The Crystal Structure of the Polymerization Catalyst of Acetaldehyde and Its Derivatives. III. The Crystal and Molecular Structure of the Bis(dimethylaluminum *N*-Phenylbenzimidate-Acetaldehyde) Complex, $[(CH_3)_2Al\cdot O\cdot C(C_6H_5):N(C_6H_5), CH_3CHO]_2$

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The molecular structure of a stereospecific (*isotactic*) polymerization catalyst of the acetaldehyde-monomer complex, $[Me_2Al\cdot O\cdot CPh: NPh,MeCHO]_2$, has been determined on the basis of three-dimensional X-ray data collected photographically. The crystal belongs to the orthorhombic system (space group *Pcca*) with four dimer formula units in a cell with the dimensions of: $a=15.83(3)$, $b=12.61(1)$, and $c=17.66(1)$ Å. The structure was established by the heavy-atom method and refined by block-diagonal, least-squares procedure. The molecule is dimeric and has a C_2-2 symmetry. A monomer molecule, acetaldehyde, is inserted in the Al–N bond of the original polymerization catalyst. The oxygen atom bridges both aluminum atoms, Al–O = 1.858(6) and 1.985(6) Å. The α-carbon atom of acetaldehyde bonds to the nitrogen atom of the amide moiety, C–N = 1.469(12) Å. The aluminum atom is penta-co-ordinated and has a trigonal bipyramidal conformation.

We have been carried out a series of molecular-structural studies of the trimethylaluminum–benzanilide system, a catalytic system of the *isotactic* polymerization of acetaldehyde, by means of X-ray diffraction. Four complexes in the series are assumed to be the key substances for obtaining useful informations about the stereospecific polymerization mechanism of acetaldehyde. They are; (I) the polymerization catalyst, $[Me_2Al\cdot O\cdot CPh: NPh]_2$;[1] (II) the polymerization catalyst-monomer complex, $[Me_2Al\cdot O\cdot CPh: NPh,MeCHO]_2$; (III) the polymerization catalyst-monomer-Lewis acid complex, $[Me_2Al\cdot O\cdot CPh: NPh,MeCHO, AlMe_3]$; and (IV) the polymerization catalyst–Lewis base complex, $[Me_2Al\cdot O\cdot CPh: NPh,ONMe_3]$.

We have already communicated the preliminary results on these four complexes[2–5] and also reported the molecular structures of complexes I[6] and IV[7] in detail. The complex I is dimeric and has a centrosymmetric eight-membered ring, where the amide moieties make bridges between two aluminum atoms by the –O–C–N– skeletons. The complex IV is composed of a monomeric unit of I and a strong Lewis base, $ONMe_3$. The amide moiety in IV takes a stable *trans* configuration, unlike that in I (*cis*).

In this paper we will describe the crystal and molecular structure of the polymerization catalyst–monomer complex, $[Me_2Al\cdot O\cdot CPh: NPh, MeCHO]_2$, which is considered to be essentially the polymerization intermediate of this catalytic system. The main purpose of this work is to clarify the co-ordination state of acetaldehyde to the polymerization catalyst.

Experimental

The crystals of $[Me_2Al\cdot O\cdot CPh:NPh, MeCHO]_2$ were prepared and supplied by Tani and Yasuda of this University. They were far more unstable than the polymerization catalyst, $[Me_2Al\cdot O\cdot CPh:NPh]_2$. Besides being very air-sensitive, they decomposed at temperatures above 20°C. A large number of well-looking crystals were taken from the mother solution; they were sealed in thin-walled glass capillary tubes in argon. During the X-ray experiment, the Weissenberg camera was placed and operated in a cool chamber. As the chamber was temporary, the temperature inside the chamber was controlled only within about 10°C.

Nickel-filtered Cu*K*α radiation ($\lambda=1.5418$ Å) was used throughout the X-ray experiments. The unit cell dimensions were determined from two zero-level Weissenberg photographs along the *a* and *c* axes. Debye powder lines of tungsten were superposed on the Weissenberg photographs for calibration, and the cell parameters were determined by the least-squares procedure. The space group was determined to be D_{2h}^{8}–*Pcca* (No. 54) on the basis of the extinctions of reflections ($l\neq 2n$ for $0kl$, $l\neq 2n$ for $h0l$, and $h\neq 2n$ for $hk0$). The crystal data are listed in Table 1. These data impose a C_i–$\bar{1}$ or C_2–2 symmetry on the dimeric molecule.

The intensity data were collected by means of multiple-film equi-inclination Weissenberg photographs along the *a* and *c* axes. As the crystal was unstable even in argon at about 10°C, four crystals of a similar size (about 0.4×0.4×1.0 mm) were used (three along the *a* axis and one along the *c* axis). 2053 reflections from $0kl$ through $11,k,l$, and 515 reflections from

Table 1. Crystal data of $[(CH_3)_2Al\cdot O\cdot C(C_6H_5): N(C_6H_5),CH_3CHO]_2$

Orthorhombic	$C_{34}H_{40}N_2O_4Al_2$ (as a dimer)
$a=15.83(3)$ Å	$M=594.6$
$b=12.61(1)$ Å	$Z=4$
$c=17.66(1)$ Å	$d_m=1.14$ g.cm^{-3}
$V=3525.2$ Å^3	$d_x=1.12$ g.cm^{-3}
	Space group *Pcca*
	$\mu=11.4$ cm^{-1} (for Cu*K*α)

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[1] Throughout the paper, the methyl and phenyl groups will be expressed as Me and Ph respectively.

