Table IV. Calculations of *ortho* Values for Bromobenzenes[a]

Group	Radius	SF	(1 − SF)	$2.4_{I,p} + (1 - SF)_{R,p}$	σ_o
CH_3	1.73	0.48	0.52	2.4(−0.05) + 0.52(−0.11)	−0.18
NH_2	1.56	0.38	0.62	2.4(0.10) + 0.62(−0.76)	−0.23
OH	1.45	0.32	0.68	2.4(0.25) + 0.68(−0.60)	0.19
OCH_3	1.47	0.33	0.67	2.4(0.25) + 0.67(−0.51)	0.26
OC_2H_5	1.47	0.33	0.67	2.4(0.25) + 0.67(−0.51)	0.26
CF_3	2.15	0.74	0.26	2.4(0.41) + 0.26(+0.09)	1.01
F	1.39	0.29	0.71	2.4(0.52) + 0.71(−0.44)	0.94
Cl	1.89	0.57	0.43	2.4(0.47) + 0.43(−0.25)	1.02
Br	2.11	0.71	0.29	2.4(0.45) + 0.29(−0.22)	1.02
C_2H_5	1.79	0.52	0.48	2.4(−0.05) + 0.48(−0.10)	−0.17
C_6H_5	2.20	0.78	0.22	2.4(0.10) + 0.22(+0.09)	0.22

[a] SF = steric factor.

inductive effect at the *ortho* position, which was treated as a constant, is an unknown combination of bond interaction and field effects. If the spatial configuration of the *ortho* substituent and the reaction site was substantially changed, it would probably affect the coefficient for the inductive effect, especially that portion which is due to field effects. Thus no system would necessarily have the same parameters as the phenyl halides unless it was completely analogous to their reduction.

There are several reducible aromatic systems in which substituent effects could be examined such as the benzyl halides, the benzyl carbonyls, and unsaturated systems such as styrene. In each of these cases, however, the reaction site is one carbon removed from the ring, and the bond between the ring and the reacting group is not broken. This is obviously a different situation from the phenyl halides which are reduced to benzene so that the bond between the aromatic nucleus and the halide atom is broken. Thus there is no reducible system which is completely analogous to the phenyl halides.

This treatment offers an explanation for a previously unexplained phenomenon, and further work on other systems is in progress to extend it.

The Crystal and Molecular Structure of $[Al(CH_3)_3]_2 \cdot C_4H_8O_2$

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Abstract: The crystal structure of $[Al(CH_3)_3]_2 \cdot C_4H_8O_2$ has been determined by three-dimensional, single-crystal, X-ray diffraction techniques. The compound crystallizes in the monoclinic space group C2/m, with two molecules per unit cell. The cell parameters are: $a = 18.84$, $b = 11.51$, $c = 6.79$ A, $\alpha = \gamma = 90°$, $\beta = 146° 15'$. The molecule, which has 2/m symmetry, contains the dioxane ring in the chair form with each oxygen atom bonded to an aluminum atom. The hybridization of the aluminum atoms is more nearly trigonal than tetrahedral. Structure solution was accomplished with the use of the symbolic addition procedure for phase determination.

As compounds of trivalent aluminum, the organoaluminum compounds are Lewis acids and will combine with Lewis bases to form molecular compounds or complex anions. When suitable electron donors (amines, ethers, or anions such as hydride or halide) combine with organoalanes, compounds containing four- or five[1]-coordinate aluminum are obtained. Bifunctional donors such as dioxane usually add 2 moles of trialkylalane.[2] Several neutral addition complexes have been studied by infrared[3] and nmr[4] techniques, but little is known in detail about their geometries. We wish to report the three-dimensional X-ray study of a neutral addition complex of trimethylaluminum, bis(trimethylaluminum) dioxanate.

Experimental Section

The material was prepared by the addition of trimethylaluminum to an excess of dioxane. The excess dioxane was then pumped off under moderate vacuum and the complex sublimed out of the residue. Two types of crystals were observed: small, colorless, regular polyhedra which give a melting point of 173 ± 1°, and a small quantity of colorless needles of undetermined melting point. Single crystals of both materials were sealed in glass capillaries as the compounds are water and oxygen sensitive. We report here the unit cell and space group for both modifications and the three-dimensional structure of the crystals characterized as small, colorless, regular polyhedra.

