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The Molecular Structures of the Complexes of Trimethylaluminium with 1,3-Epoxypropane (Oxetane) and Dimethylsulfide, $(CH_3)_3AlO(CH_2)_3$ and $(CH_3)_3AlS(CH_3)_2$, Determined by Gas Phase Electron Diffraction

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The molecular structures of $(CH_3)_3AlO(CH_2)_3$ (I) and $(CH_3)_3AlS(CH_3)_2$ (II) have been determined from gas phase electron-diffraction patterns recorded with nozzle temperatures of about 70 and 20 °C, respectively. The most important bond distances are for I: Al–C = 1.965(7) Å, Al–O = 2.03(4) Å, O–C = 1.465(2) Å, ∠OAlC = 98.8(8)°, ∠AlOC = 123(4)° and ∠COC = 94.7(12)°, and for II: Al–C = 1.985(5) Å, Al–S = 2.55(2) Å, S–C = 1.817(5) Å, ∠SAlC = 96.0(10)°, ∠AlSC = 124(2)° and ∠CSC = 99(3)°. While the configuration at the oxygen atom in the complex of $(CH_3)_3Al$ with dimethylether has been shown to be planar or near planar, the angle between the OC_2 plane of the ether and the Al–O bond being $\phi = 5(4)°$, the corresponding angle in I is 37(7)°. The deviation from planarity at oxygen in I is consistent with the suggestion that the planarity at O in the dimethylether complex is due to across angle repulsion Al–C(O). The angle between the SC_2 plane in II and the Al–S bond, $\phi = 31(5)°$, is also intermediate between the values expected for trigonal and tetrahedral hybridization of the donor atom.

Trimethylaluminium, Me_3Al, forms stable complexes with amines, phosphanes, ethers and thioethers.[1] Eyman and coworkers have determined the enthalpies of formation in the gas phase for several complexes,[2,3] eqn. (1), where D = donor atom, N, P, O or S.

$$Me_3Al(g) + DMe_n(g) = Me_3AlDMe_n(g) \quad (1)$$

$H_f(g) = -30.7(3)$ kcal mol^{-1} for NMe_3,[4]
$-21.9(2)$ kcal mol^{-1} for OMe_2, and
$-18.0(5)$ kcal mol^{-1} for SMe_2.

The gas phase enthalpy of formation of Me_3AlPMe_3 has not been determined; in hexane solution the enthalpy of formation is about 1 kcal mol^{-1} larger than for Me_3AlOMe_2.[3]

We have previously determined the molecular structures of Me_3AlNMe_3 and Me_3AlPMe_3 by gas phase electron diffraction and discussed the geometry changes in acceptor and donor on complex formation.[4,5] Other Group V–Group III donor acceptor complexes are described in Ref. 6. We have also studied the complex Me_3AlOMe_2, and found that the three valencies of the oxygen atom are coplanar or nearly coplanar.[7]

Ab initio molecular orbital calculations on the model complex H_3AlOH_2 yielded a nonplanar equilibrium conformation,[8] the angle between the plane of the water molecule and the Al–O bond being 27°. The energy of the planar configuration was calculated to be 0.19 kcal mol^{-1} above the equilibrium conformation.[8] The planar – or

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near-planar – configuration of the O atom in Me_3AlOMe_2 was therefore rationalized as being due to repulsion between the Al atom and the two carbon atoms bonded to O.[7] If this explanation is correct, the configuration around O would be expected to deviate from planarity if dimethyl-ether is replaced by a cyclic ether in which the ∠C–O–C valence angle is significantly less than tetrahedral. An investigation of a complex of Me_3Al with 1,2-epoxyethane, $O(CH_2)_2$, would therefore have been of interest. But since trialkyl-aluminium compounds, R_3Al, react with $O(CH_2)_2$ at room temperature under ring opening to yield $R_2AlOCH_2CH_2R$,[9] we have instead synthesized and studied the complex with 1,3-epoxypropane (oxetane), $O(CH_2)_3$.

At the same time we report the structure of the complex Me_3AlSMe_2. This completes our investigation of donor–acceptor complexes of trimethyl-aluminium.

