

## Mg[Al(OCH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>. A NOVEL COORDINATION COMPOUND OF A METAL ALKOXIDE AND A DONOR MOLECULE

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### SUMMARY

The crystal structure of Mg[Al(OCH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·C<sub>4</sub>H<sub>8</sub>O<sub>2</sub> has been determined by single-crystal X-ray diffraction methods. Two molecules crystallize in an orthorhombic unit cell with dimensions  $a = 13.42 \pm 0.02$ ,  $b = 10.74 \pm 0.02$ ,  $c = 7.30 \pm 0.02$  Å. The space group is *Pnmm*. Full matrix least-squares refinement with magnesium and aluminum atoms anisotropic, resulted in a final *R* value of  $R_2 = 12.1\%$ . The complex is an infinite polymer of Mg[Al(OCH<sub>3</sub>)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> units held together by dioxane molecules. About the magnesium atom the point symmetry appears to be *2/m*, with the dioxane rings disordered about the two-fold axis. The metal atoms are bridged together by essentially *sp*<sup>2</sup> hybridized oxygen atoms, which are coplanar with the methoxy methyl groups and the metal atoms.

### INTRODUCTION

Metal alkoxides, especially those of aluminum, have long been known to exhibit polymeric character both in solution<sup>1</sup> and the solid state<sup>2</sup>. The fact that they prefer this "self-complexation" to the addition of donor molecules is usually explained on the basis of a consideration of the donor properties of the alkoxide oxygen compared to the oxygen in an organic donor molecule. However, factors such as steric and charge requirements must also be considered, so that under appropriate conditions, it is not surprising to find both donor coordination and a type of alkoxide polymerization.

The metal alkoxides also afford an opportunity to study the oxygen atom in a bridging configuration. Our interest in this aspect has been stimulated by recent structural work on {Be[N(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>]<sub>3</sub><sup>3</sup>, Mg[Al(CH<sub>3</sub>)<sub>4</sub>]<sub>2</sub><sup>4</sup>, and [(CH<sub>3</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>-N(CH<sub>3</sub>)MgCH<sub>3</sub>]<sub>2</sub><sup>5</sup> in which the geometry about the bridging carbon and nitrogen atoms has been investigated.

### EXPERIMENTAL

The compound used in this X-ray investigation was prepared by the partial oxidation (O<sub>2</sub>) of the electron deficient Mg[Al(CH<sub>3</sub>)<sub>4</sub>]<sub>2</sub> in the presence of dioxane. Sublimation under a moderate vacuum allowed isolation of the complex. Single crystals of the clear, colorless, needle-like material were sealed in glass capillaries,

and subsequent Weissenberg (Cu- $K_\alpha$ ) and precession (Mo- $K_\alpha$ ) photographs showed the crystal system to be orthorhombic. Systematic absences allowed the space group to be  $Pnn2$  or  $Pnmm$ , but since statistical tests favored a centric space group,  $Pnmm$  was used in the structural solution and refinement.

The unit cell parameters are

$$\begin{aligned} a &= 13.42 \pm 0.02 \text{ \AA} \\ b &= 10.74 \pm 0.02 \text{ \AA} \\ c &= 7.30 \pm 0.02 \text{ \AA} \\ V &= 1052 \text{ \AA}^3 \end{aligned}$$

with  $Z=2$ . The calculated density is  $1.10 \text{ g/cm}^3$ . No experimental density was measured because of the small quantity of the material available.

Five layers of multiple-film equi-inclination Weissenberg data ( $hk0$  to  $hk4$ ) were obtained with Ni-filtered Cu- $K_\alpha$  radiation. 392 independent reflections were visually estimated by comparison with a calibrated intensity scale.