[2] Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo, H. Yasuda, and H. Tani, *Chem. Commun.*, **1968**, 1332.

[3] Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo, H. Yasuda, and H. Tani, *ibid.*, **1969**, 575.

[4] Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo, H. Yasuda, and H. Tani, *ibid.*, **1970**, 1243.

[5] Y. Kai, N. Yasuoka, N. Kasai, M. Kakudo, H. Yasuda, and H. Tani, *ibid.*, **1971**, 940.

[6] Y. Kai, N. Yasuoka, N. Kasai, and M. Kakudo, *J. Organometal. Chem.*, **32**, 165 (1971).

[7] Y. Kai, N. Yasuoka, N. Kasai, and M. Kakudo, This Bulletin, **45**, 3388 (1972).

*hk*0 through *hk*2 were collected. Their intensities were estimated visually, and they were corrected for the usual Lorentz and polarization factors and also for the spot-shape effect. The absorption correction was ignored (μ=11 cm^{-1} for Cu$K\alpha$). A total of 2185 independent reflections were obtained, among which 451 reflections were too weak to be measured.

Structure Determination and Refinement

The structure was established by the heavy-atom method. The initial co-ordinates of the aluminum atom were determined from the three-dimensional Patterson maps. The computations of the minimum function and a Fourier synthesis were carried out, both based on the location of the aluminum atom.[8] From these maps, three reasonable atomic locations were found close to the aluminum atom, but none of them could be identified as carbon, nitrogen, or oxygen. The atomic scattering factors of the nitrogen atoms were, therefore, assumed for these atoms in the succeeding Fourier synthesis, and 17 atomic positions out of 21 nonhydrogen atoms could be located. The remaining 4 atomic locations were determined from the successive Fourier synthesis.

Starting from the locations of these nonhydrogen atoms, the block-diagonal least-squares refinement was done, using the HBLS IV program[8] on a FACOM 230-60 computer at Kyoto University. The function minimized was $\sum w(\Delta F)^2$, and at the initial stage w was taken as unity for all reflections. The atomic scattering factors used were taken from those of Hanson and his co-workers.[9] Using the isotropic temperature factors for all the nonhydrogen atoms, the usual R index converged to 0.20 after 3 cycles. The difference Fourier map was computed, and all the hydrogen atoms could be located approximately. The refinement proceeded including these hydrogen atoms and applying the anisotropic temperature factors for nonhydrogen atoms. The weighting scheme described later was also included in the refinement. The R index was improved to 0.15 after 2 cycles. In this refinement, the locations of atoms bearing the hydrogen, especially that of the α-carbon atom in the acetaldehyde moiety, were much improved. The difference Fourier map was again computed based on the new locations of the nonhydrogen atoms, and the positions of hydrogen atoms were determined again. The final refinement was carried out considering the redetermined hydrogen atoms; the final R value is 0.143 for non-zero reflections (R=0.191 for all reflections). The weighting scheme applied in the final refinement is: $|F_o|<F_{\text{min}}$; $w=F_{\text{wt}}$, $F_{\text{min}}\leqq|F_o|\leqq F_{\text{max}}$; $w=1$, $F_{\text{max}}<|F_o|$; $w=(F_{\text{max}}/|F_o|)^2$, where $F_{\text{max}}=20.0$, $F_{\text{min}}=4.0$, and $F_{\text{wt}}=0.20$.

The final atomic co-ordinates of the nonhydrogen atoms, along with their estimated standard deviations, and the anisotropic temperature factors are listed in Tables 2 and 3 respectively. The atomic co-ordinates and isotropic temperature factors of the hydrogen atoms are listed in Table 4. Table 5 lists the observed and

TABLE 2. ATOMIC CO-ORDINATES OF THE HEAVY ATOMS (IN FRACTION OF CELL EDGES) ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS (IN 10^{-3} Å)

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Al	0.0844	3	0.1665	3	0.2081	3
O(1)	0.1978	6	0.1818	6	0.2626	6
O(2)	0.0395	5	0.1503	5	0.3046	6
N	0.1538	7	0.1999	7	0.3844	6
C(1)	0.1228	13	0.0463	13	0.1461	13
C(2)	0.0907	11	0.3107	11	0.1667	10
C(3)	0.2109	10	0.2187	8	0.3282	10
C(4)	0.2877	9	0.2789	9	0.3428	9
C(5)	0.3395	8	0.2592	9	0.4052	9
C(6)	0.4175	11	0.3162	12	0.4122	13
C(7)	0.4394	11	0.3971	12	0.3605	12
C(8)	0.3876	11	0.4141	12	0.3004	10
C(9)	0.3143	10	0.3597	11	0.2902	8
C(10)	0.1556	10	0.2625	9	0.4543	9
C(11)	0.1637	11	0.2079	10	0.5247	9
C(12)	0.1658	13	0.2750	13	0.5903	9
C(13)	0.1604	11	0.3841	11	0.5844	10
C(14)	0.1495	12	0.4339	10	0.5173	8
C(15)	0.1458	10	0.3696	9	0.4506	8
C(16)	0.0830	9	0.1265	8	0.3727	10
C(17)	0.1170	13	0.0105	10	0.3703	14