Preliminary unit cell dimensions were determined from oscillation, Weissenberg (Cu Kα), and precession (Mo Kα) photographs. With the needle-like compound, the crystal system is orthorhombic. The systematic absences allow the space group to be Pnn2 or

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Pnnm. The unit cell parameters are $a = 13.42 \pm 0.02$ A, $b = 10.96 \pm 0.02$ A, $c = 7.26 \pm 0.04$ A, $V = 1068$ A^3, $\alpha = 90°$, $\beta = 90°$, and $\gamma = 90°$. An experimental density could not be determined because of the small amount of the material obtained. However, from a consideration of the volume/molecule ratio in both this crystalline form and in the polyhedral compound, it seems likely that the two are different complexes rather than different crystalline modifications of the same complex.

The polyhedra belong to the monoclinic crystal system. Systematic absences allowed the space group to be C2, Cm, or C2/m. Statistical tests indicated the space group was centric, and therefore C2/m was taken as the correct choice. The unit cell parameters are $a = 18.84 \pm 0.02$ A, $b = 11.51 \pm 0.02$ A, $c = 6.79 \pm 0.02$ A, $V = 818$ A^3, $\alpha = 90°$, $\beta = 146.25 \pm 0.50°$, and $\gamma = 90°$ with $Z = 2$. The calculated density is 0.942 g/cm^{-3}, and the observed density was 0.91 g/cm^{-3}.

Multiple-film equiinclination Weissenberg photographs were taken along [100] from the zero through the tenth layer with Ni-filtered copper radiation (λ 1.5418 A). A total of 830 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 (μ) for this compound is 14.15 cm^{-1} with Cu Kα radiation. This gives a maximum calculated value of 0.169 for μR for the crystal used, and absorption corrections were deemed unnecessary. Fourier calculations were made with the Sly–Shoemaker–Van den Hende ERFR3[5] program. The full-matrix, least-squares refinement was carried out using the Busing and Levy program ORFLS.[6] No corrections were made for extinction or anomalous dispersion. The weighting scheme was based on

$$\sigma = 0.05\left[\frac{F_{\min}}{F_{\text{obsd}}}\right]^2 \qquad |F|_{\text{obsd}} < |F|_{\min}$$

$$\sigma = 0.05\left[\frac{F_{\text{obsd}}}{F_{\min}}\right]^2 \qquad |F|_{\text{obsd}} \geq |F|_{\min}$$

with $W = 1/\sigma^2$. Unobserved reflections were assigned an intensity and weight according to Hamilton.[7] The function $\Sigma W(|F_o| - |F_c|)^2$ was minimized. Neutral atom-scattering factors were taken from the compilations of Ibers for H, C, O, and Al.[8] The variables were scale factors, atomic coordinates, and individual atom temperature factors for isotropic refinement. Anisotropic refinement was carried out on Al with the scale factors fixed. Final bond distances, angles, and errors were computed with the aid of the Busing, Martin, and Levy ORFFE[9] program. The program ORTEP[10] was used for the crystal-structure illustrations.

Nmr spectra were measured at room temperature on a Varian A-60A spectrometer.

Structure Determination

The symbolic addition procedure of Karle and Karle[11] was used to determine the structure directly from the normalized structure factor magnitudes. A series of computer programs, FAME–MAGIC–LINK–SYMPL,[12] was used to carry out the procedure.

The normalized structure factors may be defined as

$$E(hkl) = \frac{K|F(hkl)|\exp[B(\sin\theta(hkl)/\lambda)^2]}{[\epsilon\sum_{j=1}^{N} f^2(j)n(j)]^{1/2}}$$

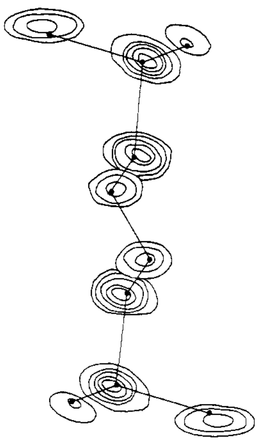

Figure 1. E map projected on the [010] plane. Contours are at equally spaced, arbitrary levels. Every other contour for the aluminum atoms has been omitted. Superimposed are lines indicating the refined configuration.

K = scale factor, $F(hkl)$ = relative structure factor, B = over-all temperature factor, $\theta(hkl)$ = Bragg angle, λ = X-ray wavelength, ϵ = systematic extinction compensation weight, $f(j)$ = form factor of atom j, $n(j)$ = number of atoms of type j in the cell, and N = number of atom types in the cell. Values of K and B were determined from a standard Wilson plot. The E's thus obtained were then rescaled such that the average $E^2 = 1.0$.

