

Stereochemistry of Polynuclear Compounds of the Main Group Elements.¹ XI. Dimethyl(methylthiol)aluminum, $[(\text{CH}_3)_2\text{AlSCH}_3]_n$, a New Type of Stereochemistry for an Organoaluminum Compound²

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Abstract: The crystal structure of dimethyl(methylthiol)aluminum, $[(\text{CH}_3)_2\text{AlSCH}_3]_n$, has been determined from three-dimensional X-ray data measured by counter methods. $[(\text{CH}_3)_2\text{AlSCH}_3]_n$ crystallizes in the orthorhombic space group Fdd2 with cell dimensions $a = 25.679$ (7) Å, $b = 7.942$ (2) Å, and $c = 12.004$ (3) Å. The calculated density of 1.13 g cm⁻³ for 16 $(\text{CH}_3)_2\text{AlSCH}_3$ units per unit cell compares well with the observed density of 1.14 ± 0.03 g cm⁻³. Three-dimensional least-squares refinement gave a conventional weighted R factor of 3.9% for 445 reflections. In the solid state, $[(\text{CH}_3)_2\text{AlSCH}_3]_n$ is a one-dimensional infinite polymer with methylthiol groups bridging dimethylaluminum groups to form zigzag infinite chains. The bridging sulfur atoms are in a pyramidal configuration. The average Al-S bond length is 2.348 (2) Å, the average Al-C bond distance is 1.944 (7) Å, and the C-S bond length is 1.806 (7) Å. The Al-S-Al' angle is 103.0 (1)°, and the S-Al-S' angle is 100.1 (1)°.

It is well known that alkyls, halogens,³ secondary amines, secondary phosphines,⁴ secondary arsines,⁵ and alcohols^{4,6} form finite polynuclear compounds with trimethylaluminum. When large, bulky groups are coordinated to the aluminum atom, monomeric species can be stabilized as in triisobutylaluminum.⁶ Somewhat smaller steric requirements result in dimeric complexes (e.g., $(\text{CH}_3)_5\text{Al}_2\text{N}(\text{C}_6\text{H}_5)_2$),⁷ and reducing the size of the bridging group even further gives trimeric compounds (e.g., $[(\text{CH}_3)_2\text{AlN}(\text{CH}_2)_2]_3$).⁸

An apparent contradiction to the above simple steric considerations arises in the systems $[(\text{CH}_3)_2\text{AlOCH}_3]_3$,⁴ $[(\text{CH}_3)_2\text{AlSCH}_3]_2$,^{4,9} $[(\text{CH}_3)_2\text{AlN}(\text{CH}_2)_2]_2$,⁴ and $[(\text{CH}_3)_2\text{AlP}(\text{CH}_2)_2]_3$.⁴ It is not obvious that nonbonded interactions should be significantly larger with a -SCH₃ than with an -OCH₃ bridging group, particularly when the converse appears to be true with -P(CH₃)₂ and -N(CH₃)₂. Indeed, since nonbonded repulsions should be a minimum with the former bridging groups, the geometries of the polynuclear compounds might be expected to be primarily the result of the different valence electron distributions about the sulfur or oxygen bridging atoms. It has been pointed out recently that three-coordinate oxygen, which is usually thought to be pyramidal in donor-acceptor complexes,¹⁰ is planar when bonded to third-row metals and metalloids.⁷ It has not been determined whether or not three-coordi-

nate sulfur, which is pyramidally coordinated in donor-acceptor molecules,¹¹ is also planar in the presence of the third-row representative metals.

Experimental Section

Dimethyl(methylthiol)aluminum was prepared under a positive pressure of N₂ at room temperature by bubbling methanethiol through a solution of trimethylaluminum in cyclohexane. The solvent was pumped off, and sublimation (65°, 2.0 mm) of the residue yielded colorless crystals, (mp 102°; reported for $[(\text{CH}_3)_2\text{AlSCH}_3]_2$,⁴ 103°).

The crystals were found to be rather insoluble in organic solvents such as benzene and cyclohexane, but were slightly soluble in toluene. Such a solution was used in the nuclear magnetic resonance experiments. All samples were sealed in standard Varian nmr tubes. The Varian A-60A and A-56/60 nuclear magnetic resonance spectrometers were used to record the spectra.

In a glove box, single crystals were mounted in thin-walled glass capillaries. The crystal used for X-ray analysis can roughly be described as a cylinder of radius 0.14 mm and of length 0.67 mm; however, the length of the cylinder was terminated by two planes which formed angles of 45 and 60° with the rotation axis of the cylinder. Precession (Mo Kα) and Weissenberg (Mo Kα) photographs showed the crystal system to be orthorhombic. The systematic absences ($hk0$, $h + k \neq 2n$, $h \neq 2n$; $k \neq 2n$; $h00$, $h \neq 4n$; $hk1$, $h \neq 2n + 1$, $k \neq 2n + 1$; $h0l$, $h + l \neq 4n$, $h \neq 2n$, $k \neq 2n$; $00l$, $l \neq 4n$; $h1l$, $h \neq 2n + 1$, $l \neq 2n + 1$; $0kl$, $k + l \neq 4n$, $k \neq 2n$, $l \neq 2n$; $0k0$, $k \neq 4n$; $1kl$, $k \neq 2n + 1$, $l \neq 2n + 1$) uniquely determined the space group Fdd2 (C_{2v}^{19}). The lattice constants and their corresponding standard deviations, as obtained from a least-squares procedure described below, are $a = 25.679$ (7) Å,¹² $b = 7.942$ (2) Å, $c = 12.004$ (3) Å. The measured density of 1.14 ± 0.03 g cm⁻³, obtained by the flotation method in C₆H₆ and C₆H₅Br at 25°, agrees satisfactorily with the density of 1.126 g cm⁻³ calculated for 16 $(\text{CH}_3)_2\text{AlSCH}_3$ units per unit cell.