Calculations were made with an IBM 7094 computer. Lorentz, polarization, and spot size corrections reduced the observed intensities to squared structure factors. The linear absorption coefficient for this compound is  $16.07 \text{ cm}^{-1}$  with Cu- $K_\alpha$  radiation. This gives a maximum calculated value of 0.081 for  $\mu R$  for the crystal used, and absorption corrections were deemed unnecessary. Fourier calculations were made with the Sly, Shoemaker, and Van den Hende ERFR3<sup>6</sup> program. Full-matrix, least-squares refinement was carried out using the Busing and Levy program ORFLS<sup>7</sup>. No corrections were made for extinction or anomalous dispersion. Unobserved reflections were assigned an intensity according to Hamilton<sup>8</sup>. The function  $\sum W(|F_o| - |F_c|)^2$  was minimized, and the weighting scheme was based on

$$\begin{aligned} \sigma^2 &= 0.05 \left| \frac{F_{\min}}{F_{\text{obs}}} \right|^2 ; F_{\text{obs}} < F_{\min} \\ \sigma^2 &= 0.05 \left| \frac{F_{\text{obs}}}{F_{\min}} \right|^2 ; F_{\text{obs}} \geq F_{\min} \end{aligned}$$

with  $W=1/\sigma^2$ . Neutral atom scattering factors were taken from the compilations of Ibers for carbon, oxygen, magnesium, and aluminum<sup>9</sup>. The variables were scale factors, atomic coordinates, and individual atom temperature factors for isotropic refinement. Anisotropic refinement was carried out on magnesium and aluminum with scale factors fixed. Final bond distances, angles, and errors were computed with the aid of the Busing, Martin, and Levy ORFFE<sup>10</sup> program. The program ORTEP<sup>11</sup> was used for the crystal structure illustrations.

#### STRUCTURE DETERMINATION

A three-dimensional Patterson function was first calculated, but the vector map showed rather large, ill-defined maxima, and allowed only a limited interpretation. Since there are two molecules per unit cell, it did not seem unreasonable to place the magnesium atom at a  $2/m$  site. A Fourier synthesis thus calculated showed other positions not at variance with the Patterson map, and further trial and error Fourier syntheses and refinements gave the coordinates of all non-hydrogen atoms in the molecular unit. However, at this point, the dioxane ring was in a planar con-

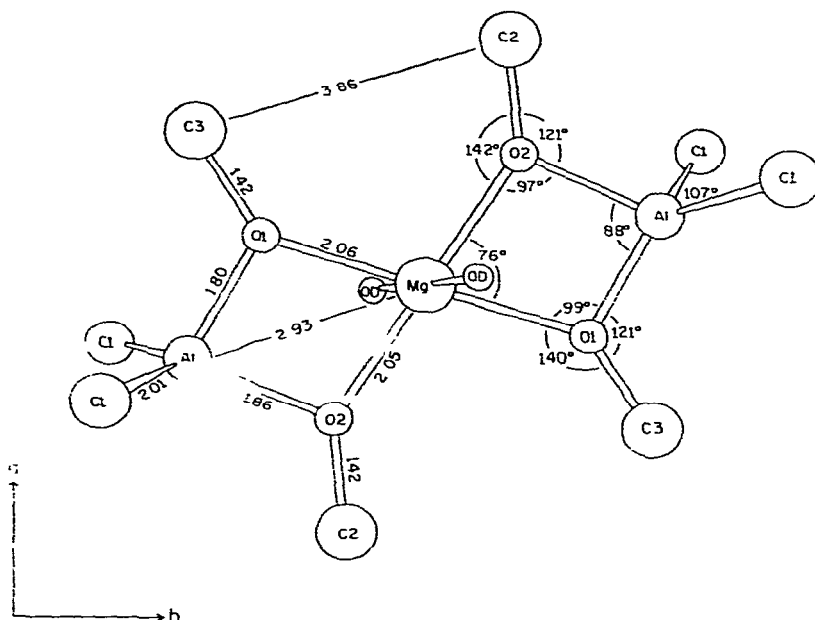


Fig. 1. Structure of  $\text{Mg}[\text{Al}(\text{OCH}_3)_2(\text{CH}_3)_2]_2 \cdot \text{C}_4\text{H}_8\text{O}_2$ . The compound is polymeric, but for clarity only the dioxane oxygen atoms bonded to the magnesium atom in the  $\text{Mg}[\text{Al}(\text{OCH}_3)_2(\text{CH}_3)_2]_2$  structural unit are shown.

