O_2F_2 signal should remain in its usual region while the $(OOF)_n$ signal would migrate with temperature until it coalesces with that of O_2F_2. Our results would indicate, and we believe that the temperature studies of Solomon, *et al.*, indicate also, that "O_3F_2" cannot be as simply described as a mixture of O_2F_2 and $(OOF)_n$.

The ease with which O_3F_2 reverts to O_2F_2, together with the fact that no really adequate structure can be drawn for O_3F_2, suggests a model of "O_3F_2" in which "interstitial" oxygen is being held by O_2F_2 molecules. Such a model fits the observations most fully. This model is further substantiated by mass spectral studies[13] which show that "O_3F_2" can be described as O_2F_2 plus O_2.

If one extends the model one step further and considers a 1:1 ratio of O_2F_2 and O_2, it becomes apparent that the most reasonable structure in this instance is $(OOF)_n$, or the model for O_4F_2 as suggested by infrared studies.[14]

An unequivocal interpretation of the ^{19}F nmr signal from O_3F_2 cannot be made at this time. It would appear that the key lies in the determination of ^{19}F nmr shifts in the O_4F_2 or in the OOF species. Our attempts to determine chemical shifts for O_4F_2 were not successful, since the instability of this species is very much greater than that associated with O_2F_2 or even "O_3F_2." With the development of more refined low-temperature nmr techniques, however, such information should be made available.

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On the Crystal Structure of Trimethylaluminum

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Abstract: The crystal structure of trimethylaluminum has been redetermined by three-dimensional, single-crystal X-ray diffraction techniques from photographic data obtained at −50°. Hydrogen as well as aluminum and carbon atoms were located. The structure consists of $Al_2(CH_3)_6$ molecules with symmetrical Al–C–Al bridges. An Al–C–Al bridge angle of 74.7 ± 0.4° and an Al–C bridge distance of 2.14 ± 0.01 A were found. The nonbridged Al–C distance is 1.97 ± 0.01 A. An Al–Al distance of 2.600 ± 0.004 A was found, ~0.1 A longer than previous results indicated. A significant molecular distortion involving the terminal carbon atoms makes the nuclear framework (excluding hydrogen) belong to point group C_{2h} instead of the idealized D_{2h}. There exists no experimental evidence to indicate that the bridge is not correctly described with a carbon sp_3 orbital participating in a four-center, four-electron, electron-deficient bridge bond.

The original example of electron-deficient methyl bridge bonding was tetramethylplatinum,[3] which is now generally recognized as nonexistent.[4] Trimethylgallium has been shown to be monomeric down to very low temperatures[5] in benzene solution and in the pure liquid at room temperature.[6] Trimethylindium[7,8] is, at best, only very weakly bonded into a higher polymer. Hence, there exist at this time only three examples of "five-coordinate carbon" or electron-deficient methyl bridge bonds: dimethylberyllium,[9] dimethylmagnesium[10] (powder data only), and trimethylaluminum.[11] Previously, Amma[12] had attempted a refinement of the three-dimensional data of trimethylaluminum collected in the original two-dimensional structure determination,[11] but the refinement failed to converge properly. Similar results have been obtained for the refinement of the photographic data of dimethylberyllium.[13] The failure of these refinements is probably due to the quality of the original diffraction data. With the availability of better vacuum-line[14] and low-temperature[15] techniques, we decided to reinvestigate this crystal structure because this compound is the prototype of methyl bridge electron-deficient bridging bonding and is important not only to the understanding of metal–alkyl bonds but also to the nature of intermediates in many organic reactions.

Experimental Section

Trimethylaluminum was purchased from the Ethyl Corp. in a small cylinder, and a sample from this was removed into a storage tube in a vacuum line. The sample was sublimed several times and then sublimed directly into very thin-walled Pyrex capillaries.[13] The capillaries were then cut off under liquid nitrogen, and the melting point of the sample in each capillary was checked. Crystals were grown in a cold room at 0° and annealed with a small electric

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Table I. Positional and Temperature Parameters and Errors ($\sigma' = \sigma \times 10^4$)

