, and stated that a number of different aggregation states are observed, depending on the substituents on the metal and the sulfur atoms. Nomura et al. [17] observed trimers for the $[\text{R}_2\text{In}(\mu\text{-SR})]_n$ system. None of these studies, however, provided any detailed information on the equilibria, and the molecular-weight studies reported provide information only about the average molecular weight of the species present in solution. Clearly, these systems involve more complex equilibria involving a variety of species and conformations present in solution.

In order to explore these processes, we have studied several aluminum and gallium systems in detail, using NMR techniques to establish the degree of aggregation and the equilibrium constants in solution. These studies

Table 4
Structural parameters for monomeric group 13 chalcogen derivatives

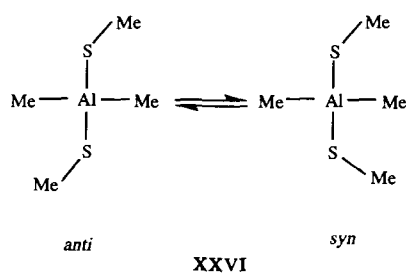
Compound	M–E bond distance (Å)	E–M–E bond angle (deg)	Ref.
Al[S(2,4,6- <i>t</i> -Bu ₃ C ₆ H ₂) ₃] ₃	2.177	115.1	[10]
	2.191	118.4	
	2.187	125.9	
Ga[S(2,4,6- <i>t</i> -Bu ₃ C ₆ H ₂) ₃] ₃	2.197	115.6	[10]
	2.207	118.5	
	2.212	125.5	
In(SeC ₆ H ₂ - <i>t</i> -Bu ₃ -2,4,6) ₃	2.510	118.5	[37]
	2.506	114.6	
	2.501	126.4	
[(Me ₃ Si) ₂ CH] ₂ GaTeSi(SiMe ₃) ₃	2.535		[33]

have established that the most common aggregation states are dimers and trimers, and that exchange between them is relatively slow on the NMR time-scale, permitting the determination of the equilibrium constants as a function of temperature in a few systems in which significant concentrations of both species are present in solution. Variable-concentration studies have established that the equilibrium is between dimer and trimer, as shown in Eq. (6). Results from a number of these studies are given in Table 5.



The energy differences typically observed between the dimers and trimers are very small (as required by the nature of the experiment) and are dependent on the nature of the substituents attached to the metal and to the chalcogen. With increasing energy differences between the dimer and the trimer, the equilibrium is shifted, leading to formation of a single species in very high concentration. Under these circumstances, the sensitivity of the measurements precludes determination of the equilibrium constants.

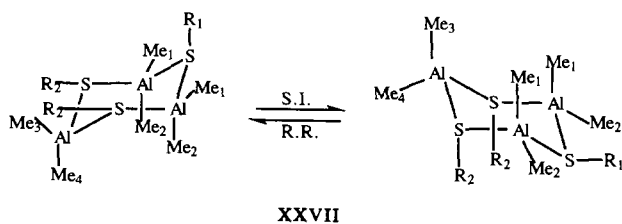
In addition to the equilibria between different aggregates, two equilibria involving conformational changes have been observed. The first, shown as



XXVI, is the anti ⇌ syn transformation observed in dimeric systems.

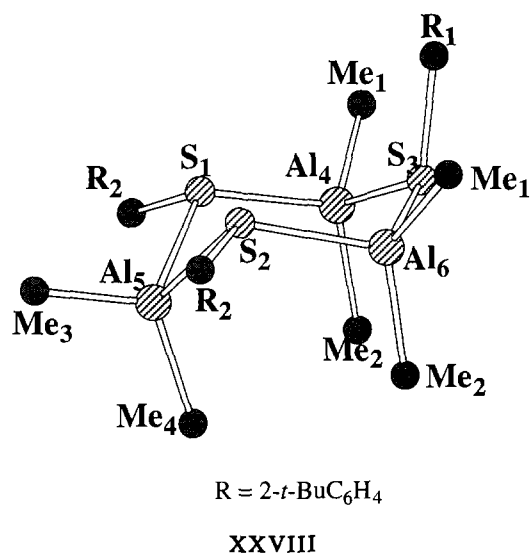
For the system [Me₂Al(μ-EMe)]_n (E = S, Se), the change from sulfur to selenium leads to a substantial

change in the observed equilibrium between dimer and trimer, as noted earlier. In the sulfur derivative, the trimer is present in high concentration, and the syn ⇌ anti equilibrium can be observed only at very low temperature. For the selenium system, the opposite is true: the dimer is the predominant form, and the syn ⇌ anti conformation is readily observed at –60 °C. The mechanism of this process has not been established, but the low value of the energy of activation, 50 kJ, appears to favor a rotation process, although other mechanisms are possible. A second type of conformational change, the conversion of one six-membered ring into another, shown as