TABLE 3. ANISOTROPIC TEMPERATURE FACTORS OF THE HEAVY ATOMS EXPRESSED IN THE FORM OF $\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)\}$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Al	0.0034	0.0062	0.0035	0.0018	−0.0008	−0.0027
O(1)	0.0036	0.0086	0.0041	0.0012	−0.0014	−0.0039
O(2)	0.0019	0.0051	0.0043	0.0006	−0.0013	0.0007
N	0.0030	0.0069	0.0032	−0.0022	−0.0016	0.0008
C(1)	0.0072	0.0137	0.0061	0.0052	−0.0026	−0.0105
C(2)	0.0054	0.0116	0.0038	−0.0012	−0.0013	0.0007
C(3)	0.0041	0.0060	0.0047	0.0046	−0.0035	0.0007
C(4)	0.0035	0.0081	0.0032	0.0017	−0.0021	−0.0044
C(5)	0.0022	0.0087	0.0045	0.0014	0.0004	−0.0028
C(6)	0.0040	0.0116	0.0058	0.0029	−0.0015	−0.0012
C(7)	0.0048	0.0112	0.0057	−0.0041	0.0030	−0.0040
C(8)	0.0050	0.0126	0.0038	−0.0036	0.0018	−0.0003
C(9)	0.0042	0.0113	0.0025	−0.0032	0.0009	0.0001
C(10)	0.0038	0.0071	0.0035	−0.0013	−0.0015	0.0028
C(11)	0.0060	0.0084	0.0039	0.0015	−0.0012	0.0058
C(12)	0.0079	0.0175	0.0016	0.0009	−0.0018	0.0021
C(13)	0.0059	0.0117	0.0036	−0.0008	−0.0012	−0.0024
C(14)	0.0067	0.0108	0.0024	0.0014	−0.0017	0.0006
C(15)	0.0049	0.0089	0.0027	0.0006	0.0001	0.0017
C(16)	0.0035	0.0058	0.0050	−0.0016	−0.0043	0.0024
C(17)	0.0083	0.0055	0.0098	−0.0026	−0.0084	0.0055

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[8] Most of the programs used in the calculations were taken from "The Universal Crystallographic Computing System (I)," edited by T. Sakurai, Japanese Crystallographic Association (1967), and the other programs were cited in our previous paper.[6,7]

[9] H. P. Hanson, F. Herman, J. D. Lea, and S. S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

TABLE 4. ATOMIC CO-ORDINATES (IN FRACTION OF CELL EDGES) ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS (IN 10^{-2} Å) AND ISOTROPIC TEMPERATURE FACTORS FOR THE HYDROGEN ATOMS (IN $Å^2$)

Atom	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	B
H(1)	0.081	10	−0.019	10	0.126	9	4.0
H(2)	0.170	10	0.060	10	0.101	10	4.2
H(3)	0.164	10	−0.001	11	0.184	10	4.1
H(4)	0.042	10	0.339	10	0.121	10	4.0
H(5)	0.160	11	0.340	10	0.159	10	3.9
H(6)	0.071	10	0.360	10	0.199	10	3.9
H(7)	0.321	10	0.198	9	0.448	9	3.0
H(8)	0.458	10	0.297	9	0.458	9	3.2
H(9)	0.497	10	0.444	10	0.367	10	3.8
H(10)	0.405	10	0.476	9	0.259	10	3.6
H(11)	0.274	10	0.379	9	0.242	10	3.7
H(12)	0.167	9	0.121	8	0.529	8	2.4
H(13)	0.173	10	0.241	10	0.645	10	3.9
H(14)	0.164	10	0.434	10	0.635	9	3.7
H(15)	0.144	10	0.519	9	0.513	9	3.2
H(16)	0.133	10	0.410	9	0.398	10	3.8
H(17)	0.038	10	0.134	10	0.419	10	3.6
H(18)	0.066	9	−0.039	9	0.356	10	3.3
H(19)	0.173	10	0.020	10	0.340	11	4.6
H(20)	0.130	10	0.018	10	0.434	10	3.7

calculated structure factors.[10]

Results and Discussion

Molecular Structure. The molecular structure viewed along the *b* axis is shown in Fig. 1, along with the numbering of the atoms. The shaded are the seven atoms of the acetaldehyde moiety. The interatomic bond distances and angles are listed in Tables 6 and 7 respectively.