Atom[a]	x/a	$\sigma'(x/a)$	y/b	$\sigma'(y/b)$	z/c	$\sigma'(z/c)$
Al	0.4708	3	0.5747	3	0.4073	2
C_1	0.6221	11	0.3814	13	0.5084	8
C_2	0.3518	12	0.4325	16	0.2701	8
C_3	0.5520	11	0.8152	13	0.4098	8
H_{1C1}	0.133	...[b]	0.183	...[b]	0.083	...[b]
H_{2C1}	0.133	...[b]	0.183	...[b]	−0.050	...[b]
H_{3C1}	0.217	...[b]	0.067	...[b]	0.058	...[b]
H_{1C2}	0.260	...[b]	0.466	...[b]	0.234	...[b]
H_{2C2}	0.366	...[b]	0.300	...[b]	0.300	...[b]
H_{3C2}	0.384	...[b]	0.517	...[b]	0.234	...[b]
H_{1C3}	0.133	...[b]	0.300	...[b]	0.416	...[b]
H_{2C3}	0.017	...[b]	0.400	...[b]	0.434	...[b]
H_{3C3}	0.00	...[b]	0.383	...[b]	0.350	...[b]

Thermal Parameters and Standard Deviations

Anisotropic Temperature Factors of the Form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta kl)]$; $\sigma' = \sigma \times 10^4$

Atom	β_{11}	σ'	β_{22}	σ'	β_{33}	σ'	β_{12}	σ'	β_{13}	σ'	β_{23}	σ'
Al	0.0025	4	0.0142	4	0.0039	1	−0.0015	3	0.0026	2	−0.0007	2
C_1	0.0067	15	0.0211	21	0.0086	8	0.0035	13	0.0055	9	0.0010	10
C_2	0.0084	17	0.0301	27	0.0072	8	−0.0051	16	0.0051	9	−0.0032	11
C_3	0.0072	15	0.0189	21	0.0089	8	−0.0018	12	0.0044	9	0.0015	10

Hydrogen atom isotropic temperature factors			Scale	
Atom	B, A^2	Layer	factor[c]	σ
H_{1C1}	3.5	0*kl*	1.002	0.034
H_{2C1}	3.5	1*kl*	1.005	0.015
H_{3C1}	3.5	2*kl*	0.985	0.024
H_{1C2}	3.5	3*kl*	1.009	0.026
H_{2C2}	3.5	4*kl*	1.009	0.022
H_{3C2}	3.5	5*kl*	1.011	0.031
H_{1C3}	3.5	6*kl*	0.999	0.022
H_{2C3}	3.5	7*kl*	0.999	0.036
H_{3C3}	3.5	8*kl*	1.007	0.036

[a] The notation H_{1C1} refers to H_1 on carbon atom C_1. [b] Hydrogen coordinates and temperature factors not varied in least squares and no estimate of coordinate or temperature factor errors given. [c] The ratio of these scale factors was fixed by the isotropic refinement. The absolute value was fixed by the anisotropic refinement using one scale factor. However, the change in going from the isotropic to the anisotropic refinement was small.

light bulb. Crystals were checked for perfection in the cold room under a polarizing microscope and then transferred *via* a dewar to a Weissenberg camera completely enclosed in a double-walled Plexiglass housing,[14] cooled to −50° by sublimation of Dry Ice.

X-Ray Data. The crystals were found to be monoclinic with unit cell constants determined by back-reflection techniques with Cu Kα (λ = 1.5405), Kα_2 (λ = 1.5443): a = 12.74 ± 0.02 A, b = 6.96 ± 0.01 A, c = 14.63 ± 0.02 A, and β = 123° 40′ ± 15′. The observed systematic extinctions (hkl, $h + k = 2n + 1$; $h0l$, $h = 2n + 1$, $l = 2n + 1$) limited the possible space groups to Cc or C2/c. The X-ray analysis indicated the correct space to be C2/c (*vide infra*). With eight molecules per unit cell the density was calculated as 0.887 g cm^{-3}, in favorable agreement with the density of liquid trimethylaluminum of 0.752 g cm^{-3}. Crystals used for the collection of intensity data were 0.2 × 0.2 × 0.3 mm or less in size. The linear absorption coefficient (μ) with Cu Kα radiation is 17 cm^{-1} and with crystals of the size indicated above, μr is sufficiently small that absorption corrections could be neglected.

It was found that crystals could be grown with any of the three crystallographic directions parallel to the capillary axis. Standard equi-inclination multiple-film intensity data were obtained using nickel-filtered Cu Kα radiation with the [100] and [010] directions as rotation axis. These data were visually estimated, correlated, and merged to yield 575 independent hkl intensities. The usual Lorentz polarization corrections were made.