figuration with the crystallographic two-fold axis passing through the oxygen atoms. The ring carbon atoms exhibited abnormally high isotropic temperature factors, and Fourier and difference Fourier maps indicated that their electron density was rather diffuse and smeared out about the Z-axis. These features could be explained by a model in which the ring carbon atoms were disordered about the crystallographic two-fold axis passing through the oxygen atoms. This information, together with the known bond distances and angles in dioxane<sup>12</sup>, allowed the calculation of the actual coordinates for the ring carbon atoms. Subsequent three-dimensional isotropic least squares refinement (unit weights) on the disordered model afforded a discrepancy factor of  $R_1 = [\sum (|F_o| - |F_c|) / \sum |F_o|] \times 100 = 18.4\%$ . The use of the weighting scheme described above, inclusion of unobserved data, and anisotropic refinement of the metal atoms (with scale factors fixed) yielded an  $R$  value of  $R_2 = [\sum W (|F_o| - |F_c|)^2 / \sum W |F_o|^2]^{1/2} \times 100 = 12.1\%$  ( $R_1 = 14.3\%$ ). Refinement in the acentric space group  $Pnn2$  was attempted but failed to produce satisfactory convergence. A final difference map based on the refinement in space group  $Pnmm$  showed no significant residual electron density. Since no peaks characteristic of hydrogen atoms were clearly resolved in the regions where they might be expected, no further attempt was made to locate their coordinates. The final calculated and observed structure factors are listed in Table 1. Final atomic parameters and standard deviations are tabulated in Table 2. Interatomic distances, angles, and errors are listed in Table 3.

#### DISCUSSION OF STRUCTURE

One may best visualize the structure as an infinite polymer consisting of

TABLE I  
OBSERVED AND CALCULATED STRUCTURE FACTORS  
Unobserved reflections are indicated by an asterisk.