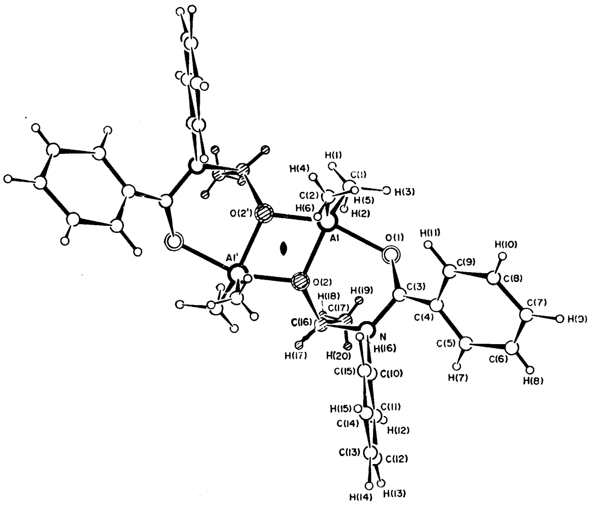

Fig. 1. The molecular structure.

TABLE 6. INTERATOMIC DISTANCES ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS

Atoms	Distance (Å)	σ (Å)	Atoms	Distance (Å)	σ (Å)
Al–O(1)	2.045	0.007	C(3)–N	1.364	0.012
Al–O(2)	1.858	0.006	C(3)–C(4)	1.455	0.013
Al–C(1)	1.965	0.013	O(2)–C(16)	1.418	0.011
Al–C(2)	1.962	0.012	C(16)–N	1.469	0.012
Al–O(2′)	1.985	0.006	C(16)–C(17)	1.559	0.017
O(1)–C(3)	1.265	0.012	N–C(10)	1.466	0.012
C(16)–H(17)	1.09	0.11			
C(4)–C(5)	1.396	0.013	C(10)–C(11)	1.426	0.015
C(5)–C(6)	1.434	0.016	C(11)–C(12)	1.436	0.018
C(6)–C(7)	1.412	0.017	C(12)–C(13)	1.382	0.017
C(7)–C(8)	1.359	0.017	C(13)–C(14)	1.353	0.016
C(8)–C(9)	1.359	0.016	C(14)–C(15)	1.431	0.015
C(9)–C(4)	1.443	0.014	C(15)–C(10)	1.361	0.014
C(1)–H(1)	1.16	0.11	C(2)–H(4)	1.11	0.10
C(1)–H(2)	1.16	0.11	C(2)–H(5)	1.11	0.10
C(1)–H(3)	0.91	0.10	C(2)–H(6)	1.11	0.11
C(17)–H(18)	1.06	0.10			
C(17)–H(19)	1.04	0.11			
C(17)–H(20)	1.14	0.10			
C(5)–H(7)	1.11	0.10	C(11)–H(12)	1.09	0.09
C(6)–H(8)	1.05	0.10	C(12)–H(13)	1.07	0.10
C(7)–H(9)	1.09	0.10	C(13)–H(14)	1.09	1.10
C(8)–H(10)	1.10	0.10	C(14)–H(15)	1.08	0.10
C(9)–H(11)	1.09	0.10	C(15)–H(16)	1.09	0.10

As may be seen in Fig. 1, the molecule is dimeric and has a C_2-2 symmetry instead of the C_i-$\bar{1}$ which was found in the catalyst, $[Me_2Al{\cdot}O{\cdot}CPh{:}\ NPh]_2$. The most interesting feature is that the aldehyde molecule is inserted between the aluminum and nitrogen atoms of the catalyst and is connected to the catalyst by two sites, O(2) and C(16). The O(2) co-ordinates to the aluminum (Al), and the C(16) bonds to the nitrogen atom of the amide moiety. These facts show that the relative position of the aldehyde molecule and the catalyst skeleton is uniquely fixed in the solid state. Such a co-ordination might be a main feature, even in the solution.

The oxygen (O(2)) of the aldehyde moiety co-ordinates to the other aluminum atom (Al′) and makes an oxonium ion-type bonding. Three bonds from the O(2) lie on the same plane (within 0.02 Å). The difference between the two Al–O(2) bond distances, (Al–O(2)=1.858(6) Å and Al′–O(2)=1.985(6) Å), is significant. The cryoscopic measurement of the molecular weight suggests that the dimeric molecule dissociates in the dilute solution under the polymerization conditions. For the dissociation, the cleavage of the Al′–O(2) bond is necessary. The rather long distance of Al′–O(2) suggests the possible fission of this bond. This was recently proved to be true by the isolation and structural determination of $[Me_2Al{\cdot}O{\cdot}CPh{:}NPh, MeCHO, AlMe_3]$.[4]

The α-carbon atom, C(16) of the aldehyde moiety shows an sp^3 hybridization; all the bond angles around the C(16) are tetrahedral (Table 7), and the bond distances, C(16)–O(2) (1.418(11) Å), C(16)–N (1.469 (12) Å), and C(16)–C(17) (1.559(17) Å), show the