Structure Refinement

A three-dimensional Patterson and electron density function were computed to check the previous structure determination.[16] A least-squares refinement was carried out by minimizing the function $\Sigma w(F_o - F_c)^2$ using the Busing and Levy program[17] on the IBM 7090. The Hughes[18] weighting scheme was used with $4F_{\min}$ = 10.0. Scattering factors were from standard sources.[19] The variables for the isotropic refinement were the atomic coordinates, individual atom isotropic temperature factors for aluminum carbon, and the scale factors. The scale factors were allowed to vary at this stage, solely to check the accuracy of our data merging. As can be seen from Table I, the interlayer scaling is quite satisfactory. The anisotropic refinement had the atomic coordinates, six β_{ij} for each atom and one scale factor as variables.

Hydrogen atom positions were located from three-dimensional difference maps after the completion of the anisotropic refinement of the nonhydrogen atoms. These difference maps were computed with arbitrary sin θ cutoffs and inclusion of F(calcd) terms for unobserved reflections. The best hydrogen atom resolution was obtained with a sin θ cutoff of 0.6. Attempts to refine the hydrogen positions by least squares were unsuccessful.

The shifts in atomic coordinates for the last least-squares cycle were less than 5 × 10^{-5} of a cell edge. The final disagreement index (R),[20] the weighted R,

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(16) Patterson and electron-density calculations made with the Sly-Shoemaker–van den Hende program, ERF-2.

(17) W. R. Busing and H. A. Levy, OR FLS Program ORNL-TM-305.

(18) E. W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).

(19) Scattering factors for neutral Al, C, and H from the compilation of J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

Table II. Interatomic Distances (A) and Angles (deg)[a]

	Bonded		
Bridge			
$Al-C_1$	2.134 ± 0.010	C_3-Al-C_2	123.1 ± 0.4
$Al-C_1'$	2.153 ± 0.012	C_2-Al-C_1'	107.2 ± 0.5
Terminal			
		$C_1'-Al-C_3$	108.7 ± 0.5
$Al-C_2$	1.983 ± 0.010	C_1-Al-C_1'	105.3 ± 0.4
$Al-C_3$	1.958 ± 0.011	C_3-Al-C_1	105.1 ± 0.5
$Al-Al'$	2.600 ± 0.004	C_2-Al-C_1	106.1 ± 0.5
Bridge, C-H		$H_1-C_1-H_2$	90
C_1-H_1	1.05	$H_1-C_1-H_3$	96
C_1-H_2	1.12	$H_2-C_1-H_3$	120
C_1-H_3	1.04	$H_1-C_2-H_2$	109
Terminal C-H		$H_1-C_2-H_3$	86
C_2-H_1	1.02	$H_2-C_2-H_3$	100
C_2-H_2	1.03	$H_1-C_3-H_2$	101
C_2-H_3	1.00	$H_1-C_3-H_3$	85
C_3-H_1	0.99	$H_2-C_3-H_3$	88
C_3-H_2	0.92	$Al-C_1-Al'$	74.7 ± 0.4
C_3-H_3	0.93	$Al'-Al-C_2$	118.2 ± 0.3
		$Al'-Al-C_3$	118.7 ± 0.3
	Nonbonded, Intramolecular		
C_1-C_1'	(bridge-bridge)		3.409 ± 0.022
C_1-C_3	(bridge-terminal)		3.251 ± 0.013
C_1-C_2	(bridge-terminal)		3.290 ± 0.016
C_2-C_3	(terminal-terminal)		3.464 ± 0.014
C_1-C_3'	(bridge-terminal)		3.342 ± 0.017
C_1-C_2'	(bridge-terminal)		3.331 ± 0.015

Nonbonded, Intermolecular

All intermolecular distance greater than 3.9 A

Dihedral angle between normals to planes defined by C_2-Al-C_3 and $C_1'-Al-C_1$, 89.2 ± 0.5

Equation of plane defined by Al, C_2, C_3 of the form

$$AX + BY + CZ - D = 0$$

$$A = 0.8501, B = 0.5169, C = -0.1010, D = +0.7240$$

Displacement of Al′, C_2', and C_3' from this plane = −0.120 A

Angle between Al-Al′ vector and Al-(C_2-C_3 bisector) 2.6 ± 0.3°

[a] Prime refers to atom related by the center of symmetry at the molecular center; *e.g.*, C_1' refers to C_1 transformed by $\bar{1}$ at center of molecule.

and the standard error were found to be 0.117, 0.145, and 2.00, respectively. Without the hydrogen contribution, the disagreement index was 0.128. Attempts at refinement of the structure in the lower symmetry space group, Cc, led to large correlations ~0.9 for atoms that were symmetry related in C2/c. Refining one set while holding the other set fixed led to the centrosymmetric structure to within less than a standard deviation. Hence, the correct space group is the centric C2/c.