The 149 data with $E > 0.9$ were input to the program MAGIC for calculation of the Σ_2 relationships and the associated probabilities. The basic set of phases used to implement the Σ_2 formula consists of arbitrary phases (+ or −) assigned to two reflections (in the space group C2/m) in order to fix the origin, plus a small number of other reflections whose phases are specified by an unknown symbol, a, b, c, etc., where each symbol has the value + or −. The initial set of knowns used in this determination is listed in Table I. Under certain conditions an unknown E will be determined. It will then be added to the list of knowns; after 15 cycles MAGIC had determined 145 knowns. The symbols (a, b, d, f) are tried in every combination of + and − For each combination, the number of inconsistencies in

Table I. Assignment of Two Origins Specifying Reflections and Four Other Reflections as a Starting Set for the Application of Σ_2

Sign	h	k	l	E
+	$\bar{2}$	9	1	2.24
+	$\bar{4}$	8	3	2.05
a	$\bar{4}$	4	$\bar{1}$	2.58
b	$\bar{7}$	3	0	1.72
d	$\bar{2}$	4	$\bar{4}$	2.50
f	$\bar{3}$	7	1	2.00

Table II. Summary of Data from Phase-Determination Program

Combination	a	b	0	d	0	f	Contradictions
1	+	+	+	+	+	+	0
2	−	−	+	+	+	+	12
3	−	−	+	−	+	+	243
4	+	+	+	−	+	+	245

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Table III. Observed and Calculated Structure Factors[a]