K	L	OBS	CAL	K	L	OBS	CAL	K	L	OBS	CAL	K	L	OBS	CAL	
*****	0	*****	40.6	5	0	44.1	40.6	*****	0	31.9	30.6	*****	0	31.9	30.6	
2	0	1.6	5.7*	6	0	11.4	11.6	7	3	12.9	22.0	8	3	12.9	22.0	
4	0	30.0	45.0	7	0	19.7	19.4	8	3	7.2	7.1*	9	3	5.5	4.4*	
6	0	34.2	6.9*	8	0	4.0	3.0*	10	3	10.0	7.8	11	3	10.9	18.7	
10	0	26.3	27.7*	0	1	13.5	3.9	10	3	8.0	6.3	1	3	18.9	6.6	
17	0	44.2	11.2*	1	1	18.9	19.7	1	4	18.7	16.3	2	3	12.7	9.3	
3	1	31.7	27.1	2	1	3.5	3.6	2	4	13.1	8.0	3	3	6.9	1.4*	
5	1	2.9	13.1	3	1	22.7	19.6	3	4	13.1	6.8	4	3	7.1	1.2*	
7	1	3.6	7.3*	4	1	28.0	24.1	4	4	11.6	8.3	5	3	7.2	0.8*	
9	1	4.2	1.8*	5	1	20.1	19.7	5	4	16.0	12.4	6	3	7.1	1.8*	
0	2	8	105.3*	6	1	19.7	21.2	*****	6	*****	*****	7	3	7.1	1.8*	
2	2	26.9	29.2	7	1	4.1	2.3*	0	0	31.9	30.6	8	3	8.9	7.7*	
4	2	31.1	35.2	9	1	10.0	10.6	1	0	9.1	10.7	0	4	10.1	5.1*	
6	2	28.7	32.9	1	2	16.9	15.2	2	0	30.3	31.5	1	4	14.7	11.5	
8	2	15.0	16.2	2	2	7.7	1.9	3	0	22.9	24.7	2	4	18.9	10.1	
10	2	5.5	5.5*	3	2	3.5	3.3*	4	0	8.4	7.6	3	4	10.3	3.5*	
3	3	10.5	7.6	4	2	6.5	3.7	5	0	22.9	21.3	4	4	10.6	6.3*	
7	3	19.1	14.6	5	2	16.8	17.4	6	0	23.4	23.1	*****	4	4	10.6	6.3*
9	3	7.2	4.3*	6	2	16.9	17.0	7	0	7.1	9.1	*****	*****	*****	*****	
11	3	9.1	11.6	7	2	6.7	7.3	8	0	4.2	2.8*	1	0	15.8	15.5	
0	4	2.4	79.3*	0	2	6.8	7.1	9	0	9.1	6.3	2	0	10.3	13.3	
2	4	21.9	21.4	0	3	5.3	1.9*	10	0	9.7	10.0	3	0	19.8	19.9	
4	4	17.1	16.6	0	3	22.5	21.9	1	1	16.6	15.9	4	0	6.1	7.1	
6	4	9.7	8.3*	1	3	11.3	8.4	2	1	18.9	18.2	5	0	5.0	3.6	
8	4	13.0	15.9	2	3	15.8	15.3	3	1	12.3	11.6	6	0	4.2	2.7*	
*****	*****	*****	*****	3	3	18.7	16.5	4	1	11.5	18.9	7	0	4.2	2.2*	
1	0	11.3	95.8	4	3	22.6	25.8	5	1	11.7	11.2	8	0	4.2	4.3*	
2	0	4.2	1.2	5	3	20.0	18.7	6	1	3.8	3.1*	9	1	11.0	12.7	
3	0	7.1	85.2	6	3	22.0	21.8	7	1	4.1	1.6*	10	1	16.8	17.0	
4	0	26.5	28.7	7	3	16.6	16.7	8	1	4.2	4.4*	1	1	15.9	18.2	
5	0	26.5	26.7	8	3	8.3	6.5	9	1	5.1	6.2	2	1	6.8	8.9	
6	0	10.7	8.4	9	3	10.1	9.0	0	2	23.7	20.2	3	1	8.3	9.9	
7	0	13.6	14.3	1	4	11.6	9.8	1	2	3.9	5.6*	4	1	9.6	8.0	
8	0	7.2	7.5	2	4	7.6	10.5	2	2	10.5	9.8	5	1	6.2	6.3	
9	0	7.7	3.6	4	4	13.2	18.4	3	2	13.4	15.9	6	2	7.2	7.2	
10	0	4.2	1.6*	7	4	16.5	12.6	4	2	18.2	15.2	7	2	7.8	6.4	
11	1	24.8	23.9	4	4	18.4	17.6	5	2	15.1	10.5	8	2	5.3	5.9*	
3	1	69.1	68.8	6	4	10.1	5.4*	6	2	19.0	16.5	9	2	6.8	2.4*	
4	1	24.8	21.5	7	4	10.5	9.8	7	2	9.0	6.5	1	3	10.5	8.0	
5	1	11.4	11.5	*****	*****	*****	*****	8	2	8.4	7.0*	2	3	13.7	20.2	
6	1	13.4	13.3	0	0	35.7	24.4	9	2	6.4	7.3	3	3	15.4	16.0	
7	1	34.2	15.6	1	0	20.3	21.0	10	2	5.1	4.7	4	3	7.1	7.1	
8	1	16.5	18.4	2	0	62.6	41.6	1	3	16.0	13.1	5	3	10.1	6.7	
9	1	4.2	1.0*	3	0	41.1	31.9	2	3	17.5	13.6	6	3	10.5	5.8	
1	2	36.7	47.0	5	0	23.3	23.5	4	3	11.3	6.3	7	4	10.6	4.7*	
2	2	29.6	22.6	6	0	26.6	24.5	5	3	17.3	14.8	8	4	10.6	6.9*	
3	2	30.1	22.5	7	0	18.8	20.0	6	3	6.9	6.8	9	4	10.6	6.9*	
4	2	4.0	1.4*	8	0	4.0	0.2*	*****	*****	*****	*****	*****	*****	*****	*****	
5	2	16.1	13.5	9	0	14.0	16.4	7	3	7.1	5.4	0	0	6.0	4.0	
6	2	11.3	12.7	10	0	7.8	8.4	8	3	7.1	2.7*	1	0	6.6	5.8	
7	2	10.9	10.8	1	1	28.9	19.3	9	3	8.4	7.9	2	0	16.8	18.4	
8	2	5.2	2.4*	2	1	12.0	17.6	0	4	8.9	6.2*	3	0	21.8	22.4	
0	3	2.9	88.5*	3	1	12.8	11.7	1	4	9.0	1.6*	4	0	6.4	5.8	
1	3	8.7	10.5	4	1	17.3	20.6	2	4	11.0	11.6	5	0	6.5	8.6	
2	3	5.9	7.0	5	1	21.4	20.1	3	4	17.0	17.9	6	0	4.0	10.3	
*****	*****	*****	*****	6	1	4.4	4.4	4	4	12.6	11.6	7	1	4.9	4.6*	