It is of considerable importance (*vide infra*) to ascertain if the bridging carbon (C_1) can be equally well described as disordered along a line parallel to the Al–Al vector. We split C_1 into two carbon half-atoms and displaced them symmetrically about the C_1 position indicated in Table I. It was found that the atomic coordinates of these half-atoms were strongly correlated (>0.9) and could not be refined even with isotropic temperature factors. Attempts at refinement by fixing the coordinates of the carbon half-atoms and varying the coordinates of the other carbon half-atoms were equally unsuccessful. We conclude that within the limits of our experimental data the structure is best described by an ordered model with the thermal parameters indicated in Table III.

Table III. Rms Component of Thermal Displacement along the Principal Axes of the Thermal Ellipsoid (1, 2, 3) and Angles between These Principle Axes and the Cartesian Coordinate System Defined by (1) $(\overrightarrow{Al-Al'})$, α; (2) $[(\overrightarrow{Al-Al'}) \times (\overrightarrow{C-C'})]$, β; and (3) $[\overrightarrow{(1)} \times \overrightarrow{(2)}]$, γ ($[\overrightarrow{(1)} \times \overrightarrow{(2)}]$ essentially $\overrightarrow{C-C'}$ direction)

Atom	Rms component, A	α, deg	β, deg	γ, deg
Al	(1) 0.074 ± 0.017	111.7	120.3	38.7
	(2) 0.166 ± 0.003	129.3	41.3	79.2
	(3) 0.193 ± 0.003	132.7	115.1	126.7
C_1	(1) 0.142 ± 0.032	95.4	94.2	6.87
	(2) 0.236 ± 0.013	143.3	125.7	96.8
	(3) 0.257 ± 0.012	53.9	143.8	90.2
C_2	(1) 0.186 ± 0.027	110.3	133.4	50.3
	(2) 0.218 ± 0.012	134.8	50.1	72.1
	(3) 0.293 ± 0.013	128.3	110.0	134.9
C_3	(1) 0.177 ± 0.020	112.7	147.5	68.1
	(2) 0.223 ± 0.014	127.9	93.7	141.8
	(3) 0.274 ± 0.013	46.5	122.2	119.6

The observed and calculated structure factors are listed elsewhere.[21] Table I contains the final parameters and errors for the same refinement. Table II gives the interatomic distances, angles, and errors.[22]

Description of Structure

The crystal structure of trimethylaluminum consists of two monomers related by a center of symmetry to form a dimer with bridging methyl groups. These dimers are then separated by ordinary van der Waals' distances (Table II) to form a molecular crystal. Although these results are in general agreement with the features of the previous structure determination,[11] significant differences were found. In particular (1) the Al–Al distance is 2.600 ± 0.005 A, ~0.1 A longer; (2) the Al–C–Al angle is now 74.7 ± 0.4° compared to 70°; (3) the Al–C bridging distance is 2.14 ± 0.01 A instead of 2.22 A. However, our Al–C terminal distance is well within error of the earlier results. This terminal distance is in good agreement with the 2.00 A observed in $KF \cdot 2Al(C_2H_5)_3$[23] and in $(C_6H_5)_3Al$[24] as well as the 2.02 A in $LiAl(C_2H_5)_4$.[25] In the latter, some elongation is to be expected on chemical grounds. Our C_2–Al–C_3 angle of 123.1° is to be compared with 112.1 and 108° in $LiAl(C_2H_5)_4$. Although previously unreported, the short bridge methyl-carbon to terminal methyl-carbon distance of 3.3 A is to be noted. The methyl-methyl nonbonded distances calculated from the sum of the van der Waals radii is 4.0 A. All the intermolecular distances remain more or less normal, *i.e.*, >3.9 A (*cf.* Figures 1 and 2).