EXPERIMENTAL

Me_3AlSMe_2 and $Me_3AlO(CH_2)_3$ were synthesized by direct combination of $(Me_3Al)_2$ and SMe_2[1] or $O(CH_2)_3$ and purified by distillation. The identity and purity of $Me_3AlO(CH_2)_3$ were confirmed by ^1H NMR, IR and Raman spectroscopy. At room temperature it is a colorless liquid.

The electron scattering patterns of both compounds were recorded on Balzers Eldigraph KDG-2. For $Me_3AlO(CH_2)_3$ we used a normal nozzle and scattering geometry. The reservoir and nozzle temperatures were about 70 °C, corresponding to a vapor pressure of about 15 Torr.

Me_3AlSMe_2 is partly dissociated in the gas phase above room temperature.[1,2] In order to keep the temperature as low as possible we used a convergent electron beam and a nozzle with wide opening.[10] The reservoir and nozzle temperatures were about 20 °C.

Exposures were made with nozzle to plate distances of 50 and 25 cm. The number of plates used were

five 50 cm plates and five 25 cm plates for Me_3ASMe_2, and
six 50 cm plates and five 25 cm plates for $Me_3AlO(CH_2)_3$.

The data were processed by standard methods.[11] The complex atomic scattering factors, $f'(s)$, were calculated from an analytical representation of the atomic potential[12] using a program written by Yates.[13] The molecular intensities were modified through multiplication by $s/|f'_C|\cdot|f'_D|$ (D=donor atom, S or O). The average modified molecular intensities ranged from

$s = 1.50$ to 15.00 Å^{-1} with $\Delta s = 0.125$ Å^{-1} and from
$s = 4.50$ to 25.00 Å^{-1} with $\Delta s = 0.25$ Å^{-1} for D=S

and from

$s = 1.375$ to 14.875 Å^{-1} with $\Delta s = 0.125$ Å^{-1} and from
$s = 2.50$ to 29.00 Å^{-1} with $\Delta s = 0.25$ Å^{-1} for D=O.

STRUCTURE ANALYSES

Molecular models of Me_3AlSMe_2 and $Me_3AlO(CH_2)_3$ are shown in Fig. 1. The following assumptions were made regarding the structure of both complexes: (i) The molecular symmetry is C_s with the symmetry plane perpendicular to the plane through D, C(4) and C(5), (and the plane of the paper in Fig. 1). (ii) The symmetry of the Me_3AlD fragments is C_{3v}. The orientation of the methyl groups bonded to Al is such that one C–H bond is *anti* the Al–D bond. (iii) All C–H bond distances are equal. All Me groups have C_{3v} symmetry with the threefold axes coinciding with the C–Al or C–S bonds. After these assumptions have been made, the structure of the Me_3AlDC_2 fragment of each molecule is determined by the four bond distances C–H, Al–C, Al–D and D–C and the four valences angles ∠Al–C–H, ∠D–Al–C, ∠Al–D–C and ∠C–D–C.

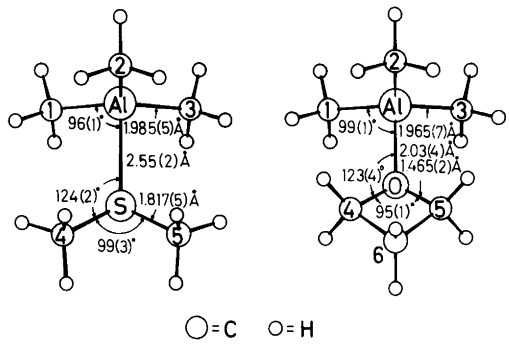

Fig. 1. Molecular models of $(CH_3)_3AlS(CH_3)_2$ and $(CH_3)_3AlO(CH_2)_3$. Both molecules are assumed to have C_s symmetry. Hydrogen atoms are numbered according to the carbon atom to which they are bonded.

For Me_3AlSMe_2 it was finally assumed that the orientation of the Me groups bonded to S is such that one C–H bond is *anti* the S–C′ bond. From the assumptions which have been made, it follows that the SMe_2 fragment has C_{2v} symmetry, and the list of independent structure parameters needs only to be augmented by ∠S–C–H to give a total of nine.