$\text{Mg}[\text{Al}(\text{OCH}_3)_2(\text{CH}_3)_2]_2$  units held together by dioxane molecules in the chair form. The apparent site symmetry at the magnesium atom is  $2/m$ , with the dioxane rings disordered about the two-fold axis (Fig. 2).

It is important to note that the aluminum and magnesium atoms, as well as the oxygen and carbon atoms of the methoxy groups, lie in a crystallographic mirror plane. The isotropic temperature factors for both oxygen and carbon atoms are normal, and attempted refinement of the structure with the methoxy groups dis-

3	3	6.8	13.1	7	1	6.0	3.5	*****H=7*****	1	0	16.7	15.7	4	1	4.2	1.0*
4	3	33.3	40.5	8	1	4.1	5.0*	2	0	11.6	7.2	5	0	0.2	1.3*	
5	3	11.6	9.9	0	2	7.5	6.3	3	0	11.6	7.2	1	2	8.2	13.6	
6	3	6.1	2.7*	1	2	3.2	3.0	4	0	11.8	11.4	2	1	10.5	9.1	
7	3	13.6	12.1	2	2	0.1	3.4	5	0	11.8	10.2	3	2	16.6	16.0	
8	3	16.6	18.7	3	2	30.4	33.4	6	0	11.8	10.2	4	2	5.5	2.6	
1	4	15.1	15.7	6	2	20.5	18.1	7	0	4.0	2.5*	5	2	7.9	5.8	
2	4	9.0	6.2	5	2	27.7	26.3	8	0	7.3	7.8	6	2	5.5	2.2	
3	4	7.4	8.2*	7	2	20.6	18.4	9	0	6.3	4.6	2	3	10.1	4.0	
4	4	15.5	14.7	8	2	7.7	4.5	0	9.0	9.8	12.2	1	3	10.1	6.8	
5	4	10.0	5.7	9	2	10.3	11.9	1	1	12.8	12.2	2	3	11.0	8.8	
6	4	9.7	4.2*	2	3	15.9	16.6	2	1	25.8	25.0	3	3	7.2	2.2*	
7	4	10.4	8.3	2	3	14.8	17.3	3	1	6.7	10.7	4	3	7.2	2.2*	
8	0	156.8	107.6	4	3	10.0	11.1	4	1	7.4	9.2	5	3	7.1	5.1*	
1	0	45.6	43.7	3	3	21.3	21.7	5	1	3.8	2.8*	*****H=11*****	*****H=11*****	*****H=11*****	*****H=11*****	
2	0	16.4	10.1	4	3	12.6	9.2	6	1	9.9	8.4	1	0	4.1	2.6	
3	0	16.4	13.1	5	3	23.9	22.4	7	1	4.2	1.4	2	0	4.1	1.8	
4	0	56.0	54.0	6	3	9.8	6.8	8	1	4.1	4.4*	3	0	14.0	14.0	
5	0	2.9	2.2*	7	3	7.1	5.1*	9	1	4.1	4.4*	4	0	4.2	0.8*	
6	0	21.9	23.6	8	3	7.1	6.8	0	2	23.0	22.2	5	0	7.9	7.9	
7	0	22.8	21.5	0	4	7.5	1.1	1	2	4.6	3.3	6	1	6.2	6.9	
8	0	13.7	17.3	1	4	16.7	14.6	2	2	8.1	4.3	7	1	4.2	4.0*	
9	0	9.2	9.7	2	4	13.0	15.6	3	2	5.4	2.2*	8	2	4.2	4.0*	
1	1	21.1	12.9	3	4	13.9	11.3	4	2	8.1	4.3	9	1	6.6	6.3	
2	1	17.9	17.1	4	4	13.9	11.3	5	2	5.4	2.2*	0	1	4.2	4.6	
3	1	7.7	7.8	5	4	16.4	15.1	6	3	3.9	3.3	1	2	5.5	3.4*	
4	1	33.5	32.7	6	4	15.6	12.8	7	2	7.6	7.5	2	1	2	5.5	
5	1	21.1	20.7	7	4	10.6	11.5	8	3	9.8	7.8	3	2	7.9	4.8	