XXVII, has also been observed.

To help in understanding this interchange, the relationship of the substituents on a typical six-membered ring in the chair conformation is shown by



XXVIII. There are four different methyl group environments indicated, in a ratio of 2:2:1:1. If the ring conformation is fixed on the NMR time-scale, these groups should give rise to four signals with this intensity ratio. If rapid ring inversion/fluctuation occurs, all groups bound to the metal will become equivalent. We have observed that with 2-*t*-BuC₆H₄ groups attached to the sulfur, the ring is rigid at room temperature on the

Table 5
Thermodynamic parameters for the equilibrium process, 2 Trimer \rightleftharpoons 3 Dimer, in selected $[R_2M(\mu-ER')_n]$ systems

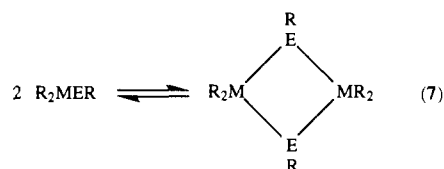
Compound	K_{eq} 25°	ΔH° kJ mol ⁻¹	ΔS° J mol ⁻¹	ΔG° kJ mol ⁻¹
$[Me_2Al(\mu-SMe)]_n$	0.4	23.1	70.0	12.8
$[Me_2Al(\mu-SeMe)]_n$	180.0	11.5	81.5	8.5
$[Me_2Al(\mu-SSiPh_3)]_n$	31.0	5.8	220.0	9.4
$[Me_2Al(\mu-S-2-FC_6H_4)]_n$	44.5	68.0	260.0	1.5
$[Me_2Al(\mu-S-2,6-C_6H_3)]_n$	0.6	26.5	85.0	2.2

NMR time-scale, giving rise to the anticipated four-line patterns (Fig. 1). In this process the ring undergoes an inversion that can be detected by the variation in the line shape with temperature.

Consideration of all of the data makes it possible to provide a significantly better description of the Group 13 organometallic chalcogen derivatives. These species are found to show at least five different arrangements in the solid state: monomers, dimers, trimers, tetramers and polymers. The first question to be addressed is what determines the solid-state structure. The related question is what determines the aggregate state in solution.

An analysis of these systems shows that, in the transformation from monomer to dimer, the total number of bonds and the bond type are changed. In the two monomers, there are two M–E single bonds which are

replaced by four M–E–M bridge bonds in the dimer (Eq. (7)).



The driving force for the reaction is the formation of these additional bonding interactions, which are energetically favored. The entropy term is unfavorable because of the decrease in the number of free molecules and the