The most pronounced difference between our structure determination and earlier results is that we find a nonnegligible molecular distortion (Table II). The aluminum and terminal atoms of one dimer are not

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(20) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; weighted $R = \Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2$; standard error $= [\Sigma(F_o - F_c)^2/(NO - NV)]^{1/2}$ (NO = number of observations = 575; NV = number of variables = 37).

(21) This tabulation and a more detailed form of this paper (or extended version, or material supplementary to this article) has been deposited as Document No. 9373 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(22) All distances, angles, and errors were computed with a Busing-Levy OR FFE, ORNL-TM-306.

(23) G. Allegra and G. Perego, *Acta Cryst.*, **16**, 185 (1963).

(24) H. McBride, private communication.

(25) R. L. Gerteis, R. E. Dickerson, and T. L. Brown, *Inorg. Chem.*, **3**, 872 (1964).

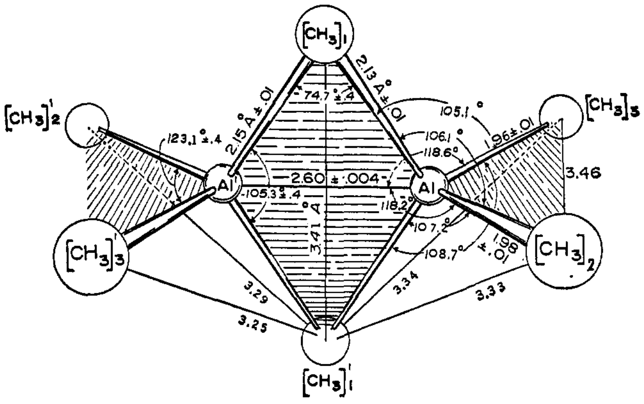


Figure 1. Geometry, bond distances, and bond angles in the dimeric trimethylaluminum molecule. Methyl distances refer to carbon distances. Hydrogen atoms are not shown for reasons of simplicity.

coplanar. A separation of 0.12 A is found between the parallel planes defined by AlC_2C_3 and $Al'C_2'C_3'$. This distortion can also be seen from the angle of 2.6 ± 0.3° between the Al–Al′ line and the line defined as Al–(bisector of C_2–C_3). Since the dihedral angle between the planes defined by C_2, Al, C_3 and C_1', Al, C_1 is 89.2 ± 0.5°, the molecular symmetry (exclusive of hydrogen) is C_{2h} with the twofold rotation axis bisecting the Al–Al′ line and perpendicular to the Al–C_1–Al′C_1' plane. The origin of this distortion is not clear at this time.

Although we report hydrogen atom positions, the errors in these atomic coordinates are probably sufficiently large so that no physical significance should be attached to the differences in C–H bond distances and H–C–H bond angles.

Discussion

Since it is now clear that only the aluminum alkyls of the group III metal alkyls are dimerized with relatively strong Al–C–Al bridge bonds, the nature of this bridge is of particular importance. The aluminum alkyls have been extensively studied by infrared, Raman,[26] and nmr[27] spectroscopy, and it seems worthwhile at this point to relate our structure results to these other measurements.

The nmr spectrum of trimethylaluminum at room temperature consists of a sharp singlet in contrast to the two expected for the bridging and terminal groups. This indicates that the two species are either magnetically equivalent or are involved in a rapid exchange process.[28] At −75° the spectrum[27a] consists of two resonances with an area ratio of 2:1, indicating a rapid exchange process at room temperature. At this time it is not possible to distinguish between two mechanisms for this exchange: (1) the breaking of one Al–C bridge bond which may re-form with a different methyl group in the bridge and (2) a deformation of the molecule in which no bonds are broken, leading to an intermediate with four bridging methyl groups. These processes are shown in Scheme I.[27b]