6	1	11.0	12.9	*****H=5*****	*****H=5*****	*****H=5*****	*****H=5*****	9	3	26.0	27.7	4	2	5.5	3.4*	
7	1	11.9	16.1	1	0	21.7	21.4	0	3	3	26.0	27.7	5	2	7.9	4.8
8	1	20.1	22.9	2	0	23.3	22.9	1	3	3	11.8	5.9	6	2	5.5	1.7*
9	1	10.9	4.5	3	0	3.4	0.7	2	3	5	5.6	1.8*	7	2	5.5	2.9
1	2	23.4	27.2	4	0	26.8	23.9	3	5	3	6.9	0.7*	8	3	7.2	3.7*
2	2	3.7	0.6*	5	0	14.0	10.8	4	6	3	13.9	12.6	9	1	3	7.1
3	2	25.0	26.6	6	0	12.2	13.2	5	7	3	7.2	0.3*	0	2	3	7.1
4	2	25.6	22.5	7	0	12.2	13.2	6	8	3	7.1	2.2*	1	3	7.1	5.7
5	2	4.5	2.1*	8	0	4.3	4.2	7	9	3	6.7	3.3	2	3	0.1	5.9
6	2	21.7	21.3	0	0	4.3	4.2	8	0	4	13.1	12.1	3	3	10.0	7.7
7	2	8.2	7.6	0	1	17.5	14.6	9	3	4	0.7	5.8	*****H=12*****	*****H=12*****	*****H=12*****	*****H=12*****
8	2	22.8	24.8	1	1	17.2	14.6	0	4	3	13.1	7.6*	0	0	6.5	6.2
9	2	12.7	13.0	2	1	37.5	38.8	1	5	4	10.4	1.6*	1	0	4.2	2.1*
1	3	16.4	16.4	3	1	20.8	22.7	2	4	4	10.4	1.6*	2	0	4.0	6.1
2	3	15.7	15.1	4	1	3.8	1.5	3	5	4	13.0	4.0	3	0	10.4	1.4*
3	3	23.0	22.8	5	1	30.3	29.7	4	6	0	12.3	13.7	4	0	10.4	9.9
4	3	13.4	15.0	6	1	20.6	18.9	5	7	0	32.1	32.9	5	0	4.1	4.7
5	3	16.5	17.4	7	1	15.2	15.2	6	8	0	6.7	9.8	1	1	4.2	4.8*
6	3	7.1	0.8*	8	0	5.0	5.6	7	3	0	3.7	6.4*	2	1	4.2	2.0*
7	3	7.2	2.4*	9	1	7.2	9.6	8	4	0	3.9	0.2*	3	1	4.2	4.0
8	3	7.0	1.8*	10	1	5.0	6.1	9	0	0	11.1	10.5	4	1	4.2	4.3*
9	3	6.2	6.0	1	2	16.1	17.1	0	6	0	3.1	4.7	5	2	5.5	0.7*
10	3	6.2	6.0	2	2	21.3	19.7	1	7	0	4.2	2.0*	1	2	5.5	5.3*
11	3	6.2	6.0	3	2	9.2	8.3	2	8	0	3.1	4.7	2	2	5.5	1.8
1	4	17.9	21.1	4	2	10.8	11.7	3	9	0	4.0	3.0*	3	2	5.5	5.1*
2	4	11.9	9.5	5	2	9.6	9.0	4	0	0	15.7	16.4	4	2	3.4	5.0*
3	4	7.6	5.0	6	2	6.0	4.7	5	1	1	4.9	6.2	5	2	3.4	5.1*
4	4	20.4	22.1	7	2	5.3	3.6	6	2	1	8.2	5.7	1	3	7.1	1.3*
5	4	10.2	7.4	8	2	5.5	3.9	7	3	1	3.6	1.1*	2	3	7.0	0.6*
6	4	11.0	8.2	9	2	5.5	4.3	8	4	1	3.6	1.1*	3	3	9.7	6.4
7	4	13.6	12.9	0	8	2	5.5	9	5	1	4.0	0.2*	*****H=13*****	*****H=13*****	*****H=13*****	*****H=13*****
1	0	35.3	34.3	1	0	35.3	34.3	0	6	1	4.1	0.2*	1	0	5.1	5.9
2	0	60.5	50.6	2	0	10.2	5.5	1	7	1	4.2	3.4*	2	0	4.1	2.1*
3	0	15.9	15.4	3	3	17.3	19.1	2	8	0	7.1	7.6	3	0	6.4	5.9
4	0	16.9	17.2	4	0	20.2	19.6	3	9	1	12.5	8.8	*****H=14*****	*****H=14*****	*****H=14*****	*****H=14*****
5	0	16.9	17.2	5	3	20.2	19.6	4	2	2	11.6	11.5	0	0	7.4	6.8