K	L	OBS	CAL
******H= 0*******			
4	0	12.8	12.2
8	0	37.3	39.7
10	0	23.4	22.6
12	0	12.4	14.0
14	0	5.0	6.3
2	1	21.1	20.3
4	1	9.3	9.3
6	1	14.9	17.2
8	1	16.7	15.4
10	1	6.6	6.5
12	1	3.6	4.8
14	1	1.7	2.8
0	2	8.9	9.0
2	2	5.4	3.1
4	2	9.0	7.9
6	2	13.7	13.8
8	2	4.1	3.9
10	2	3.5	1.8
0	3	1.1	4.2*
2	3	3.5	2.1
4	3	3.9	4.6
6	3	4.5	5.7
8	3	1.0	.7*
10	3	3.0	3.0
0	4	5.0	7.6
2	4	5.6	7.4
4	4	5.5	5.1
6	4	3.8	4.4
8	4	2.0	4.0
******H= -1******			
1	0	23.9	23.2
3	0	21.2	18.7
5	0	16.5	17.2
7	0	9.1	9.8
9	0	12.5	9.1
11	0	8.6	5.5
13	0	2.3	2.2*
1	1	25.1	27.5
3	1	1.4	1.3*
5	1	31.1	30.0
7	1	26.0	27.5
9	1	7.8	6.7
11	1	2.7	4.4*
13	1	6.0	7.0
1	-1	19.6	19.2
3	-1	1.7	1.8*
5	-1	11.5	9.0
7	-1	9.7	6.1
9	-1	2.7	7.5*
11	-1	2.6	1.5*
1	2	50.0	53.2
3	2	15.5	15.2
5	2	21.5	19.9
7	2	26.3	25.6
9	2	17.0	17.5
11	2	9.8	10.5
1	-2	12.6	11.4
3	-2	21.2	21.9
5	-2	20.9	24.4
7	-2	11.6	14.9
11	-2	5.6	4.7
1	3	15.4	13.7
3	3	2.6	4.4*
7	3	6.7	4.2
9	3	6.6	5.8
1	-3	6.3	6.6
3	-3	8.1	11.0
5	-3	9.0	12.9
7	-3	5.0	8.1
1	4	6.3	7.5
3	4	2.7	1.4*
5	4	2.5	1.6*
7	4	2.1	3.5*
******H= -2******			
0	0	21.8	20.4
2	0	32.4	30.4
4	0	46.3	55.1
6	0	34.7	37.1
8	0	14.0	13.8
10	0	5.7	5.7
12	0	7.9	6.8
0	1	21.7	22.9
2	1	11.4	10.8
4	1	31.0	34.7
6	1	13.4	13.1
8	1	5.5	1.7
10	1	1.7	2.2*
12	1	1.6	.8*
4	-1	29.7	32.9
6	-1	28.7	32.0
8	-1	19.7	21.9
10	-1	13.1	13.3
12	-1	8.7	8.8
0	2	20.5	20.4
2	2	18.2	17.5
4	2	12.0	12.2
6	2	5.5	4.0
8	2	1.7	2.7*
10	2	6.2	4.0
12	2	1.5	1.6*
0	-2	18.2	19.2
2	-2	8.4	6.1
4	-2	6.3	5.9
8	-2	6.4	6.2
10	-2	4.3	4.4
0	3	14.9	13.5
2	3	15.6	14.7
4	3	19.7	21.1
6	3	19.4	21.2
8	3	10.3	9.3
10	3	1.6	2.2*
0	-3	8.4	10.6
8	-3	2.9	3.3
0	4	11.2	8.8
2	4	9.3	8.0
4	4	9.0	9.1
6	4	8.7	9.6
8	4	5.1	4.8
******H= -3******			
3	0	19.9	17.3
5	0	9.1	7.0
7	0	12.2	14.1
9	0	11.4	10.7
11	0	5.7	6.1
13	0	1.2	2.9*
3	1	14.6	13.6
5	1	27.0	27.9
7	1	35.8	37.2
9	1	27.4	27.2
11	1	16.7	17.9
13	1	7.4	8.9
1	-1	8.3	9.2
3	-1	8.7	6.9
5	-1	5.8	3.7
7	-1	8.0	7.1
9	-1	1.6	1.3*
11	-1	1.4	1.6*
1	2	6.9	7.9
3	2	3.4	1.8
5	2	10.4	8.4
7	2	12.6	12.2
9	2	7.6	7.8
11	2	4.4	5.8
13	2	3.3	3.9
3	-2	5.2	2.2
5	-2	4.5	5.6
7	-2	4.7	3.1
9	-2	4.2	4.0
1	3	6.2	7.0
3	3	8.6	7.9
5	3	13.7	14.5
7	3	7.2	6.3
9	3	1.6	.6*
11	3	1.3	.3*
1	-3	6.0	9.0
3	-3	7.2	8.3
5	-3	4.0	4.8
7	-3	3.7	3.8
1	4	4.8	3.4
3	4	1.6	3.6*
5	4	1.6	5.9*
7	4	1.6	1.3*
9	4	1.3	1.4*
1	5	5.7	5.8
3	5	5.0	5.2
5	5	4.1	5.3
******H= -4******			
0	0	9.2	9.2
2	0	16.3	17.2
4	0	10.0	9.6
6	0	14.3	12.3
8	0	2.3	1.1*
10	0	9.4	7.9
12	0	2.1	1.2*
4	1	18.3	20.1
6	1	11.6	12.2
8	1	8.2	4.3
10	1	16.5	12.4
12	1	3.7	7.1
0	-1	13.0	13.5
2	-1	24.7	26.0
4	-1	30.4	31.7
6	-1	18.0	18.5
8	-1	9.2	10.7
10	-1	8.9	9.4
12	-1	5.4	5.6
2	2	10.5	9.1
4	2	7.5	5.6
6	2	23.0	26.4
8	2	14.9	14.8
10	2	4.0	4.7
12	2	6.2	5.6
0	-2	4.5	3.1
2	-2	11.3	10.1
4	-2	15.6	16.5
6	-2	9.8	11.2
2	3	27.6	27.4
4	3	12.6	11.6
6	3	19.2	10.0
8	3	18.6	19.9
10	3	12.5	13.4
12	3	7.4	7.4
0	4	15.3	15.7
2	4	8.3	7.3
4	4	2.2	7.5*
6	4	4.2	.5
8	4	6.2	5.3
10	4	4.0	4.7
0	5	4.5	5.7
4	5	2.7	3.4*
6	5	3.4	3.6
******H= -5******			
1	0	33.8	26.6
3	0	37.3	42.2
5	0	38.6	34.5
7	0	20.6	19.2
9	0	14.5	14.0
11	0	11.1	10.4
13	0	5.7	6.6
1	1	20.3	19.0
3	1	48.9	52.9
5	1	44.2	41.2
7	1	13.5	12.7
9	1	7.4	9.5