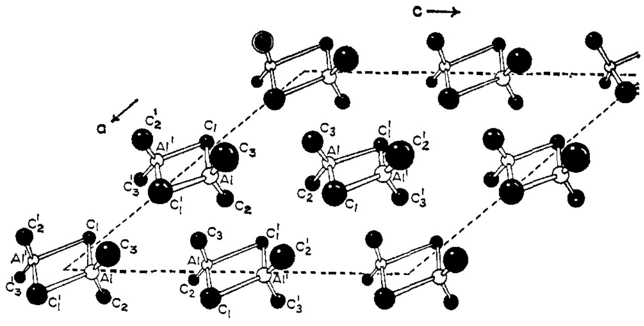
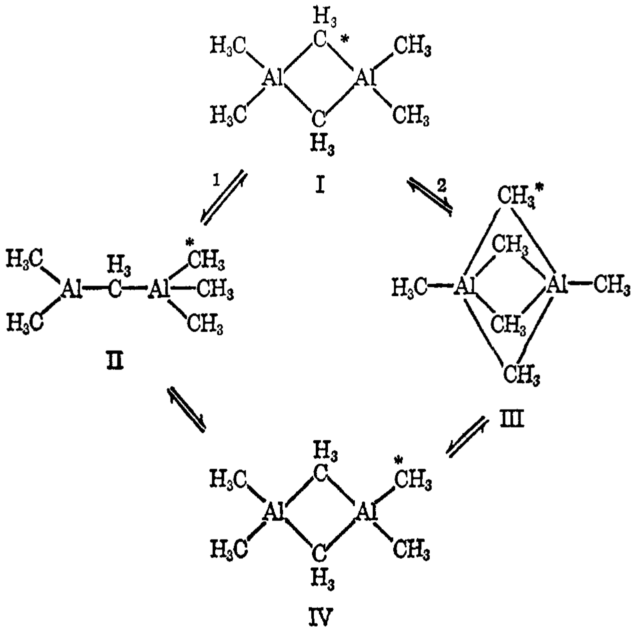
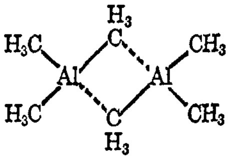


Figure 2. Perspective down the *b* axis indicating the arrangement of the dimeric molecules in the unit cell.

Scheme I



Neither the nmr spectra, the infrared solution, nor vapor phase spectra down to 300 cm^{-1} can distinguish between the symmetrically bridged structures I and IV (D_{2h} symmetry) or the asymmetric bridge (C_{2h} symmetry) structure V. This has led to speculation that



V

trimethylaluminum actually exists in dynamic equilibrium between the two asymmetrically bridged structures (VI). An equilibrium of this type would facilitate a bridge opening such as II and help to explain the rapid exchange process. Because of the limitations in the earlier diffraction data as well as the lack of computing facilities in that era of crystallography, neither structure V nor the dynamic equilibrium could be fully ruled out. The Al–C distances had an estimated stand-

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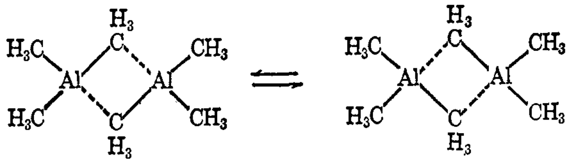
[26] (a) K. Pitzer and H. Gutowsky, *J. Am. Chem. Soc.*, **68**, 2204 (1946); (b) C. P. Van der Kelen and M. A. Herman, *Bull. Soc. Chim. Belges*, **65**, 362 (1956); (c) E. G. Hoffman, *Z. Electrochem.*, **64**, 616 (1960); (d) E. G. Hoffman and G. Schomburg, *ibid.*, **61**, 1101 (1957); (e) A. P. Gray, *Can. J. Chem.*, **41**, 1511 (1963).

[27] (a) N. Muller and D. E. Pritchard, *J. Am. Chem. Soc.*, **82**, 248 (1960); (b) K. C. Ramey, J. F. O'Brien, I. Hasegawa, and A. E. Borchert, *J. Phys. Chem.*, **69**, 3418 (1965); (c) C. P. Poole, Jr., H. E. Swift, and J. F. Itzel, Jr., *ibid.*, **69**, 3663 (1965).

[28] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 218.

ard deviation of ±0.02 A, but a more realistic appraisal would have been ±0.04–0.05 A.[11]



VI

We feel that our structure determination rules out the asymmetric bridge features of structure V, but the molecular symmetry of the dimer is, nevertheless, C_{2h} due to the fact that the aluminum and terminal carbon atoms are not coplanar.