Intensity data were measured manually on a Picker four-circle X-ray diffractometer using Cu Kα radiation. This radiation was selected on the basis of the presence of the rather large a axis and of the increase in measured intensities available with this radiation. The crystal was aligned on the diffractometer in such a way that the [026] direction and the ϕ axis coincided in order to minimize multiple scattering effects. Twelve reflections were carefully top-bottom and left-right centered using the Cu Kα component of the

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incident radiation (λ 1.54178 Å, 25°). The observed diffraction angles formed a basis for the least-squares refinement of the unit cell parameters using the program B-101,¹³ which also gave diffractometer settings for measuring the rest of the Bragg reflections. The average peak width and deviation over $\sin \theta$, as measured by an ω scan technique over various regions in 2θ , was $1.60 \pm 0.13^\circ$. Accordingly, the collimators used for the incident and diffracted beam were 1.0 and 3.0 mm, respectively, with a take-off angle of 3.0° . A 0.0005-in. nickel foil filter was placed between the crystal and the scintillation counter which was mounted 20 cm from the crystal.

All data were measured by the θ - 2θ scan technique at a scan rate of $2.0^\circ/\text{min}$. Reflections with $2\theta < 30^\circ$ were given a symmetrical 2.0° scan, and reflections with $2\theta \geq 30^\circ$ were given an asymmetrical scan of 1.2° before the peak maximum and 1.46° after the peak maximum. Stationary-counter-stationary-crystal background counts of 10 sec were taken at the beginning and end of the scan. All scans were recorded on a chart recorder and, since the diffractometer was operated manually, all peaks were checked for centering, peak shape, and overlap. The lower level discriminator of the pulse height analyzer was adjusted to minimize streaking effects.

Three forms (hkl , $\bar{h}kl$, and $h\bar{k}l$) of data were collected to $2\theta_{\text{max}} = 95.0^\circ$. Additional data (hkl , $\bar{h}kl$) were then collected to $2\theta_{\text{max}} = 115.0^\circ$. All of the forms are equivalent, even in the presence of anomalous dispersion.¹⁴ Two standard peaks were measured periodically throughout data collection. A systematic, but not linear with respect to time, decline of about 8% in the intensities of the standard peaks was observed. Reflections with $2\theta_{\text{max}} = 95.0^\circ$ were scanned first and their intensities were not scaled; however, the intensities of reflections with $95.0^\circ < 2\theta \leq 115.0^\circ$ were scaled up by 3.8%, a value which placed these data on the same average counting scale as the data with $2\theta_{\text{max}} = 95.0^\circ$. In spite of this crude method of correction for crystalline decomposition, it is estimated that no systematic errors in intensity greater than 4% were introduced. A total of 1147 reflections were measured of which 445 reflections were unique. Because of the rather large crystal dimensions and moderate absorption coefficient ($\mu = 47.3 \text{ cm}^{-1}$), an absorption correction was considered necessary. The data were corrected for background, Lorentz-polarization, and absorption using the program ACAC.¹⁵ An estimation of the standard deviations, $\sigma(|F|)$, of the structure factors derived from the background corrected intensities I is given by

$$\sigma(|F|) = \frac{|F|}{2I} [C_N + 0.25(T_C/T_B)^2(B_1 + B_2) + (0.05I)^2]^{1/2}$$

where C_N is the total integrated peak counts in a time T_C and B_1 and B_2 are the background counts in a time T_B .¹⁶ The weighting scheme was based on $1/\sigma^2(|F|)$. Unobserved reflections ($I_o < 3\sigma^2(I)$, where $\sigma^2(I) = [C_N + (T_C/T_B)^2(B_1 + B_2)]^{1/2}$) were given a raw intensity of $1.5\sigma^2(I)$ ¹⁷ and initially assigned standard deviations of $I_{\text{min}}/\sqrt{12}$, where $I_{\text{min}} = 3\sigma^2(I)$.¹⁷ All forms of data were then averaged to give the 445 unique reflections, of which 38 were unobserved reflections.