11	1	8.6	7.8
13	1	6.8	6.1
7	-1	9.8	8.6
9	-1	5.7	4.3
11	-1	3.0	2.8
1	2	39.8	43.1
3	2	18.5	15.9
5	2	10.6	9.2
7	2	9.7	4.3
9	2	1.9	1.6*
11	2	1.8	2.1*
1	-2	7.0	7.0
1	3	4.5	10.7
3	3	8.8	9.1
5	3	1.6	.7*
7	3	5.5	1.0
9	3	6.0	6.5
11	3	5.7	5.6
1	4	15.9	14.0
3	4	14.0	15.6
5	4	15.3	20.3
7	4	12.6	14.4
9	4	1.8	3.7*
1	5	7.9	8.1
3	5	5.3	5.7
5	5	5.2	6.5
7	5	4.7	5.9
******H= -6******			
2	0	6.8	6.2
4	0	7.0	8.3
6	0	1.7	1.7*
8	0	3.6	.2
10	0	1.9	.7*
0	1	28.9	25.4
2	1	3.2	10.3
4	1	12.1	8.1
6	1	7.2	2.9
8	1	7.9	9.8
10	1	10.9	10.9
12	1	4.5	4.1
0	-1	8.1	4.1
2	-1	8.9	5.5
6	-1	4.8	3.7
8	-1	4.1	2.2
10	-1	5.1	4.7
4	2	34.3	31.9
6	2	28.2	25.5
8	2	25.6	24.6
10	2	21.3	21.7
12	2	11.9	11.8
0	-2	9.0	10.3
2	-2	9.6	9.9
4	-2	7.0	6.4
6	-2	3.9	3.5
8	-2	3.6	5.1
0	3	1.7	7.5*
2	3	13.7	12.6
4	3	23.9	23.6
6	3	15.0	13.4
8	3	7.6	6.6
10	3	6.3	6.3
12	3	4.8	4.4
0	4	3.8	4.9
2	4	8.3	6.6
4	4	15.8	16.1
6	4	10.3	11.6
8	4	1.9	1.6*
10	4	1.7	.5*
0	5	1.8	1.5*
2	5	1.9	7.9*
4	5	1.5	.1*
0	6	1.5	4.0*
******H= -7******			
1	0	19.5	18.2
3	0	27.4	27.5
5	0	20.4	19.7
7	0	11.7	11.1
9	0	10.2	10.3
11	0	5.9	7.3
1	1	2.9	1.7
3	1	6.1	5.0
5	1	14.4	9.7
7	1	7.9	4.4
9	1	9.7	7.9
11	1	6.3	5.5
1	-1	5.4	4.6
3	-1	15.7	15.5
5	-1	13.8	13.8
7	-1	5.3	6.1
1	2	7.7	16.9
3	2	5.2	8.9
5	2	9.1	4.5
7	2	1.7	.3*
9	2	12.3	9.2
11	2	7.4	6.3
1	-2	1.4	2.3*
1	3	33.3	30.0
3	3	17.7	17.2
5	3	16.0	16.3
7	3	14.2	15.2
9	3	9.1	9.3
11	3	7.1	6.0
13	3	4.3	3.6
1	4	30.4	40.9
3	4	18.0	20.4
5	4	14.2	13.9
7	4	13.9	15.2
9	4	11.3	15.1
11	4	7.0	9.7
1	5	8.6	8.0
3	5	5.5	4.3
5	5	5.0	1.0
7	5	4.0	2.2
9	5	1.4	4.1*
1	6	1.7	2.5*
3	6	1.5	4.9*
5	6	2.3	4.7
******H= -8******			
0	0	2.4	2.0*
2	0	2.4	3.3*
4	0	2.5	3.2*
6	0	6.7	2.1
10	0	2.0	3.1*
0	1	13.0	8.4
2	1	29.2	29.0
4	1	40.6	41.6
6	1	26.0	23.8
8	1	14.5	12.9
10	1	14.2	11.0
12	1	8.2	7.4
2	2	20.5	21.4
4	2	42.0	45.3
6	2	22.4	21.1
8	2	9.7	9.4
10	2	9.9	8.9
12	2	7.9	6.3
0	3	11.2	9.8
2	3	11.2	10.8
4	3	17.6	17.5
6	3	2.1	3.0*
8	3	2.5	3.6*
10	3	7.6	6.4
12	3	2.0	2.9*
0	4	19.5	21.7
2	4	12.0	15.9
4	4	7.1	6.1
6	4	2.5	.7*
8	4	2.3	5.3*
10	4	7.1	7.8
0	5	7.4	7.3
2	5	6.2	8.3
4	5	7.7	12.4
6	5	7.9	12.5
8	5	2.3	5.6*
0	6	2.4	5.5*
2	6	2.4	5.3*
4	6	2.2	3.6*
******H= -9******			
1	0	9.7	6.5
3	0	2.0	2.3*
5	0	2.0	.3*
7	0	2.1	1.9*
9	0	4.4	3.2
1	1	1.4	1.3*
3	1	1.6	.9*
5	1	1.8	5.9*
7	1	6.6	4.9
9	1	2.0	.8*
11	1	1.7	.7*
1	-1	11.7	10.9
3	-1	6.7	6.9
5	-1	3.8	3.7
7	-1	2.9	4.5
1	2	12.7	17.9
3	2	13.9	18.2
5	2	1.9	1.1*
7	2	2.2	.1*
9	2	11.5	10.3
11	2	9.6	7.2
1	3	41.2	47.6
5	3	32.8	33.5
7	3	20.7	19.5
9	3	21.1	19.1
11	3	14.8	14.0
13	3	5.0	6.2
1	4	10.9	2.5
3	4	24.9	25.0
5	4	21.9	21.5
7	4	9.2	7.3
9	4	6.0	4.8
11	4	5.6	4.7
1	5	5.6	1.7
3	5	14.5	14.9
5	5	12.6	15.3
7	5	8.2	5.5
9	5	2.0	1.6*
1	6	2.0	1.3*
3	6	2.0	4.0*
******H=-10******			
0	0	6.3	4.8*
2	0	11.5	9.7
4	0	16.6	13.7
6	0	10.2	8.6
0	1	14.7	21.5
2	1	17.8	20.1
4	1	18.7	16.2
6	1	14.2	13.9
8	1	14.3	11.3
10	1	5.4	8.6*
2	2	3.3	5.1*
4	2	4.4	3.7*
6	2	5.5	.4*
8	2	6.3	7.6*
10	2	6.7	7.5*
4	3	5.2	3.0*
6	3	6.3	5.6*
8	3	7.1	8.2*
10	3	5.7	5.8*
4	4	5.8	7.2*
6	4	6.5	4.5*
8	4	7.2	7.0*
10	4	6.7	7.7*
4	5	6.0	11.9*
6	5	6.3	8.1*
8	5	6.0	10.7*
10	5	6.7	10.6*
0	6	6.3	2.2*
2	6	7.1	4.4*
4	6	6.9	4.0*
6	6	6.3	.8*