Initially the $O(CH_2)_3$ ligand was also assumed to have C_{2v} symmetry. This implies that the ring is planar. The ∠H–C–H valence angles of the methylene groups were assumed equal, and the lines bisecting these angles were assumed to bisect the endocyclic valence angles at C. The list of independent structure parameters must then be augmented by the C–C bond distance and the ∠H–C–H valence angle. In the final refinements the assumption that the four-membered ring is planar, was abandoned and a folding angle, β, equal to the angle between the planes through OC(4)C(5) and C(4)C(5)C(6) was introduced as an additional independent structure parameter. The folding angle

Table 1. Interatomic distances, valence angles and root-mean-square vibrational amplitudes (l) of $(CH_3)_3AlO(CH_2)_3$ and $(CH_3)_3AlS(CH_3)_2$. Estimated standard deviations in parentheses in units of the last digit. The angles have not been corrected for shrinkage.

	r_a/Å	l/Å		r_a/Å	l/Å
$(CH_3)_3AlO(CH_2)_3$			$(CH_3)_3AlS(CH_3)_2$		
Al–C	1.965(7)	0.062(4)	Al–C	1.985(5)	0.075(6)[a]
Al–O	2.03(4)	0.084(ass)	Al–S	2.55(2)	0.105(8)
O–C	1.465(2)	0.049(ass)	S–C	1.817(5)	0.063(6)[a]
C–C	1.547(3)	0.050(ass)			
C–H(mean)	1.106(2)	0.082(2)	C–H(mean)	1.101(2)	0.075(4)
Al---C(4)	3.07(3)	0.15(9)	Al---C(4)	3.87(3)	0.24(3)
Al---C(6)	3.95(3)	0.15(3)			
Al---H(1)	2.60(2)	0.14(1)	Al---H(1)	2.50(6)	0.22(4)[b]
O---C(1)	3.03(3)	0.12(4)	S---C(1)	3.39(2)	0.15(1)
O---C(6)	2.10(3)	0.062(ass)	S---H(4)	2.41(7)	0.19(4)[b]
C(1)---C(2)	3.36(2)	0.14(4)	C(1)---C(2)	3.42(1)	0.133(ass)
C(1)---C(4)	3.54(2)	0.33(3)	C(1)---C(4)	4.10(5)	0.70(22)[c]
C(1)---C(5)	4.45(2)	0.18(3)	C(1)---C(5)	5.13(2)	0.55(26)
C(1)---C(6)	4.90(2)	0.18(3)			
C(2)---C(4)	3.56(7)	0.53(38)	C(2)---C(4)	4.24(8)	0.70(22)[c]
C(2)---C(6)	4.17(5)	0.29(22)			
C(4)---C(5)	2.16(2)	0.062(ass)	C(4)---C(5)	2.77(7)	0.096(ass)
	(°)			(°)	
∠O–Al–C	98.8(8)		∠S–Al–C	96.0(10)	
∠C–Al–C	117.7(4)		∠C–Al–C	118.9(3)	
∠Al–O–C	123 (4)		∠Al–S–C	124 (2)	
∠C–O–C	94.7(12)		∠C–S–C	99 (3)	
∠O–C–C	88.2(16)				
∠C–C–C	88.3(11)				
∠Al–C–H	112.4(10)		∠Al–C–H	105 (4)	
∠H–C(4)–H ∠H–C(6)–H	113 (4)		∠S–C–H	109 (5)	
ϕ[d]	37 (7)		ϕ[d]	31 (5)	
β[e]	8 (10)				

[a,b,c] These amplitudes were refined with constant difference. [d] The angle between the Al–D bond (D=O or S) and the DC_2 plane of the electron donor. A positive ϕ corresponds to an approximately staggered conformation of the C atoms in donor and acceptor as indicated in Fig. 1. [e] Folding angle of the $O(CH_2)_3$ ring. For definition of sign see text.