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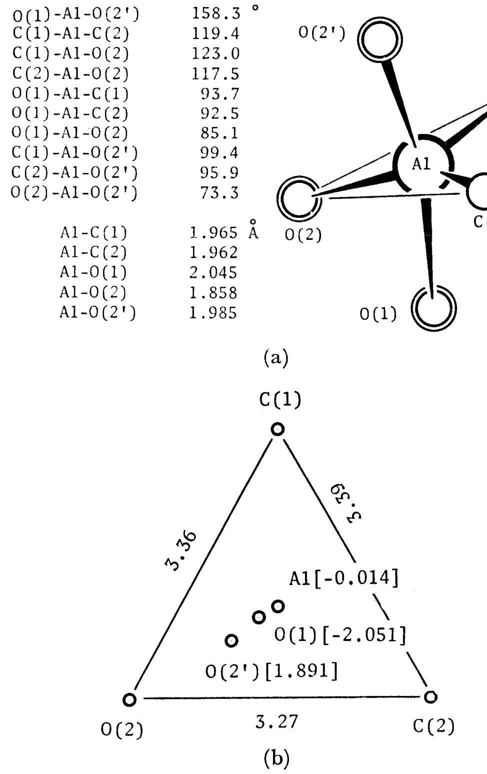
[10] Table 5 has been submitted to and is kept as Document No. 7210 by, the office of the Bulletin of the Chemical Society of Japan, 1-5, Kanda-Surugadai, Chiyoda-ku, Tokyo. A copy may be secured by citing the Document number and by remitting, in advance, ¥300 for photo prints. Pay by check or money order payable to: Chemical Society of Japan.

TABLE 7. INTERATOMIC ANGLES ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS

Atoms	Angle (deg.)	σ (deg.)	Atoms	Angle (deg.)	σ (deg.)
C(1)-Al-O(1)	93.7	0.4	C(3)-N-C(16)	120.8	0.7
C(2)-Al-O(1)	92.5	0.4	C(3)-N-C(10)	120.5	0.7
O(2)-Al-O(1)	85.1	0.3	C(10)-N-C(16)	118.3	0.7
C(1)-Al-O(2′)	99.4	0.4	Al-O(2)-Al′	105.3	0.3
C(2)-Al-O(2′)	95.9	0.4	Al-O(2)-C(16)	128.0	0.5
O(2)-Al-O(2′)	73.3	0.3	C(16)-O(2)-Al′	126.7	0.5
O(2′)-Al-O(1)	158.3	0.3	O(2)-C(16)-C(17)	110.1	0.8
C(1)-Al-O(2)	123.0	0.4	O(2)-C(16)-N	110.9	0.7
C(2)-Al-O(2)	117.5	0.4	N-C(16)-C(17)	109.4	0.8
C(1)-Al-C(2)	119.4	0.5	H(17)-C(16)-O(2)	107	6
Al-O(1)-C(3)	127.6	0.6	H(17)-C(16)-C(17)	109	6
O(1)-C(3)-N	119.6	0.8	H(17)-C(16)-N	110	6
O(1)-C(3)-C(4)	119.4	0.8			
N-C(3)-C(4)	121.0	0.8			
C(3)-C(4)-C(5)	122.6	0.8	N-C(10)-C(11)	118.4	0.8
C(3)-C(4)-C(9)	119.9	0.8	N-C(10)-C(15)	119.5	0.8
C(4)-C(5)-C(6)	119.1	0.9	C(10)-C(11)-C(2)	115	1
C(5)-C(6)-C(7)	121	1	C(11)-C(12)-C(13)	122	1
C(6)-C(7)-C(8)	118	1	C(12)-C(13)-C(14)	122	1
C(7)-C(8)-C(9)	123	1	C(13)-C(14)-C(15)	118	1
C(8)-C(9)-C(4)	121	1	C(14)-C(15)-C(10)	121	1
C(5)-C(4)-C(9)	117.5	0.9	C(11)-C(10)-C(15)	122.1	0.9
H(1)-C(1)-H(2)	107	7	H(4)-C(2)-H(5)	116	7
H(1)-C(1)-H(3)	99	8	H(4)-C(2)-H(6)	90	8
H(2)-C(1)-H(3)	97	8	H(5)-C(2)-H(5)	100	8
Al-C(1)-H(1)	124	5	Al-C(2)-H(4)	120	5
Al-C(1)-H(2)	119	5	Al-C(2)-H(5)	113	5
Al-C(1)-H(3)	105	6	Al-C(2)-H(6)	113	7
			H(18)-C(17)-H(19)	127	8
			H(18)-C(17)-H(20)	115	7
			H(19)-C(17)-H(20)	110	8
			C(16)-C(17)-H(18)	107	5
			C(16)-C(17)-H(19)	102	5
			C(16)-C(17)-H(20)	88	5
H(7)-C(5)-C(4)	120	5	H(12)-C(11)-C(10)	123	5
H(7)-C(5)-C(6)	121	5	H(12)-C(11)-C(12)	122	5
H(8)-C(6)-C(5)	118	6	H(13)-C(12)-C(11)	120	6
H(8)-C(6)-C(7)	121	6	H(13)-C(12)-C(13)	119	6
H(9)-C(7)-C(6)	122	5	H(14)-C(13)-C(12)	121	5
H(9)-C(7)-C(8)	120	5	H(14)-C(13)-C(14)	117	5
H(10)-C(8)-C(7)	119	5	H(15)-C(14)-C(13)	122	5
H(10)-C(8)-C(9)	119	5	H(15)-C(14)-C(15)	120	5
H(11)-C(9)-C(8)	120	5	H(16)-C(15)-C(14)	117	5
H(11)-C(9)-C(4)	119	5	H(16)-C(15)-C(10)	122	5

normal values of the single covalent bond.