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[a] Unobserved reflections are indicated by an asterisk.

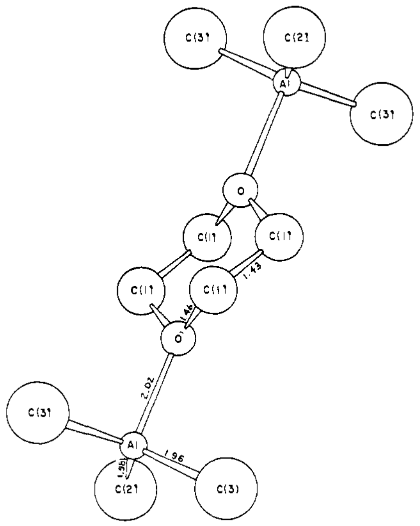

Figure 2. Molecular structure of $[Al(CH_3)_3]_2 \cdot C_4H_8O_2$.

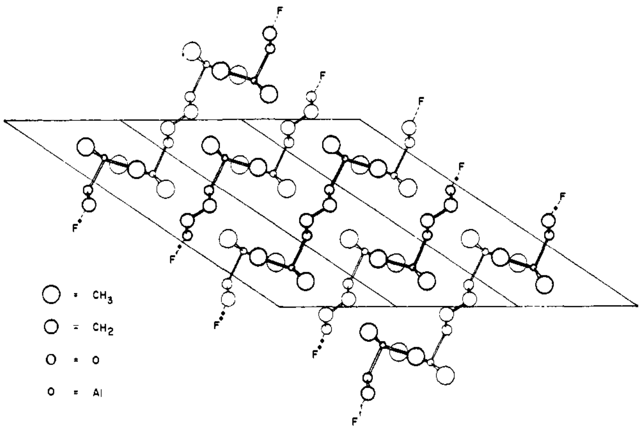

Figure 3. Packing in $[Al(CH_3)_3]_2 \cdot C_4H_8O_2$ crystals, as viewed along [010]. F indicates a portion of the molecule is not shown.