ordered about the mirror plane failed to yield an  $R$  value of less than 20%. Bond angles are consistent with essentially  $sp^2$  hybrid orbitals on the bridging oxygen atoms, but methyl-methyl repulsions open the carbon-oxygen-magnesium angles to  $140^\circ$ . The resulting methyl-methyl distance of 3.86 Å, is to be compared with 3.24 Å, the methyl-methyl approach if the carbon-oxygen-magnesium angle were to equal the carbon-oxygen-aluminum bond angle. However, this repulsion is not seen as a dominant structural force, since in  $[\text{Be}(\text{N}(\text{CH}_3)_2)_2]_3^3$  the methyl-methyl nonbonded

TABLE 2

FINAL FRACTIONAL COORDINATES AND TEMPERATURE FACTORS

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$\beta$
Mg	0.0000	0.0000	0.0000	<sup>a</sup>
Al	0.0709(4)	-0.2585(5)	0.0000	<sup>b</sup>
O(1)	0.0482(7)	0.1825(9)	0.0000	5.88
O(2)	0.1291(7)	-0.1014(9)	0.0000	4.71
O(dioxane)	0.0000	0.0000	0.3068(21)	6.21
C(1)	0.1034(9)	-0.3510(12)	0.2312(24)	9.03
C(2)	0.2344(11)	-0.0867(15)	0.0000	5.66
C(3)	0.1383(13)	0.2520(18)	0.0000	7.08
C(dioxane)	0.0948(16)	-0.0089(22)	0.4150(46)	7.62
C(dioxane)	0.0799(13)	0.0637(18)	0.4173(38)	5.50

<sup>a</sup>  $\beta_{11} = 0.0101$ ;  $\beta_{22} = 0.0079$ ;  $\beta_{33} = 0.0079$ ;  $\beta_{12} = \beta_{13} = \beta_{23} = 0.0$ . <sup>b</sup>  $\beta_{11} = 0.0092$ ;  $\beta_{22} = 0.0084$ ;  $\beta_{33} = 0.0209$ ;  $\beta_{12} = \beta_{13} = \beta_{23} = 0.0$ .

TABLE 3

BOND DISTANCES AND ANGLES

Bond	Distance (Å)	Angle	Degrees
Mg-Al	2.93(1)	O(2)-Al-O(1)'	87.80(30)
Mg-O(1)	2.06(1)	O(2)-Mg-O(2)'	76.11(26)
Mg-O(2)	2.05(1)	Al-O(1)-Mg	98.80(32)
Mg-O(D)	2.24(2)	Al-O(2)-Mg	97.29(45)
Al-O(1)	1.80(2)	Al-O(2)-C(2)	121.21(90)
Al-O(2)	1.86(1)	Al-O(1)-C(3)	121.28(64)
Al-C(1)	2.01(2)	Mg-O(2)-C(2)	141.51(93)
O(1)-C(3)	1.42(2)	Mg-O(1)-C(3)	139.91(1.01)
O(2)-C(2)	1.42(1)	C(1)-Al-C(1)'	106.61(38)
O(D)-C(D1)	1.50(3)	Mg-O(D)-C(D1)	121.77(1.37)
O(D)-C(D2)	1.51(2)	Mg-O(D)-C(D2)	122.39(1.12)
C(D1)-C(D2)'	1.46(4)	C(D1)-O(D)-C(D1)'	116.46(1.47)
C(D2)-C(D1)'	1.46(4)	C(D2)-O(D)-C(D2)'	115.24(1.22)
<i>Nonbonded distances (Å)</i>			
O(1)-O(2)	3.24(2)	C(D1)-C(2)	3.66(3)
C(2)-C(3)	3.86(3)	C(D2)-C(3)	3.74(3)