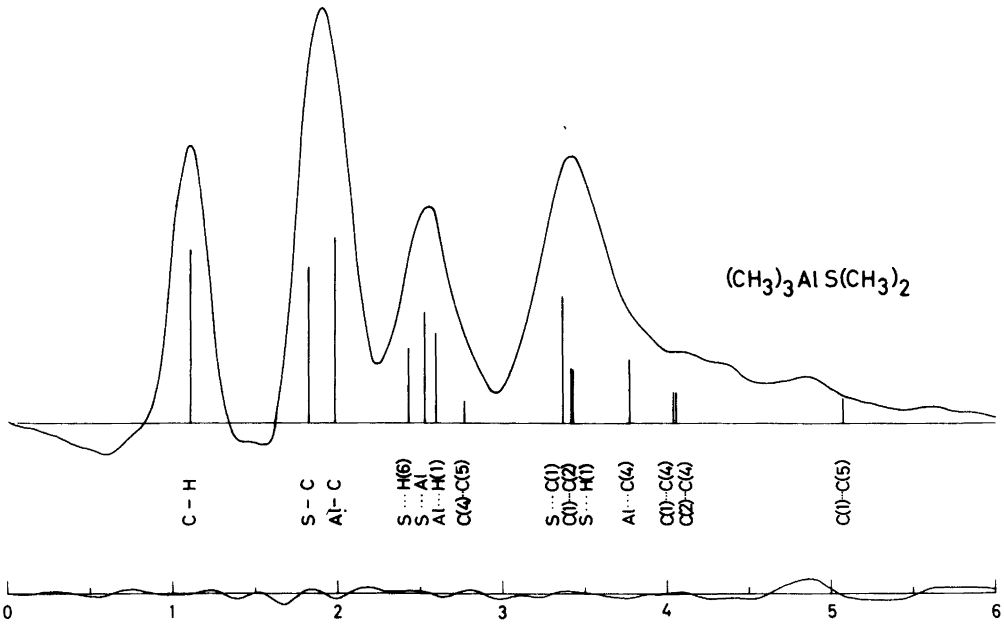

Fig. 2. Above: Experimental radial distribution curve for $(CH_3)_3AlS(CH_3)_2$. Artificial damping constant $k=0.002$ Å^2. Major interatomic distances are indicated by bars of height proportional to the area under the corresponding peak. *Below:* Difference between the experimental curve and the theoretical curve calculated for the best model.

β is zero when the ring is planar and the sign was defined as positive when the ring is folded in such a manner that C(6) in Fig. 1 moves further away from the viewer.

The independent structure parameters were refined by least-squares calculations with diagonal weight matrices under the constraints of geometrically consistent r_a structures.[14] In the case of Me_3AlSMe_2 eight r.m.s. vibrational amplitudes were included in the refinement, in the case of $Me_3AlO(CH_2)_3$ twelve amplitudes were refined.

The refinements converged to yield the structure parameters listed in Table 1. The estimated standard deviations have been multiplied by a factor of two to include the uncertainty due to correlation in the experimental data and possible errors introduced by the assumptions made regarding the molecular model.

Experimental radial distribution curves calculated by Fourier inversion of experimental molecular intensity curves are shown in Figs. 2 and 3 along with the difference between the experimental RD curves and their theoretical counterparts calculated for the best models. We consider the agreement satisfactory.

A referee has suggested that our model for Me_3AlSMe_2 is inadequate and that the neglect of torsional motion about the Al–S bond may be responsible for the discrepancy between experimental and theoretical RD curves around 4.9 Å, and may have introduced systematic errors into our estimate of other parameters, particularly the angle ϕ. We have therefore carried out additional refinement on a dynamic model:[15] The dihedral angle τ was defined as zero for the C_{2v} model shown in Fig. 1. $\tau=60°$ then corresponds to a conformation in which the Me groups of donor and acceptor are approximately eclipsed. The potential energy was assumed to be $V(\tau)=0.5\ V_o[1-\cos(3\tau)]$. The gas was assumed to consist of conformers with τ equal to about 10, 30 and 50°, each with relative weight proportional to the Boltzmann factor $\exp(-V(\tau)/RT)$. The root-mean-square vibrational amplitudes of all torsion-dependent C–C distances were assumed equal and refined along with V_o and the other structure parameters. The resulting value