the symbol equivalence found by MAGIC is determined. The four best sets of signs are shown in Table II. If a, b, d, f were all positive, then all phases would be positive; therefore, this combination was eliminated. Combination 2 was selected, and on that basis the corresponding E map was computed. E maps are Fourier maps in which E values rather than F values are used as coefficients.[13] The advantage of using E maps is that the atoms are represented essentially as point atoms. Since many of the reflections with large E values have high indices, the resolution on an E map is very good. Upon examination of the E map (Figure 1), the coordinates of all nonhydrogen atoms were found. Several cycles of isotropic least-squares refinement with unit weights resulted in a discrepancy factor of $R_1 = [\Sigma(|F_o| - |F_c|)/\Sigma|F_o|] \times 100 = 17.9\%$ for observed data, and a subsequent difference Fourier indicated the positions of the hydrogen atoms. By allowing the positional parameters of the hydrogen atoms to vary, but holding the isotropic temperature factors constant (at the value indicated by the Wilson plot), R_1 was reduced to 15.1%. Unobserved data were then included and the aluminum atom was refined anisotropically with scale factors fixed to a value of

$$R_2 = [\Sigma W(|F_o| - |F_c|)^2/\Sigma W|F_o|^2]^{1/2} \times 100 = 12.6\% \; (R_1 = 14.0\%)$$

At this point, the average C–H bond length was 1.00 A. The final calculated and observed structure factors are listed in Table III. Final atomic parameters and standard deviations are tabulated in Table IV. Interatomic distances, angles, and errors are listed in Table V.

Discussion

The molecule, which has 2/m symmetry, consists of two $Al(CH_3)_3$ groups bonded, one each, to the oxygen atoms in the dioxane ring, which is in the chair form. About the aluminum atoms the hybridization appears to be more nearly trigonal than tetrahedral. The terminal carbon bond lengths (1.96 A) agree to within experimental error with those reported for the trimethylaluminum dimer (1.98 A)[14] and the methylaluminum dichloride dimer (1.93 ± 0.03 A).[15] The Al–O bond length (2.02 A) is notably longer than the Al–O bond in $AlCl_3 \cdot C_6H_4COCl$ (1.82 A),[16] but this is not unexpected since the coordinate bonding is stronger in the latter where the acceptor character of the aluminum atoms is increased by the more ionic character of the aluminum–chlorine bond. Distortion from tetrahedral coordina-

Table IV. Final Fractional Coordinates and Temperature Factors

Atom	x/a	y/b	z/c	B
Al	0.2930 (4)	0.5000	0.3989 (9)	...[a]
O	0.1199 (7)	0.5000	−0.1322 (14)	3.14
C(1)	0.0381 (7)	0.3972 (5)	−0.3249 (16)	4.00
C(2)	0.2461 (17)	0.5000	0.5735 (35)	6.97
C(3)	0.3627 (11)	0.3554 (7)	0.4505 (24)	6.36
H1 (C(3))	0.3738 (68)	0.3701 (49)	0.3386 (153)	3.28
H2 (C(3))	0.4324 (66)	0.3507 (55)	0.6519 (161)	3.28
H3 (C(3))	0.3426 (74)	0.3260 (50)	0.5237 (183)	3.28
H4 (C(2))	0.1681 (90)	0.5000	0.5347 (218)	3.28
H5 (C(2))	0.2896 (58)	0.4162 (37)	0.6283 (138)	3.28
H6 (C(1))	0.0323 (71)	0.4112 (48)	−0.2269 (154)	3.28
H7 (C(1))	0.1175 (70)	0.3088 (47)	−0.1730 (166)	3.28

[a] $\beta_{11} = 0.0078$; $\beta_{22} = 0.0057$; $\beta_{33} = 0.0850$; $\beta_{12} = 0.0$; $\beta_{13} = 0.0237$; $\beta_{23} = 0.0$.

Table V. Bond Distances and Angles

Bond	Distance, A	Angle	Degrees
Al–O	2.02 (2)	C(3)–Al–C(3)	116.01 (78)
Al–C(2)	1.98 (2)	C(3)–Al–C(2)	117.25 (40)
Al–C(3)	1.96 (1)	C(3)–Al–O	99.59 (42)
O–C(1)	1.46 (1)	C(2)–Al–O	101.90 (59)
C(1)–C(1)	1.43 (2)	Al–O–C(1)	122.27 (46)
		O–C(1)–C(1)	91.08 (52)
		C(1)–O–C(1)	108.21 (89)
Nonbonded Intermolecular Distances (A)			
Al–C(2)	4.89 (2)	C(1)–C(2)	4.23 (3)
O–C(2)	4.19 (3)	C(2)–C(3)	4.62 (3)
O–C(3)	4.76 (1)	C(3)–C(3)	4.26 (3)
C(1)–C(3)	3.91 (1)		

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(13) I. L. Karle, H. Hauptman, J. Karle, and A. B. Wing, *Acta Cryst.*, **11**, 257 (1958).