If the bridge distortion as in structure V was significant, it should manifest itself in one or more of the following ways. One is a significant asymmetry in Al–C and Al′–C bridge distances. This is not observed. The Al–C–Al′ bridge is symmetric well within statistical error (Table III). Another is a statistical disordering of the molecules corresponding to two orientations related by a twofold rotation about an axis perpendicular to the Al–Al′ line lying in the Al–C_1–Al′C_1′ plane. Hence, the bridging atoms could be described by two half carbon atoms symmetrically displaced along the Al–Al′ direction. This model would also require the C_2 and C_3 atoms to be disordered above and below a plane passing through Al and Al′ perpendicular to the Al–C_1–Al′C_1′ bridge plane. There is no evidence for any disorder of the terminal carbon atoms. No satisfactory refinement could be achieved with our data on a disordered bridging carbon half-atom model (see above). Further, this model would require at least a pronounced C_1 thermal motion parallel to the Al–Al′ line. This is not observed (Table III). Although we make no claims for accuracy of hydrogen positions, any disordering of carbon atoms would make the location of hydrogen atoms virtually impossible.

If the dynamic equilibrium VI existed in the solid state, then the disorder or thermal motion behavior delineated above should again be observed. These have already been ruled out. Therefore, we conclude that trimethylaluminum does not exist as the dynamic equilibrium VI. The correct description of the geometry of trimethylaluminum is a dimer with symmetric methyl bridge bonds and of point symmetry C_{2h} exclusive of hydrogen. The true over-all symmetry of the molecule would be $\bar{1}$ (Ci).

As put forth earlier by Rundle,[11] the bridge bonding in trimethylaluminum can be described either as a combination of tetrahedral orbitals from aluminum and carbon or as a "methylated double bond," the difference being mostly a matter of taste. In the former description two bonding four-center MO's can be constructed from the carbon and aluminum tetrahedral orbitals of symmetry a_{1g} and $b_{3\mu}$, respectively (assuming D_{2h} symmetry). The four electrons (one from each aluminum and carbon) then completely fill these two bonding molecular orbitals to give the closed-shell electronic structure. The $b_{3\mu}$ MO has a nodal plane passing through the aluminum and terminal carbon atoms, and consequently this is a distorted π orbital. With some overlap of the aluminum tetrahedral orbitals a metal–metal bent σ bond may be considered present as well. This formulation[29] bears a one-to-one correspondence to the description of diborane.[30]

Rundle[11] proposed that four principal factors govern the stability of dimers held together by alkyl bridges. Association is favored by (1) a large difference in electronegativity between the metal and carbon; (2) a low value for the energy required to promote an electron from an s to a p orbital in the valence shell of the metal; (3) a large bond energy for a normal single bond between the metal and carbon; (4) a minimal amount of inner shell repulsion between the two metal atoms separated by internuclear distances demanded by the geometry of the dimer. The first two make dimerization difficult for trimethylboron, and the last two probably act against formation of dimers by Ga, In, and Tl. If one examines the angles about Al, it is found that the C_3–Al–C_2 angle is 123.1°, the C_3–Al–Al′ angle is 118.7°, and the C_2–Al–Al′ angle is 118.2°. These are strikingly close to the ideal 120° for sp^2 hybridization. We would like to suggest, in addition to the above four factors (these are really not four independent variables), that overlap of metal–metal orbitals or metal–metal bonding is also important in the dimerization of the aluminum alkyls. Since the metal–metal bonding, in general, decreases in going down the periodic table (particularly after the 3rd row metals, *e.g*,, Si, Ge, Sn, Pb), this also tends to destabilize the dimer for the group IIIb metal alkyls after aluminum.

If factor 1 above is important, then it is not clear why dimethylberyllium[9] and dimethylmagnesium[10] are polymeric with methyl bridges but dimethylzinc[31] is monomeric—particularly since Be and Zn have essentially the same electronegativity (1.5, 1.6)[32a] and the tetrahedral covalent radius of Zn (1.31) is less than that of Mg (1.40).[32b] However, when viewed in terms of metal–metal bonding, the fact that dimethylzinc is monomeric is not surprising. Alternatively, this trend is also understandable in terms of factor 3.

An examination of the tabulated s → p excitation energies[33] shows that factor 2 cannot be the important factor for the lack of dimerization of trimethylboron. (B 2s → 2p $\sim$ 29,000 cm^{-1} $\sim$ Al 3s → 3p). The most likely reason for the lack of dimerization of trimethylboron is probably a simple steric effect. An examination of the methyl–methyl nonbonding intramolecular distances in trimethylaluminum (Table II, Figure 1) shows that the methyl groups are already tightly packed and a substantial reduction in the size of the metal atom would create a good deal of van der Waals repulsion (covalent radii (A): Al = 1.26, B = 0.88, but Be = 1.06). Therefore, with the additional data now available, factors 3 and 4 seem to be the most important. However, metal–metal bonding as well as steric repulsions are not to be neglected.