length is 3.13 Å. The only other instance of three-coordinate oxygen exhibiting this type of geometry is in dimeric (trimethylsiloxy)dimethylaluminum<sup>13</sup>; however, no bond lengths or angles are quoted for the structure.

The bonding between metal atoms in  $\text{Mg}[\text{Al}(\text{OCH}_3)_2(\text{CH}_3)_2]_2 \cdot \text{C}_4\text{H}_8\text{O}_2$  should be similar to that in  $\text{Mg}[\text{Al}(\text{OCH}_3)_4]_2$ , a "double alkoxide salt" first prepared by Meerwein in 1929<sup>14</sup>. The very formulation of the material as a "salt" suggests a pertinent question upon which the present structure may shed light: to what extent can these materials be termed *-ate* complexes<sup>15</sup>? Although caution must be exercised in the interpretation of the metal-oxygen (bridge) bond lengths since the aluminum atoms are four-coordinate and the magnesium atom is six-coordinate, the short

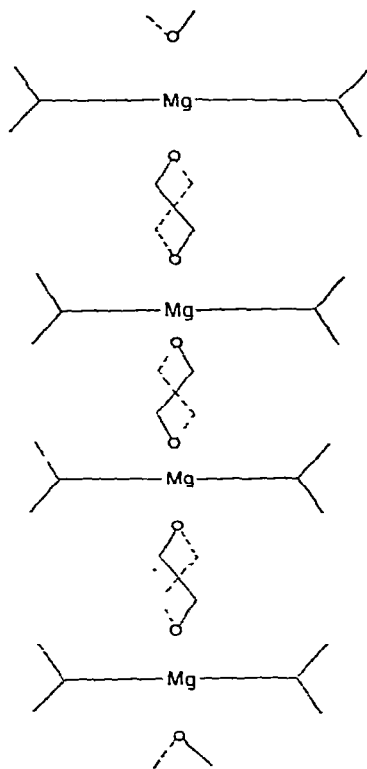


Fig. 2. View of the disorder of the dioxane rings about the two-fold axis in the Z-direction

magnesium–oxygen (2.05 Å) and aluminum–oxygen (1.85 Å) bond lengths do not indicate the existence of discrete  $\text{Mg}^{++}$  and  $[\text{Al}(\text{OCH}_3)_2(\text{CH}_3)_2]^-$  ions. The aluminum–carbon (methyl) distance of 2.01 Å agrees well with aluminum–carbon (terminal) lengths found in  $[\text{Al}(\text{CH}_3)_3]_2$  (1.97 Å)<sup>16</sup>, and  $[\text{Al}(\text{CH}_3)_3]_2 \cdot \text{C}_4\text{H}_8\text{O}_2$  (1.98 Å)<sup>12</sup>. However, the magnesium–aluminum distance of 2.93 Å is considerably larger than the sum of their covalent radii (2.64 Å), and the metal–oxygen–metal bridging angle of about  $98^\circ$  is substantially greater than that reported in other bridged Group II and III organometallic structures<sup>3–5,16</sup>. Thus, while the bridge bonding exhibits covalent character, some ionic contribution is implied by the large bridging angle and magnesium to aluminum atom distance.

Bond distances and angles for each of the dioxane rings which compose the disordered model are given in Table 3. The parameters agree well with each other, and with those reported for  $[\text{Al}(\text{CH}_3)_3]_2 \cdot \text{C}_4\text{H}_8\text{O}_2$ <sup>12</sup>.

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