The most remarkable features are that the aluminum atom is penta-co-ordinated, and that a distorted trigonal-bipyramid is formed. The geometry around the aluminum atom is shown in Fig. 2. The aluminum atom lies exactly on the C(1)–C(2)–O(2) plane (within 0.01 Å), and the three bond angles around the aluminum in this basal plane show little deviation from 120°, the value expected for the typical trigonal bipyramid. The O(1) atom is just beneath the aluminum atom, and the three bond angles, O(1)–Al–C(1), O(1)–Al–C(2), and O(1)–Al–O(2), show a relatively good coincidence with the expected value of 90°. The interatomic vector, O(1)–Al, makes an angle of 84.6° with the basal plane, while the angle between the O(2′)–Al vector and the basal plane is 73.7°. The latter shows a great deviation from 90°. The distortion of the geometry around the aluminum atom from the trigonal bipyramid may be attributed to the formation of an additional four-membered ring, $\mathrm{Al}\overset{\diagup\mathrm{O(2')}\diagdown}{\underset{\diagdown\mathrm{O(2)}\diagup}{\qquad}}\mathrm{Al'}$.



O(1)-Al-O(2')	158.3 °
C(1)-Al-C(2)	119.4
C(1)-Al-O(2)	123.0
C(2)-Al-O(2)	117.5
O(1)-Al-C(1)	93.7
O(1)-Al-C(2)	92.5
O(1)-Al-O(2)	85.1
C(1)-Al-O(2')	99.4
C(2)-Al-O(2')	95.9
O(2)-Al-O(2')	73.3
Al-C(1)	1.965 Å
Al-C(2)	1.962
Al-O(1)	2.045
Al-O(2)	1.858
Al-O(2')	1.985

Fig. 2. The co-ordination geometry around the penta-co-ordinated aluminum atom. (a) Bond distances and angles. (b) Projection onto the basal plane (deviation from the plane are given in the brackets in Å unit).

The geometry around the penta-co-ordinated aluminum atom is summarized in Table 8. In [AlH_3, $2NMe_3$],[11] the aluminum atom lies on the crystallographic center of symmetry and two nitrogen and one aluminum atoms lie on a straight line. Because of the disorder, the presence of the six half-hydrogen atoms was assumed on the plane perpendicular to the N–Al–N axis in the hexagonal array. In the infinite-chain molecule with the molecular unit of [Me_2N–CH_2–CH_2–NMe_2]–AlH_3,[12] two aluminum atoms of the asymmetric unit do not lie at any crystallographic special positions. Two nitrogen atoms from two different diamine molecules occupy the apical positions of the trigonal bipyramid, with N–Al–N angles of 178.0° and 176.5°. The three hydrogen atoms around the aluminum atom, which were located by the difference Fourier synthesis, lie on an equatorial plane with an approximate three-fold symmetry. μ-Oxo-di[bis(2-methyl-8-quinolinolato-

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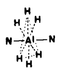
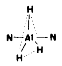
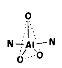
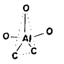
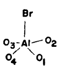
11) C. W. Heitsch, C. E. Nordman, and R. W. Parry, *Inorg. Chem.*, **2**, 508 (1963).

12) G. J. Palenik, *Acta Crystallogr.*, **17**, 1573 (1964).

aluminum(III)][13] also contains two penta-co-ordinated, slightly distorted trigonal bipyramidal, aluminum atoms in an asymmetric unit. Three oxygen and one aluminum atoms lie on the equatorial plane, and two nitrogen atoms occupy the apical positions. The average value of the N–Al–N is 163°. On the other hand, in the present complex, two carbon and one oxygen atoms lie on the equatorial plane and two oxygen atoms occupy the apical positions. The O–Al–O angle is 158°; much distortion is seen. In $C_8H_{24}Al_3Br_5O_6Si_4$,[14] each aluminum atom is co-ordinated by four oxygen and one bromine atoms, but the distortion is too large to interpret the geometry as either a trigonal bipyramid or a square pyramid.

Crystal Structure. Figure 3 shows the crystal structure projected along the *b* axis. Intermolecular atomic contacts of less than 3.8 Å are shown by broken lines. They are all considered as normal van der Waals' contacts.