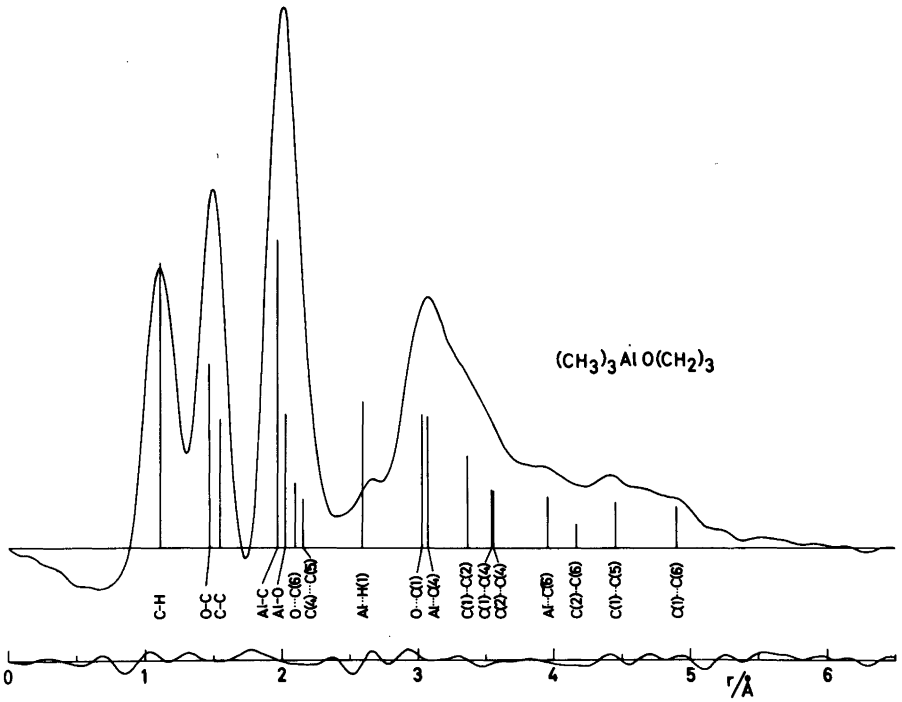

Fig. 3. Above: Experimental radial distribution curve for $(CH_3)_3AlO(CH_2)_3$. Artificial damping constant $k=0.002$ Å^2. Major interatomic distances are indicated by bars of height proportional to the area under the corresponding peak. *Below:* Difference between the experimental curve and the theoretical curve calculated for the best model.

of V_0 was $-1(4)$ kcal mol^{-1}, and the mean value for the torsion-dependent CC amplitudes was 0.43(14) Å. None of the other structure parameters changed more than one fourth standard deviation, in particular ϕ remained unchanged at 31(5)°: The *R*-factor was 6.67 % as compared to 6.84 % for the static model. The *RD*-curve difference decreased by nearly a factor of two near $r=4.9$ Å, but increased somewhat elsewhere.

We have also carried out refinements with ϕ fixed at 55°, corresponding to approximately tetrahedral valence angles. l(Al···C(4)) then refines to values above 0.8 Å, and when ϕ is released, the refinement converges to the $\phi=31°$ minimum.

DISCUSSION

Composition of the molecular beam of Me_3AlSMe_2. As already pointed out, Me_3AlSMe_2 is partly dissociated in the gas phase above room temperature.[1,2] Using the thermodynamic relationship determined by Henrickson and Eyman[2] we calculate that at 20 °C (the temperature of our experiment) and under equilibrium conditions the total vapor pressure is 2.06 Torr, while the partial pressures of the various species are $p(Me_3AlOSMe_2)=1.73$ Torr, $p(SMe_2)=0.22$ Torr, $p(Me_6Al_2)=0.10$ Torr and $p(Me_3Al)=0.01$ Torr. The degree of dissociation of the complex at equilibrium is thus 13 %. But since the driving force for dissociation is the formation of trimethylaluminium dimers, and 95 % of the free Me_3Al is present as dimer at equilibrium, equilibrium need not be established in the short time that the gas needs to travel from the reservoir to the diffraction point.