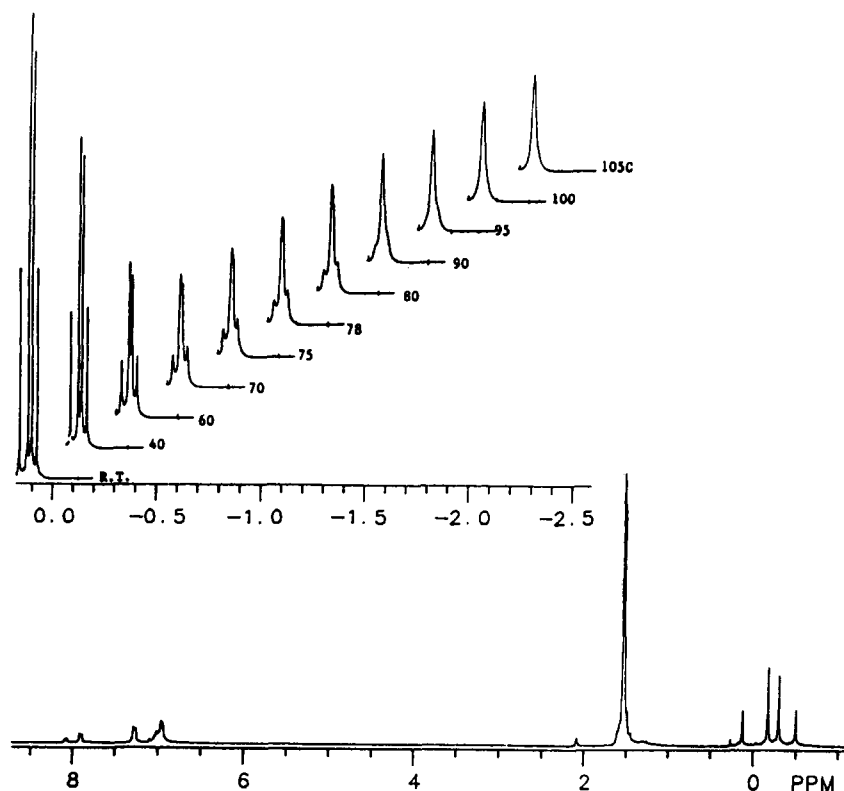


Fig. 1. Proton NMR spectrum of $[Me_2Al(\mu-S-2-t-BuC_6H_4)]_3$. The inset shows the temperature dependence of the Al–Me resonance lines.

potential decrease in freedom of motion within the dimer. The reason for the formation of the higher aggregate is less clear. In these cases, the total number of bonds of each type remains the same; i.e. in conversion of three dimers to two trimers, the number of M–E–M bridge bonds remains six. At the same time, the entropy becomes less favorable. Thus, the energy for the formation of the higher aggregates must come from the increased strength of the M–E–M bridge bond or from reduction of ring strain that offsets the unfavorable entropy term. There is at present no definitive evidence to establish what contribution is made by each of these terms.

From the influence of the substituent on the size of the aggregate, it appears that the steric bulk of the substituents on the chalcogen and on the metal plays an important role. Most of the higher aggregates are observed with methyl substituents on the metal, and reasonably bulky substituents such as 2-*t*-BuC₆H₄ or 2,6-Me₂C₆H₃ on the chalcogen. When bulky substituents are placed on both the chalcogen and the metal, dimers are most common. The only reported chain structure is that for [Me₂Al(μ-SMe)]_n. The morphology, mass spectrum and other properties of [Me₂Al(μ-SeMe)]_n suggest a similar structure, but crystals of X-ray quality have not yet been obtained.

Dimers and trimers are the primary structures observed for all of these derivatives in solution. In the absence of packing effects, it appears that the entropy term is sufficient to prevent formation of significant concentrations of any higher aggregates. The equilibrium constants provide a measure of the relative stability of dimer and trimer. The data establish that, for a number of systems, the dimer is the stable form, although in some cases the equilibrium between dimer and trimer is established, with the concentration of each species sufficient to allow measurements by integration of the NMR spectrum. In these cases, the equilibrium constants are in the range 10⁻² to 10², and the standard free energy ΔG° are in the range of -3 to +3 kJ mol⁻¹. Some systems are found to be exclusively trimers in solution. The energy change required from all-dimer to all-trimer is only a few kilojoules per mol; this is consistent with all of the observations and with the fact that there are equivalent sets of bonds on each side of the equilibrium.

The wide variety of structures observed and the complex equilibria and exchange processes that occur in solution suggest that the Group 13 chalcogen derivatives [R₂M(μ-ER)]_n, [RM(ER)₂]_n and [M(ER)₃]_n will continue to offer a fruitful area for research. A better understanding of the factors that govern solid-state structures, i.e. the aggregation states and conformations, awaits further studies of compounds with substituents having a broad range of steric requirements and electronic properties. To understand the complex processes

that occur in solution, quantitative investigation of the effect of the organic substituents and the chalcogen on the equilibria between aggregation states will be required, with special attention paid to the determination of the mechanisms of exchange reactions. Both the solid-state and solution studies would be enhanced by theoretical studies, which could provide an understanding of the steric interactions and electronic structures of the molecules.

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