The form factors for Al³⁺, S²⁻, and C⁰ were taken from the compilations of Hanson, *et al.*¹⁸ Anomalous dispersion corrections for Al and S were taken from the compilations of Berghuis, *et al.*¹⁹ The spherical scattering factors for H were those of Stewart, Davidson, and Simpson.²⁰ The program ERFR-3 was used to compute electron density and Patterson maps,²¹ the program ORFLSD, a local version of ORFLS,²² was used in the least-squares refinement, the

program ORFFE was used to calculate bond lengths and angles and corresponding standard deviations,²³ and the program ORTEP was used to draw the structural illustration.²⁴

The structure was solved by sharpened Patterson and Fourier techniques. Initially a Patterson map was calculated, but it was uninterpretable in terms of any simple, cyclic compound. Next a sharpened Patterson map was calculated, and it revealed a large peak on the Harker plane $2u, 2v, 0$ which later proved to be due to the overlap of sulfur-sulfur and aluminum-aluminum vectors. The coordinates (0.1060, 0.2083, 0.2500) were assigned to a sulfur atom, the z coordinate being assigned arbitrarily to define the origin along the z axis and to facilitate the search for other atoms on subsequent Fourier maps. A Fourier synthesis phased on the sulfur atom indicated another large peak which was also treated as a sulfur atom. An electron density map was calculated on the basis of these two atoms, and this map revealed the positions of the remaining nonhydrogen atoms. The first "sulfur" atom was shown by the coordination about it to be an aluminum atom. Two cycles of full-matrix least-squares refinement incorporating the positional parameters of all nonhydrogen atoms and using all observed reflections up to $2\theta = 95^\circ$ yielded $R_1 = \Sigma[|F_o| - |F_c|]/\Sigma|F_o| = 0.127$. The real and imaginary anomalous dispersion corrections for the aluminum and sulfur atoms were then applied to the calculated structure factors, and all observed data were included. One cycle of refinement on the positional and isotropic thermal parameters was carried out yielding an R_1 of 0.151. Three cycles with anisotropic temperatures dropped R_1 to 0.076. A plot of $w(|F_o| - |F_c|)^2$ vs. $|F_o|$, $w = 1$, showed that the weighting scheme mentioned above would satisfy Cruickshank's criterion that $w(|F_o| - |F_c|)^2/|F_o|$, where $w = \text{weight}$, would be constant if the weights assigned to the unobserved reflections would be increased by a factor of 12. As a result, the unobserved reflections were all given a $\sigma(|F_o|)$ such that the average value of $w(|F_o| - |F_c|)^2/|F_o|$ for all of the unobserved reflections would be the same as the average value of this quantity for the observed reflections.²⁵ Using these $\sigma(|F_o|)$'s, two more cycles of refinement gave a value of $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2} = 0.068$. The presence of hindered rotation of the methyl groups was indicated in a difference Fourier by the presence of relatively low peaks ($0.3 \text{ e}/\text{\AA}^3$) at somewhat reasonable hydrogen atom positions in a continuous ring of low electron density ($0.1 \text{ e}/\text{\AA}^3$) about the carbon atoms. Nevertheless, hydrogen atoms were placed in the positions indicated. Four cycles of least-squares refinement incorporating all 42 positional parameters, 30 anisotropic temperature factors, and 9 isotropic temperature factors of the hydrogens yielded convergence. The final R factors were $R_1 = 0.033$ (excluding unobserved data) and $R_2 = 0.0403$ (including unobserved data). The estimated standard deviation of an observation of unit weight (ERF) given by $[\Sigma w(|F_o| - |F_c|)^2]^{1/2}/(N_o - N_v)$, where N_o is the number of observations and N_v is the number of variables, was 1.33. On a final difference Fourier map no peaks larger than $0.4 \text{ e}/\text{\AA}^3$ or smaller than $-0.5 \text{ e}/\text{\AA}^3$ appeared, and none of the larger peaks were near the coordinates of an atom.

In order to determine whether the three forms of data belonged to the $+l$ or $-l$ hemisphere, as these hemispheres are not equivalent in the presence of anomalous dispersion,¹⁴ least-squares refinement was carried out with the indices changed from h, k, l to $-h, -k, -l$. The final residuals were $R_1 = 0.032$ (excluding unobserved data) and $R_2 = 0.0387$ (including unobserved data). The value of ERF was 1.28. In each refinement, no systematic variation of $W(|F_o| - |F_c|)^2$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was observed. Since the ratio $R_2(+)/R_2(-) = 1.04$ and since $R_{1, 3\sigma, 0.005} = 1.011$, the h, k, l refinement can be rejected on the 99.5% confidence level.²⁶ An additional check on the validity of this choice was made. An investigation of the z coordinate of Al, C(1), C(2), and C(3) revealed that at the end of the h, k, l refinement each of these atoms was shifted in the positive z direction from its location at the end of