TABLE 8. GEOMETRY AROUND THE PENTA-CO-ORDINATED ALUMINUM ATOM

[AlH_3, $2NMe_3$][11]		∠N-Al-N=180° *Trigonal bipyramid* Al on $\bar{1}$. 6/2H on the plane perpendicular to N-Al-N axis in the hexagonal array by the disorder
[AlH_3, $Me_2NCH_2CH_2$-NMe_2][12]		$\angle N\text{-}Al\text{-}N=\begin{cases}178.0°\\176.5°\end{cases}$ *Trigonal bipyramid* Infinite chain, ···–C–C–N–Al–N–···
[$Al_2O(C_{10}H_8NO)_4$][13]		$\angle N\text{-}Al\text{-}N=\begin{cases}162.2°\\163.5°\end{cases}$ *Distorted trigonal bipyramid*
[$Me_2Al\cdot O\cdot CPh:NPh$, $MeCHO]_2$[a]		∠O-Al-O=158.3° *Distorted trigonal bipyramid*
[$C_8H_{24}Al_3Br_5O_6Si_4$][14]		$\angle O_1\text{-}Al\text{-}O_3=132°$ $\angle O_2\text{-}Al\text{-}O_4=158°$ Difficult to interpret as either trigonal bipyramid or square pyramid

a) Present work

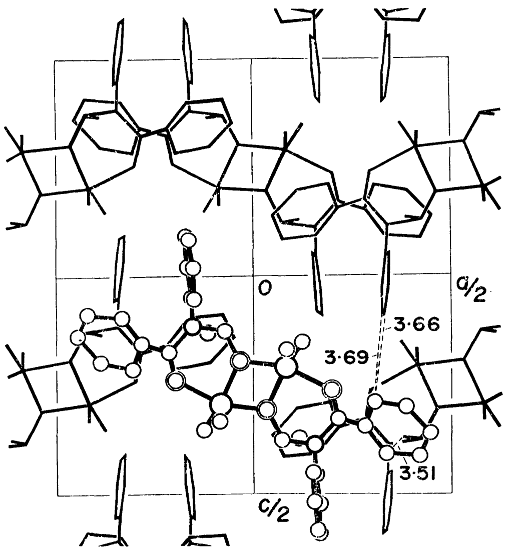


Fig. 3. The crystal structure projected along the *b*-axis.

Some Reactions about the Present Complex. From among the reactions of the trimethylaluminum–benzanilide catalyst system, some important reactions related with the present complex are shown in Fig. 4. In a previous paper,[7] the reaction from complex I to IV was discussed from a molecular-structural point of view. Very recently, Tani and his co-workers discovered that complex IV can also be obtained from complex II (the present complex) and $ONMe_3$ under conditions similar to those above. The complex II is obtained from complex I and MeCHO as has been described before. From these facts, the reaction scheme can be redrawn as is in Fig. 4 by drawing the molecular structures of these complexes.

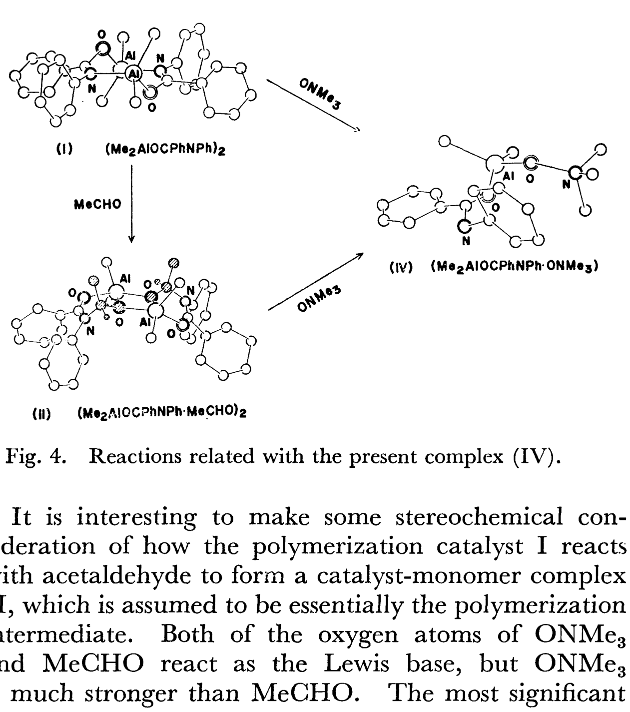


Fig. 4. Reactions related with the present complex (IV).

It is interesting to make some stereochemical consideration of how the polymerization catalyst I reacts with acetaldehyde to form a catalyst-monomer complex II, which is assumed to be essentially the polymerization intermediate. Both of the oxygen atoms of $ONMe_3$ and MeCHO react as the Lewis base, but $ONMe_3$ is much stronger than MeCHO. The most significant difference between these two bases is that $ONMe_3$ is unifunctional, whereas MeCHO is bifunctional; when the oxygen atom of MeCHO acts as a Lewis base, the α-carbon can act like Lewis acid. In Fig. 5, the postulated molecule (ii) may, therefore, not be so stable as (i), which is identical with the complex IV (IV in Fig. 4), even though the amide moiety takes a stable *trans* configuration. The interaction between the electron-deficient α-carbon atom of acetaldehyde and the electron-rich nitrogen atom of the amide moiety can be expected. The subsequent configurational change of the amide moiety from *trans* to *cis* is required to make the interaction possible. This is shown by the postulated molecule (i) in Fig. 6. An additional rotation about the Al–O bond (Fig. 6 (ii)) is necessary to strengthen the interaction. Another rotation about the O–C bond (Fig. 6 (iii)) completes the formation of a half of the complex II (Fig. 6 (iv)). The present complex, (II) is then formed by the association of these two halves.