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In order to eliminate confusion,[34] it should be pointed out that a recent complete matrix least-squares anisotropic temperature factor refinement of trimethylindum[35] gave In–C distances of In–C_1, –C_2, –C_3 of 2.24 ± 0.06, 2.25 ± 0.06, and 2.16 ± 0.04 A and C–In–C angles of C_3–In–C_1 120.5 ± 1.8°, C_2–In–C_3 117.3 ± 1.3°, and C_2–In–C_1 122.2 ± 1.8°. These distances and angles are not statistically different from the earlier results,[7] but the estimates of error are probably more realistic. It is to be noted that $In(CH_3)_3$ is still planar well within statistical error, and the "pseudotetramer" should be viewed as very weakly bonded together, if at all. Where weak chemical bonds begin and end is by no means a clear-cut, unambiguous decision.

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Steric Effects in Fast Metal Complex Substitution Reactions. II[1]

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Abstract: The rate constants for the formation and dissociation of nickel(II) and cobalt(II) complexes with α- and β-aminobutyric acids have been determined by the temperature-jump method. Although rate constants for formation of higher order as well as monosubstituted complexes were measured, the most significant results with respect to a comparison between the two different metal ions concern the rate constants (k_1) for the first substitution. It was determined that substitution for both nickel(II) and cobalt(II) is faster with α-aminobutyric acid than with the β acid. That is, at 20° an ionic strength = 0.1 M for nickel(II) with α-aminobutyrate, $k_1 = 1.0 \times 10^4$ M^{-1} sec^{-1}; with β-aminobutyrate, $k_1 = 4.0 \times 10^3$ M^{-1} sec^{-1}. Under the same conditions, for cobalt(II) with α-aminobutyrate, $k_1 = 2.5 \times 10^5$ M^{-1} sec^{-1}; with β-aminobutyrate, $k_1 = 2.0 \times 10^4$ M^{-1} sec^{-1}. The relative error for these rate constants is ±20%. The rate constants determined for α-aminobutyric acid are consistent with a mechanism in which release of a water molecule from the metal ion's inner coordination sphere is rate determining. In reaching this conclusion, it is shown that an empirical factor of $^1/_2$, to account for the partial absence of spherical symmetry in these chelating agents, must be used when comparing these (and the β) values with rate constants previously determined for other ligands. The slower reactions with β-aminobutyric acid are explained by the kinetic chelate effect, in which chelate ring closure is the rate-determining step. The steric effect is appreciably greater for cobalt(II) than for nickel(II) because of the inherently greater lability of the former ion.

Studies of fast metal complex substitution reactions can be explained by a previously proposed mechanism for the formation of complexes between divalent ions and simple anionic ligands.[3–6] The initial process is the diffusion-controlled, ion-pair formation between the aquated metal ion and ligand. For most monodentate and certain polydentate ligands, the rate-determining step is the loss of a water molecule with concomitant substitution of the reactant ligand into the inner coordination shell. Since the rate-determining step is controlled by the rate of release of a water molecule from the inner coordination sphere, it is therefore a characteristic of the metal ion.

For metal complexes with multidentate ligands, the stability of the metal chelate is, in part, governed by the chelate structure.[7] The thermodynamic data for divalent metal ions with amino acids show that a five-membered ring is more stable, unless a linear complex is formed. For example, the stability constants for α- and β-aminobutyric acids differ by over a factor of 10 (see Table I).

Recently, evidence has been reported that there is also a kinetic chelate effect.[6] Studies of divalent metal chelates with α- and β-alanine show that there is a decrease in rate when changing the ligand from α-alanine to β-alanine. This decrease in rate is explained by the difficulty in forming a six-membered, as opposed to a five-membered, ring with an aminocarboxylic acid ligand. The mechanism is the same as that originally proposed, but the rate-determining step is believed to be closing of the chelate ring rather than the release of a water molecule from the inner coordination sphere of the metal ion.

The kinetics for the formation of nickel(II) and cobalt(II) chelates with α- and β-aminobutyric acid (α-

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