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Table I. Positional and Thermal Parameters for $[(\text{CH}_3)_2\text{AlSCH}_3]_n$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	0.12718 (6)	0.1745 (2)	0.0 ^b	0.00240 (3)	0.0170 (2)	0.0048 (1)	0.0001 (1)	0.0001 (1)	-0.0015 (1)
Al	0.11033 (6)	0.2039 (2)	-0.1910 (2)	0.00239 (3)	0.0166 (3)	0.0051 (1)	0.0003 (1)	-0.0001 (1)	-0.0012 (1)
C(1)	0.0371 (3)	0.2523 (10)	-0.2171 (7)	0.0031 (2)	0.0281 (15)	0.0080 (5)	0.0020 (4)	-0.0028 (8)	-0.0028 (8)
C(2)	0.1654 (3)	0.3458 (10)	-0.2504 (7)	0.0037 (2)	0.0244 (15)	0.0065 (5)	-0.0011 (4)	0.0009 (3)	0.0001 (8)
C(3)	0.0644 (3)	0.1181 (11)	0.0568 (7)	0.0032 (1)	0.0264 (15)	0.0078 (5)	-0.0024 (4)	0.0014 (3)	-0.0021 (8)
H(1)C(1)	0.020 (4)	0.123 (14)	-0.176 (9)	12.6 (28) ^c					
H(2)C(1)	0.029 (3)	0.363 (11)	-0.215 (8)	7.8 (21)					
H(3)C(1)	0.021 (3)	0.202 (9)	-0.260 (7)	8.1 (23)					
H(1)C(2)	0.169 (2)	0.344 (8)	-0.320 (6)	5.3 (14)					
H(2)C(2)	0.159 (2)	0.460 (8)	-0.231 (5)	5.6 (15)					
H(3)C(2)	0.204 (3)	0.299 (9)	-0.213 (8)	8.1 (20)					
H(1)C(3)	0.041 (3)	0.222 (10)	0.080 (6)	7.6 (18)					
H(2)C(3)	0.062 (4)	0.015 (14)	0.030 (8)	9.5 (26)					
H(3)C(3)	0.064 (3)	0.117 (10)	0.139 (8)	7.7 (18)					

^a The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. ^b The *z* coordinate of the sulfur atom was held constant during refinement. ^c The hydrogen atoms were given isotropic temperature factors of the form $\exp[-\beta(\sin^2 \theta/\lambda^2)]$.

the $-h$, $-k$, $-l$ refinement. The direction and magnitude of these shifts would be in excellent agreement with the polar dispersion error calculations of Cruickshank and McDonald²⁷ only if the data belonged to the $-l$ hemisphere. Finally, this choice of data labeling is of some importance to the chemical interpretation. The h , k , l refinement yielded Al-S and Al'-S bond distances of 2.328 (2) and 2.357 (2) Å, respectively, which are significantly different. On the other hand, the $-h$, $-k$, $-l$ refinement yielded Al-S and Al'-S bond distances of 2.345 (2) and 2.351 (2) Å, respectively, which are not significantly different. Since no steric interactions could be found to explain the different bond lengths obtained in the h , k , l refinement, the $-h$, $-k$, $-l$ refinement is again favored. All of the results discussed, therefore, will deal with the latter refinement. Refinement of the structure formed by a reflection of the $-h$, $-k$, $-l$ structure through the (001) plane would not converge. Table I contains a listing of the final coordinates and temperature factors. Table II contains the final calculated and observed structure factors amplitudes in electrons. Selected bonded and nonbonded interatomic distances appear in Table III, and selected bond angles are listed in Table IV. Our numbering system is indicated on Figure 1. A listing of the root-mean-square displacement of the nonhydrogen atoms, as calculated by ORFFE, appears in Table V.

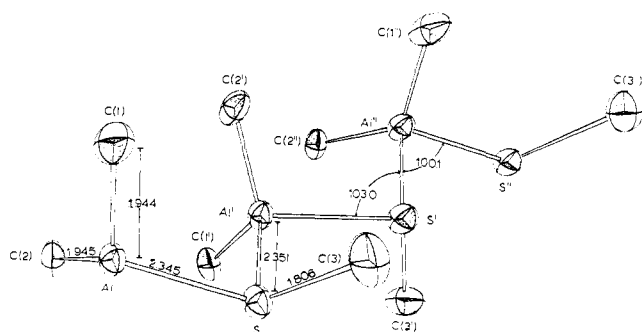


Figure 1. A perspective drawing of three $(\text{CH}_3)_2\text{AlSCH}_3$ units in the infinite chain.

Discussion of the Structure

Dimethyl(methylthiol)aluminum has been found to exist in the solid state as a one-dimensional infinite polymer, three units of which are shown in Figure 1. No previous infinite polymeric structures, $[(\text{CH}_3)_2\text{AlX}]_n$, where X is a bridging group, have been shown to exist in the solid state. However, mixtures of cyclic oligomers and higher polymers have been postulated for the glassy forms of $(\text{CH}_3)_2\text{AlN}(\text{CH}_3)_2$.²⁸ The polymer