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13) Y. Kushi and Q. Fernando, *J. Amer. Chem. Soc.*, **92**, 91 (1970).

14) M. Bonamico, *Chem. Commun.*, **1966**, 135.

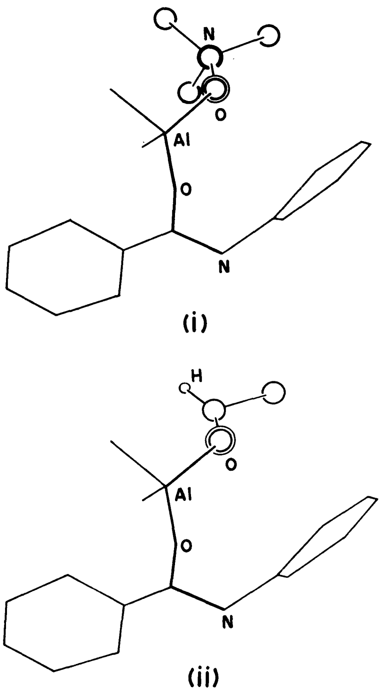

Fig. 5. The comparison of the molecular structure of [$Me_2Al \cdot O \cdot CPh\colon NPh, ONMe_3$] (i) and a postulated molecule [$Me_2Al \cdot O \cdot CPh\colon NPh, MeCHO$] (ii).

The molecular-structural change in the reaction of the complex II with $ONMe_3$ (Fig. 4) can also be discussed in a similar manner, but in the reverse direction. The stronger Lewis base $ONMe_3$ attacks and replaces the aldehyde moiety of a half of the dissociated complex II to form the complex IV.

The α-carbon atom of the acetaldehyde moiety in the complex II is an asymmetric carbon. Since the molecule has a crystallographic C_2-2 symmetry, there are two asymmetric carbon atoms of the same configuration in a molecule. The space group belongs to a centrosymmetric *Pcca*, and there are an equal number of optical isomers in the crystal. The absolute configuration of these asymmetric carbon is, therefore, S–S or R–R. A hypothetical molecule, which has a C_i-$\bar{1}$ symmetry instead of C_2-2, is shown in Fig. 7; the absolute configuration of the asymmetric carbon atoms is S–R or R–S. In the postulated molecule, if the geometry around the aluminum atom is kept significantly unchanged from that of the actual molecule, a rather short contact C(2)···C(17′), 3.3 Å, results between the two methyl groups in a molecule (one attached to the aluminum atom and the other from the aldehyde moiety). Such a steric hindrance probably make it difficult for the molecule of C_i-$\bar{1}$ symmetry to exist or at least makes the molecule unstable.

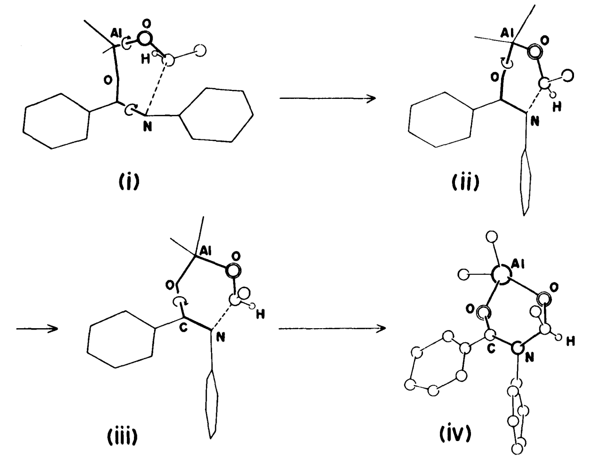

Fig. 6. Schematic representation of a conversion of the postulated molecule, [$Me_2Al \cdot O \cdot CPh\colon NPh, MeCHO$] into the real structure, which is a half of the [$Me_2Al \cdot O \cdot CPh\colon NPh, MeCHO]_2$ molecule.

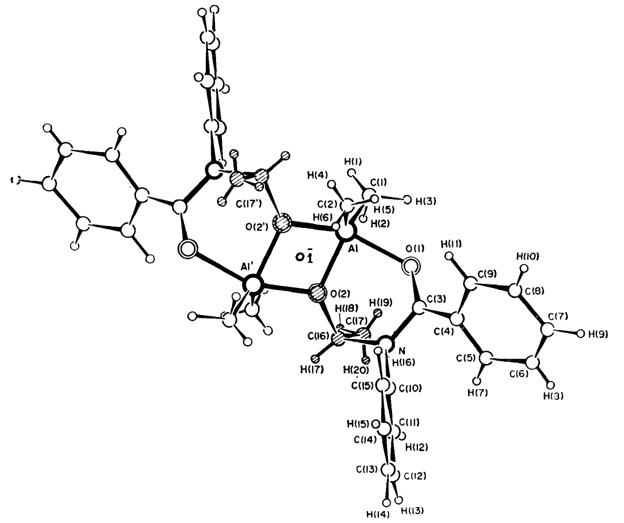

Fig. 7. A hypothetical molecule for [$Me_2Al \cdot O \cdot CPh\colon NPh, MeCHO]_2$ with C_i-$\bar{1}$ symmetry instead of C_2-2.

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