The electron scattering pattern obtained is consistent with a complex concentration equal to 100 %. The disagreement between experimental and theoretical *RD* curves around $r=4.9$ Å cannot be due to dissociation, since Me_6Al_2 has no distances in this region. The experimental *RD* curve for

Me_6Al_2 shows distinct peaks at 4.0 and 5.6 Å where the *RD* curve obtained for Me_3AlSMe_2 is nearly horizontal.[16] We believe, therefore, that the structure parameters in Table 1 may be used with confidence as long as their rather wide error limits are kept in mind.

The structure of $Me_3AlO(CH_2)_3$. The Al–O bond distance in this complex is similar to that in Me_3AlOMe_2, 2.01(2) Å.[6] Both these dative bond distances are significantly larger than the Al–O (bridge) bond distances in the dialkylalkoxides, $[(CH_3)_2AlOCH_3]_3$ and $[(CH_3)_2AlOC(CH_3)_3]_2$, 1.851(3) Å[17] and 1.864(6) Å,[18] respectively. In these compounds the Al–O bonds may be regarded as 50 % covalent and 50 % dative. The average Al–O (terminal) bond distance in trimeric aluminium triisopropoxide which must be regarded as 100 % covalent, is 1.68 Å.[19] We have previously pointed out a similar linear variation of Al–N bond distances with % covalent character.[5]

While the configuration at the oxygen atom in Me_3AlOMe_2 is found to be planar or nearly planar, the angle between the Al–O bond and the OC_2 plane of the ether being $\phi = 5(4)°$, the configuration at the oxygen atom in $Me_3AlO(CH_2)_3$ is nonplanar with $\phi = 37(7)°$. This angle is thus intermediate between those expected for trigonally and tetrahedrally hybridized oxygen, 0 and 55°, respectively. The Al–C(4) distances in the two complexes are, however, very similar, 3.04(2) Å in the dimethylether and 3.07(3) Å in the epoxypropane complex. The results of the present study are therefore consistent with the suggestion that the planar configuration at O in the dimethyl ether complex is due to repulsion between the Al atom and the C atoms bonded to O.

In all the complexes of Me_3Al which we have studied, the Al–C bond distance is found to be slightly larger and the ∠CAlC angle considerably smaller than in free monomeric Me_3Al.[16] Comparison with the structure of free 1,3-epoxypropane as determined by MW spectroscopy[20] [ring planar or quasiplanar, C–O = 1.448(5) Å, C–C = 1.546(5) Å, ∠COC = 91.9(10)° and ∠CCC = 84.6(10)°] indicates that the C–O bond distance and the ∠COC angle both increase on complex formation. Similar, statistically significant changes were found in Me_3AlOMe_2. The folding angle β, in the complex is not significantly different from zero.

The structure of Me_3AlSMe_2. The Al–S bond distance is similar to the dative Al–S bond distance in the anionic complex K $(Me_3AlSCNAlMe_3)$, 2.489(2) Å.[21] As expected, it is about 0.18 Å longer than the Al–S (bridge) bond distance in $(Me_2AlSMe)_2$ where the Al–S bond may be described as 50 % dative and 50 % covalent.[22] The latter is in turn about 0.08 Å longer than the Al–S bond distance in the cubic high pressure modification of Al_2S_3, 2.29 Å; this bond may be regarded as 25 % dative and 75 % covalent.[23]

Somewhat surprisingly the configuration at the sulphur atom is found to deviate considerably from that expected for tetrahedral hybridization, the angle between the SC_2 plane and the Al–S bond being $\phi = 31(5)°$: The Al–C(4) distance is too large to allow the deviation from tetrahedral configuration to be rationalized as due to Al–C repulsion. In addition the large values obtained for the Al–C(4) and C(Al)–C(S) vibrational amplitudes indicate that the molecule undergoes large amplitude wagging of the SMe_2 fragment as well as virtually non-hindered internal rotation about the Al–S bond. A theoretical study of the energy of the model complex H_3AlSH_2 as a function of ϕ would clearly be of interest and has been initiated.

The standard deviations obtained in the present study are too large to allow a meaningful comparison with the structure of free SMe_2.[24]

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