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is generated from the repeating units $(\text{CH}_3)_2\text{AlSCH}_3$ by alternate applications of the diamond glide $1/4 - x$, $1/4 + y$, $1/4 + z$, and of the translational operation x , $1/2 + y$, $1/2 + z$. The geometry about the aluminum atom is distorted from tetrahedral symmetry with a C(1)-Al-C(2) angle of 122.0 (4)°, C-Al-S angles of 110.8 (2) and 106.4 (3)° or C'-Al'-S angles of 105.7 (3) and 109.7 (3)°, and a S-Al-S' angle of 100.1 (1)°. The large C(1)-Al-C(2) angle is consistent with the angle formed by the terminal methyl groups and aluminum atom in $[(\text{CH}_3)_3\text{Al}]_2$, 123.1 (4)°, and suggests that this relatively large angle is due to methyl-methyl repulsion forces. The geometry about the sulfur atom is pyramidal with a C(3)-S-Al angle of 103.3 (3)°, a C(3)-S-Al' angle of 104.0 (3)°, and an Al-S-Al' angle of 103.0 (1)°. The Al-C bond distances of 1.944 (8) and 1.945 (7) Å agree within experimental error with aluminum-terminal methyl bond distances in $(\text{CH}_3)_5\text{Al}_2\text{N}(\text{C}_6\text{H}_5)_2$, 1.98 Å,⁷ in $[(\text{CH}_3)_2\text{AlN}(\text{CH}_2)_3]_3$, 1.96 Å,⁸ and in $[(\text{CH}_3)_3\text{Al}]_2$, 1.97 Å.²⁹ The S-C bond length is 1.806 (7) Å. The Al-S bond lengths of 2.345 (2) and 2.351 (2) are somewhat shorter than 2.40 Å found in $\text{AlBr}_3 \cdot \text{H}_2\text{S}$.³⁰ Subtracting Pauling's single-bond, covalent radius of carbon (0.77 Å)³¹ from the average Al-C bond distance (1.95 Å) yields 1.18 Å, an estimate of the aluminum atom covalent radius. Similarly, one obtains 1.04 Å for the covalent radius of the sulfur atom. Adding these values yields a single-bond Al-S distance of 2.22 Å. The difference between the observed and "calculated" Al-S bond lengths is similar to that observed for bridging and terminal Cl atoms (2.25 and 2.05 Å, respectively) in $[(\text{CH}_3)_3\text{AlCl}_2]_2$.³² The average C-H bond distance of 0.97 (13) Å is normal for X-ray data, but as indicated by the rather high standard deviations of the hydrogen positional and thermal parameters (Table I), the data were not very sensitive to the hydrogen atom positions. The root-mean-square amplitudes of thermal vibration are listed in Table V. No abnormally short interpolymer distances were found.

An interesting feature of this crystal analysis is that $[(\text{CH}_3)_2\text{AlSCH}_3]_n$ can exist as an infinite polymer in the

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Table II. Observed and Calculated Structure Factor Amplitudes in Electrons^a ($F(000) = 896$)