(14) R. G. Vranka and E. L. Amma, Abstracts, Annual Meeting of the American Crystallographic Association, Bozeman, Mont., July 1964, p 61.

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tion around the aluminum atoms may be explained by considering the electrostatic repulsion between pairs of bonding electrons. Since oxygen is more electronegative than carbon, the Al–C bonding electron pairs are closer to the aluminum atom than the more strongly polarized Al–O bonding pair. Thus the C–Al–C angles become larger (116–117°) and the C–Al–O angles become smaller (100°) than the tetrahedral value. Figures 2 and 3 show the molecular structure of $[Al(CH_3)_3]_2 \cdot C_4H_8O_2$ and packing in the crystals, respectively.

Three-coordinate oxygen is usually found in a pyramidal configuration; an exception is reported[17] for tetramethyl-O,O′-bistrimethylsilylcyclodialumoxane, where the three oxygen valencies are coplanar. In the present study, the Al–O–C(1) angle (122°) and the C(1)–O–C(1) angle (108°) are not what would be expected on the basis of sp^3 hybridization for the oxygen atoms, nor do they indicate that the oxygen is in a planar configuration.

The nmr spectra using tetramethylsilane as an internal standard indicate a chemical shift of τ 10.93 for the protons of the $(CH_3)_3Al$– group. This suggests a higher electron density at these partly negative carbon atoms than is found at the terminal carbon atoms in the trimethylaluminum dimer[18] (τ 10.67). The protons on the dioxane ring carbon atoms in the complex are in resonance at lower fields with a chemical shift of τ 6.19 compared with the protons in *p*-dioxane (τ 6.30).

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A Compound Containing a Tetrahedral Cluster of Nickel Atoms[1]

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Abstract: The crystal structure—and simultaneously the true empirical and molecular formulas—for a compound, $Ni_4(CO)_6[P(C_2H_4CN)_3]_4$, first reported but incorrectly formulated in 1959, has been determined. The compound crystallizes in the space group $R\bar{3}$ with hexagonal unit cell dimensions $a = 18.78 \pm 0.02$ A and $c = 26.12 \pm 0.02$ A, and six formula units per cell. The molecules have nearly perfect tetrahedral symmetry aside from small deformations attributed to packing effects, although, crystallographically, only C_3 symmetry is required. In the tetrahedron of nickel atoms the mean Ni–Ni distance is 2.508 ± 0.004 A. There is a symmetrical bridging carbonyl group across each edge of the tetrahedron and a P–Ni bond collinear with each threefold axis of the tetrahedron. A qualitative discussion of the bonding would suggest that the molecule should be inherently diamagnetic. Observed paramagnetism is thus attributed to contamination by nickel metal and other magnetic impurities in bulk samples of this rather unstable substance.

Some years ago Meriwether, Colthup, Fiene, and Cotton[2] reported that the reaction of nickel carbonyl with tris(β-cyanoethyl)phosphine, $P(CH_2CH_2CN)_3$, led not only to the expected product of the $Ni(CO)_2(PR_3)_2$ type, which may be obtained with phosphines generally, but also to a red-orange product (mp 160° dec) containing less CO *and* less phosphine per metal atom. This compound, which was then formulated as $[Ni(CO)P(C_2H_4CN)_3]_n$, was found to have no infrared absorption attributable to terminal CO groups but it did exhibit one strong band at 1815 cm^{-1}. Moreover, only a single C≡N stretching band was observed at 2245 cm^{-1}, suggesting that none of the cyano groups was coordinated. It was also reported that the substance was paramagnetic, but with less than one unpaired electron per metal atom. It was suggested on the basis of this evidence that the substance was likely to be a polymer of some sort, either linear or cyclic, with the polymerization number, *n*, equal to at least 2.

In the years since this preliminary study was reported, the widespread occurrence of metal atom cluster compounds in general[3a,4] and those of the polynuclear metal carbonyl type[3b] in particular has been recognized. This prompted a reconsideration of the nature of this substance. Since it did form crystals, albeit rather unstable ones, a reinvestigation of it was undertaken using, as the principal tool, single-crystal X-ray diffraction.

As will be seen, the compound has now been shown to have the formula $Ni_4(CO)_6[P(C_2H_4CN)_3]_4$ and to contain a tetrahedral cluster of nickel atoms.

Experimental Section

Crystals of $Ni_4(CO)_6[P(CH_2CH_2CN)_3]_4$ were prepared by a modification of the method of Meriwether, *et al.*[2] Dry methanol (75

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[4] F. A. Cotton, *Quart. Rev.* (London), 20, 389 (1966).