H	K	OBS	CAL	H	K	OBS	CAL	H	K	OBS	CAL	H	K	OBS	CAL	H	K	OBS	CAL
*****L= 0*****																			
-4	0	365.0	372.6	-11	-7	21.3	20.4	-3	-7	26.8	26.4	-9	-7	20.3	19.5	-18	-2	25.1	26.9
-8	0	158.1	158.5	-13	-7	29.0	29.6	-5	-7	46.1	44.6	-11	-7	22.0	20.8	-20	-2	22.4	26.1
-12	0	170.5	164.2	-15	-7	11.6	12.5	-7	-7	18.5	16.6					0	-4	47.1	47.4
-16	0	77.1	74.0					-9	-7	40.1	39.9	*****L= -6*****				-2	-4	11.6	9.6
-20	0	46.7	44.5	*****L= -2*****				-11	-7	6.5	4.4*	-2	0	25.3	25.4	-4	-4	46.9	46.4
-24	0	19.1	17.1	-2	0	16.4	14.6	-13	-7	26.7	27.4	-6	0	48.4	44.8	-6	-4	21.4	21.7
-28	0	6.1	2.8*	-6	0	68.4	67.0	-15	-7	6.0	3.3*	-10	0	76.2	75.9	-8	-4	39.9	41.1
-2	-2	67.4	69.5	-10	0	107.3	102.7					-14	0	73.8	74.1	-10	-4	29.6	29.2
-4	-2	154.6	159.1	-14	0	142.7	143.0	*****L= -4*****				-18	0	24.4	24.0	-12	-4	20.8	20.4
-6	-2	8.6	10.3	-18	0	59.9	59.4	0	0	417.5	420.2	-22	0	14.2	14.5	-14	-4	33.2	33.5
-8	-2	73.4	75.1	-22	0	38.7	35.7	-4	0	233.2	205.5	0	-2	149.2	148.6	-16	-4	9.8	9.3
-10	-2	36.4	37.7	-26	0	21.7	22.7	-8	0	129.4	122.8	-2	-2	154.8	151.0	-18	-4	26.3	30.6
-12	-2	6.1	6.3*	0	-2	135.4	137.7	-12	0	121.0	115.1	-4	-2	129.8	128.9	-2	-6	6.7	6.8*
-14	-2	82.9	82.6	-2	-2	191.1	189.3	-16	0	54.6	54.3	-6	-2	136.8	133.6	-4	-6	12.3	11.1
-16	-2	6.8	4.7*	-4	-2	77.8	81.2	-20	0	46.0	44.4	-8	-2	101.9	102.5	-6	-6	13.3	11.5
-18	-2	31.1	30.1	-6	-2	88.6	92.1	-24	0	32.9	34.0	-10	-2	90.6	88.5	-8	-6	24.3	23.2
-20	-2	15.1	13.0	-8	-2	71.1	67.9	-2	-2	48.9	50.0	-12	-2	69.1	67.2	-10	-6	12.2	11.7
-22	-2	16.9	13.5	-10	-2	53.5	52.5	-4	-2	69.9	67.7	-14	-2	45.7	46.0				
-24	-2	7.1	3.1*	-6	-2	44.1	44.8	-6	-2	44.1	44.8	-16	-2	35.3	36.1	*****L= -9*****			
-26	-2	10.1	7.3	-8	-2	39.5	40.4	-8	-2	39.5	40.4	-18	-2	28.2	28.3	-1	-1	33.0	35.0
0	-4	25.0	25.3	-10	-2	51.8	51.3	-10	-2	51.8	51.3	-20	-2	18.1	17.5	-3	-1	68.4	64.4
-2	-4	176.1	187.3	-12	-2	19.8	19.8	-12	-2	19.8	19.8	-22	-2	19.7	20.7	-5	-1	31.2	29.8
-4	-4	28.7	28.5	-14	-2	68.0	69.1	-14	-2	68.0	69.1	-24	-2	6.6	6.2*	-7	-1	73.2	70.6
-6	-4	170.7	182.9	-16	-2	32.1	31.3	-16	-2	32.1	31.3	-2	-4	25.7	25.3	-9	-1	43.2	43.3
-8	-4	16.1	16.5	-18	-2	32.9	32.0	-18	-2	32.9	32.0	-4	-4	22.1	20.4	-11	-1	62.7	63.3
-10	-4	139.0	144.8	-20	-2	28.7	27.4	-20	-2	28.7	27.4	-6	-4	18.9	16.9	-13	-1	20.3	19.5
-12	-4	19.3	17.8	-22	-2	17.7	18.3	-22	-2	17.7	18.3	-8	-4	33.0	32.8	-15	-1	36.5	37.7
-14	-4	78.1	77.1	-24	-2	11.9	12.1	-24	-2	11.9	12.1	-10	-4	7.3	6.7*	-17	-1	16.3	18.0
-16	-4	27.6	27.1	0	-4	41.4	42.6	0	-4	41.4	42.6	-12	-4	35.5	34.3	-19	-1	16.7	18.5
-18	-4	36.7	35.6	-2	-4	117.5	119.2	-2	-4	117.5	119.2	-14	-4	17.0	16.0	-1	-3	38.7	37.9
-20	-4	16.4	15.5	-4	-4	45.3	47.3	-4	-4	45.3	47.3	-16	-4	26.7	26.5	-3	-3	39.6	39.4
-22	-4	11.4	13.0	-6	-4	113.4	115.4	-6	-4	113.4	115.4	-18	-4	15.9	15.2	-5	-3	25.4	23.8
-24	-4	6.5	6.2*	-8	-4	16.9	15.7	-8	-4	16.9	15.7	-20	-4	17.9	18.0	-7	-3	22.9	21.6
-2	-6	17.5	18.8	-10	-4	41.7	40.6	-10	-4	41.7	40.6	0	-6	58.3	59.1	-9	-3	35.8	35.8
-4	-6	6.9	4.6*	-12	-4	13.1	11.2	-12	-4	13.1	11.2	-2	-6	63.3	63.8	-11	-3	17.0	16.0
-6	-6	13.5	12.6	-14	-4	33.0	31.9	-14	-4	33.0	31.9	-4	-6	54.9	55.5	-13	-3	32.6	33.8
-8	-6	25.9	26.1	-16	-4	7.0	8.3*	-16	-4	7.0	8.3*	-6	-6	43.3	44.2	-15	-3	18.0	19.0
-10	-6	7.0	1.3*	-18	-4	18.3	19.8	-18	-4	18.3	19.8	-8	-6	52.5	50.1	-17	-3	19.4	20.9
-12	-6	42.9	42.5	0	-6	56.5	57.6	-20	-4	12.0	11.1	-10	-6	31.3	30.3	-1	-5	44.7	43.8
-14	-6	6.9	1.9*	-2	-6	58.2	57.9	-22	-4	21.6	23.6	-12	-6	43.4	42.6	-3	-5	28.0	27.2
-16	-6	26.0	26.0	-4	-6	49.5	48.7	-2	-6	13.4	13.1	-14	-6	20.4	20.3	-5	-5	52.0	50.7
-18	-6	6.4	3.6*	-6	-6	31.8	32.1	-4	-6	13.6	11.5	*****L= -7*****				-7	-5	22.2	21.4
-20	-6	11.4	13.7	-8	-6	58.8	56.8	-6	-6	14.3	13.8	-1	-1	36.9	35.1	-9	-5	35.8	33.7
0	-8	43.2	43.8	-10	-6	16.6	16.3	-8	-6	29.5	29.5	-3	-1	74.7	72.9	-11	-5	16.3	16.6
-2	-8	6.9	6.3*	-12	-6	59.9	57.8	-10	-6	12.3	12.8	-5	-1	62.1	62.4	*****L= -10*****			
-4	-8	49.2	51.8	-14	-6	12.3	11.6	-12	-6	40.1	39.3	-7	-1	106.0	99.4	-2	0	12.6	13.8
-6	-8	6.9	2.9*	-16	-6	31.5	31.3	-14	-6	10.5	9.6	-9	-1	32.1	30.3	-6	0	28.5	26.8
-8	-8	43.1	44.0	-18	-6	6.5	7.1*	-16	-6	25.5	25.0	-11	-1	77.3	75.3	-10	0	41.2	43.6
-10	-8	14.0	11.5	-2	-8	6.3	4.3*	-18	-6	6.1	6.2*	-13	-1	33.8	33.8	-14	0	28.4	29.4
				-4	-8	6.5	3.7*	0	-8	27.4	27.1	-15	-1	38.6	38.7	-18	0	12.6	13.0
				-6	-8	16.7	16.5	-2	-8	24.8	24.6	-17	-1	35.2	35.9	0	-2	90.8	89.0
				-8	-8	6.3	7.2*	-4	-8	32.8	32.6	-19	-1	25.1	25.4	-2	-2	91.4	90.0
				-10	-8	17.2	13.9	-6	-8	21.0	21.2	-21	-1	20.0	21.6	-4	-2	80.5	77.1
*****L= -1*****												-23	-1	12.2	15.0	-6	-2	85.1	83.0
-1	-1	141.3	142.7	*****L= -3*****				*****L= -5*****				-1	-3	27.9	28.1	-8	-2	65.3	64.6
-3	-1	174.1	178.2	-1	-1	77.7	76.9	-1	-1	103.1	96.8	-3	-3	21.2	20.9	-10	-2	55.3	56.5
-5	-1	102.2	100.4	-3	-1	80.9	79.3	-3	-1	151.0	147.0	-5	-3	35.6	35.3	-12	-2	44.9	46.6
-7	-1	83.7	85.9	-5	-1	124.7	121.4	-5	-1	74.0	73.4	-7	-3	21.2	21.6	-14	-2	26.6	27.9
-9	-1	141.4	140.2	-7	-1	70.8	65.3	-7	-1	134.3	132.2	-9	-3	27.2	27.0	-16	-2	18.7	20.7
-11	-1	73.6	74.3	-9	-1	67.8	67.0	-9	-1	100.8	93.3	-11	-3	38.6	38.6	-2	-4	7.4	9.7*
-13	-1	103.9	105.4	-11	-1	38.6	37.9	-11	-1	113.4	110.1	-13	-3	36.2	36.8	-4	-4	13.9	11.5
-15	-1	46.5	46.3	-13	-1	84.7	83.1	-13	-1	45.9	46.4	-15	-3	31.8	32.6	-6	-4	7.3	9.4*
-17	-1	71.1	70.4	-15	-1	13.7	15.3	-15	-1	63.6	63.2	-17	-3	30.3	30.4	-8	-4	17.4	16.0
-19	-1	24.7	23.4	-17	-1	75.1	74.8	-17	-1	18.2	18.8	-19	-3	18.4	19.2	-10	-4	11.5	8.9
-21	-1	30.0	28.9	-19	-1	14.7	13.4	-19	-1	31.8	30.8	-21	-3	14.4	16.8	-12	-4	19.4	18.8
-23	-1	11.9	9.4	-21	-1	42.5	41.2	-21	-1	7.1	3.7*	-1	-5	64.6	65.6				
-25	-1	16.6	16.2	-23	-1	10.9	7.9	-23	-1	16.7	17.2	-3	-5	50.1	50.8	*****L= -11*****			
-27	-1	6.6	5.0*	-25	-1	24.1	26.5	-25	-1	6.6	2.6*	-5	-5	56.1	56.1	-1	-1	47.2	47.3
-1	-3	144.8	157.6	-27	-1	6.8	10.5*	-1	-3	118.1	119.8	-7	-5	25.8	24.8	-3	-1	62.5	63.5
-3	-3	151.3	158.9	-29	-1	52.5	56.8	-3	-3	119.7	126.0	-9	-5	51.9	52.3	-5	-1	44.8	43.9
-5	-3	74.4	79.3	-3	-3	53.9	58.3	-5	-3	72.7	72.6	-11	-5	27.1	27.4	-7	-1	67.9	69.2
-7	-3	91.0	94.6	-5	-3	24.0	25.4	-7	-3	61.6	62.5	-13	-5	34.3	34.8	-9	-1	32.6	34.2
-9	-3	84.0	84.9	-7	-3	58.3	60.0	-9	-3	82.4	81.6	-15	-5	24.7	25.3	-11	-1	49.8	51.1
-11	-3	106.0	108.3	-9	-3	28.9	28.7	-11	-3	42.6	44.1	-17	-5	20.3	21.8	-13	-1	16.5	18.3
-13	-3	58.4	59.1	-11	-3	102.7	106.9	-13	-3	66.8	65.0	-1	-7	6.4	6.5*	-15	-1	24.2	27.0
-15	-3	67.5	68.7	-13	-3	11.1	7.7	-15	-3	21.7	22.5	-3	-7	15.5	14.3	-1	-3	44.1	43.7
-17	-3	26.6	25.7	-15	-3	72.8	74.2	-17	-3	37.3	37.8	-5	-7	13.3	12.9	-3	-3	41.0	38.9
-19	-3	30.5	29.0	-17	-3	14.7	14.5	-19	-3	10.3	9.4	-7	-7	8					

Table III. Interatomic Distances (Å) for the Nonhydrogen Atoms^a

Bonded Distances	
Al-S	2.345 (2)
Al'-S	2.351 (2)
Al-C(1)	1.944 (8)
Al-C(2)	1.945 (7)
S-C(3)	1.806 (7)
Nonbonded Distances	
Al-Al'	3.676 (1)
Al-C(3)	3.272 (8)
Al-C(3)	3.293 (8)
C(1)-C(2)	3.402 (12)
C(1)-C(3)	3.527 (12)
S-C(1)	3.538 (8)
S-C(2)	3.443 (8)
S-C(1')	3.432 (8)
S-C(2')	3.530 (8)
S-S'	3.600 (1)

^a Errors in the lattice parameters are included in the estimated standard deviations.

Table IV. Bond Angles (Deg)^a

Al-S-Al'	103.0 (1)
S-Al'-S'	100.1 (1)
C(1)-Al-C(2)	122.0 (4)
S-Al-C(1)	110.8 (3)
S-Al-C(2)	106.4 (3)
S-Al'-C(1')	105.7 (3)
S-Al'-C(2')	109.7 (3)
Al-S-C(3)	103.3 (3)
Al'-S-C(3)	104.0 (3)

^a See Table III.

Table V. Root-Mean-Square Amplitudes of Vibration (Å) along the Principle Axes R_i ^a

Atom	R_1	R_2	R_3
Al	0.180 (2)	0.238 (2)	0.283 (1)
S	0.188 (2)	0.233 (2)	0.294 (2)
C(1)	0.226 (9)	0.272 (9)	0.353 (9)
C(2)	0.212 (9)	0.276 (8)	0.358 (9)
C(3)	0.220 (8)	0.262 (8)	0.361 (9)

^a See Figure 1.

about the remaining aluminum-bridging methylthiol bond. The reverse process would regenerate the dimer from the infinite polymer. Another possibility is a simple solid-state reaction which occurs as the dimers are deposited on the sublimation tube walls. A route is through the interaction of a lone pair of electrons on a sulfur with an aluminum atom in another dimer to yield a five-coordinate aluminum atom intermediate.

It has been suggested³³ that by decreasing the electronegativity of the bridging group and therefore the ionic character of the metal-bridge bond in nonelectron-deficient dimeric systems metal-metal repulsions should increase. In the case of second-row bridging groups, the increase of metal-metal repulsion can be relieved and better bridge bonding can be obtained by forming

(33) L. F. Dahl, private communication, Oct 1968.

trimeric systems with correspondingly large Al-bridge-Al angles as in $[(\text{CH}_3)_2\text{AlN}(\text{CH}_2)_2]_3$.⁸ However, in the case of the sulfur bridging groups, Gillespie has suggested³⁴ that nonbonding lone pairs hinder the formation of large bond angles at the sulfur atom. Thus, the sulfur-bridged dimeric systems cannot easily reduce metal-metal repulsions by the formation of trimeric systems. This reasoning would imply that the polymeric form, $[(\text{CH}_3)_2\text{AlSCH}_3]_n$, with larger metal-metal distances should be more stable than dimeric or trimeric species.

One objective of this study was to determine the geometry about three-coordinate sulfur when bonded to a main group metal. The anomalous behavior of oxygen in this connection has been noted previously.⁷ It is obvious from the structural results that pyramidal, three coordination of sulfur atoms does occur in the main group as well as in transition element compounds. This effect may be due to the inability of the sulfur atom to form dative sulfur-metal π bonds. It has been pointed out recently by Donohue,³⁵ however, that planar, three coordination for oxygen exists in hydrogen-bonded compounds in which the oxygen atom is coordinated to three hydrogen atoms. It does not, then, appear to be necessary to invoke dative π bonding involving oxygen p orbitals and empty metal d orbitals in order to explain the coplanarity of the oxygen atoms with its coordinated atoms in the bridged metal systems. A structural study of alkoxy-bridged beryllium or boron atoms would be of interest in this connection.

The nuclear magnetic resonance spectrum of this compound was also measured. The spectrum of 44° in toluene contains a peak at τ 10.18 \pm 0.02 (integrated intensity of 11.0 \pm 1.0), which is probably due to the resonance of the terminal methyls on the aluminum atoms and also a peak at τ 8.09 \pm 0.02 (integrated intensity of 5.7 \pm 0.05), which may be assigned to the resonance of the methyl group bonded to the sulfur atom. These assignments are supported by the occurrence of the terminal methyl resonances of $[(\text{CH}_3)_3\text{Al}]_2$, $[(\text{CH}_3)_2\text{AlCl}]_2$, and $[(\text{CH}_3)_2\text{AlBr}]_2$ in toluene at τ 10.28 (-50°), 10.10 (-50°), and 10.00 (40°),³⁶ respectively, and by the value of τ 7.90 found for the methylmercapto resonance of $\text{CH}_3\text{SC}_2\text{H}_5$. At 0° , the methylmercapto resonance of $[(\text{CH}_3)_2\text{AlSCH}_3]_n$ broadens. If the $(\text{CH}_3)_2\text{AlSCH}_3$ species is indeed a dimer in toluene solution,⁹ the broadening effect at lower temperatures may be due to quenching of exchange between *cis* and *trans* configurations of the methylthiol group. Such an exchange has been proposed in other systems.³⁷ Attempts to observe the resonance at lower temperatures were hindered by precipitation of the sample.

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