Molecular Structure of the Polymerization Catalyst–Monomer Complex, $(\mathrm{Me_2AlOCPhNPh,MeCHO})_2$

By YASUSHI KAI, NORITAKE YASUOKA, NOBUTAMI KASAI,* and MASAO KAKUDO
(*Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamada-Kami, Suita, Osaka,* **564**, *Japan*)
and HAJIME YASUDA and HISAYA TANI
(*Department of Polymer Science, Faculty of Science, Osaka University, Toyonaka, Osaka,* 560, *Japan*)

RECENTLY we reported the molecular structure of a stereospecific polymerization catalyst for acetaldehyde, $(\mathrm{Me_2AlOCPhNPh})_2$.[1] We now describe the *X*-ray structure analysis of the catalyst–acetaldehyde complex $(\mathrm{Me_2AlOCPhNPh, MeCHO})_2$ which is most important in attempts to clarify the initiation mechanism of acetaldehyde polymerization.[2]

As the complex is very unstable in air, and also at temperatures above 20°, the crystal chosen was sealed in a thin-walled glass capillary tube in argon, and the temperature was strictly controlled (not exceeding 15° during the experiments). However, this was not enough to prevent the decomposition and four crystals were used for the intensity data collection. *Crystal data*: $(\mathrm{Me_2AlOCPhNPh, MeCHO})_2$; $a = 15·83 \pm 0·03$, $b = 12·61 \pm 0·01$, $c = 17·66 \pm 0·01$ Å; space group *Pcca*, D_c 1·12, D_m 1·14 g.cm.$^{-3}$, $Z = 4$ (as a dimer).

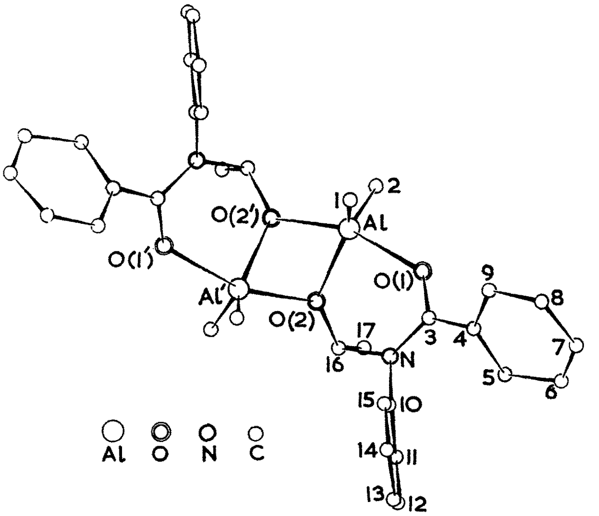


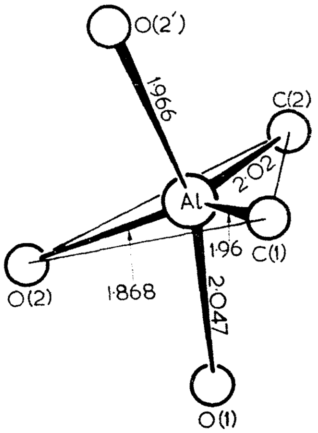
FIGURE. *Molecular structure of* $(\mathrm{Me_2AlOCPhNPh,MeCHO})_2$.

With nickel-filtered Cu-K_α radiation, multi-film equi-inclination Weissenberg photographs were taken around the *a* and *c* axes, and 2185 independent reflexions were obtained out of 2053 0*kl* to 11,*k*,*l* and 515 *hk*0 to *hk*2 reflexions. By starting with the three-dimensional Patterson function, which allowed the location of the aluminium atom, the structure was solved through the minimum function, Fourier synthesis, and the block-diagonal least-squares refinement. For non-zero reflexions $R = 0·147$ (including hydrogen atoms), which is relatively large but is sufficient to determine the co-ordination of the acetaldehyde to the catalyst.

The molecular structure is shown in the Figure. The molecule is dimeric about the crystallographic two-fold axis. The most interesting feature of the molecule is the co-ordination of acetaldehyde to the catalyst, particularly the formation of C(16)–N single bond. The acetaldehyde molecule is connected to the catalyst by both O(2) and C(16). The oxygen atom is bridged between two aluminium atoms. The Al–O(2′) distance [**1·966 Å**; e.s.d., **σ = 0·006 Å,** abbreviated as (6) hereafter] is significantly longer **than** Al–O(2) [1·868(6) Å], which may support the **chemical**

Geometry around the penta-co-ordinated aluminium (estimated standard deviations are shown in parentheses)

O(1)–Al–O(2′)	158·4°	(0·3°)
C(1)–Al–C(2)	123·2	(0·6)
C(1)–Al–O(2)	116·7	(0·4)
C(2)–Al–O(2)	121·1	(0·5)
C(1)–Al–O(2′)	95·8	(0·4)
C(2)–Al–O(2′)	99·2	(0·5)
O(2)–Al–O(2′)	73·0	(0·3)
C(1)–Al–O(1)	92·2	(0·4)
C(2)–Al–O(1)	93·3	(0·5)
O(1)–Al–O(2)	92·2	(0·4)



evidence that the dimeric molecule dissociates to monomeric units under polymerization conditions.[2]

In the aldehyde moiety, the O(2)–C(16) distance [1·43(1) Å] is longer than that in the acetaldehyde monomer [1·22 Å (vapour)[3] or 1·25 Å (crystal)][4] and is equal to the ordinary C–O single-bond distance. The α-carbon of the acetaldehyde moiety assumes sp^3 instead of the ordinary sp^2 hybridization due to the bonding to the nitrogen atom, as had been suggested by n.m.r. studies.[2] The C(16)–N distance [1·49(1) Å] is equal to the sum of the covalent radii, 1·47 Å, within experimental error.

Another interesting feature is that the aluminium atom is penta-co-ordinated, and that a distorted trigonal-bipyramid is formed (Table). This is the first example of penta-co-ordinated aluminium determined definitely by *X*-ray analysis, although such co-ordination was suggested in $AlH_3,2NMe_3$.[5]

The Al–O(1) distance in the catalyst moiety [2·047(7) Å] is much longer than that in the catalyst itself [1·81(1) Å].

The conformation of the amide group in the catalyst moiety does not show any great deviation from that of the catalyst. The two benzene rings adopt a *cis*-configuration, and the dihedral angle of their best planes is 62°.

The contribution of this structure determination to the polymerization mechanism, including the co-catalytic action of water,[6] will be the subject of a future paper.

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

[2] H. Tani, T. Araki, and H. Yasuda, *J. Polymer Sci., Part B, Polymer Letters*, 1968, **6**, 389.

[3] D. Stevenson, H. D. Burnham, and V. Schomaker, *J. Amer. Chem. Soc.*, 1939, **61**, 2922.

[4] M. Letort, and A-J. Richard, *J. Chem. Phys.*, 1960, **57**, 752.

[5] C. W. Heitsch, C. E. Nordman, and R. W. Parry, *Inorg. Chem.*, 1963, **2**, 508.

[6] H. Tani, and H. Yasuda, *J. Polymer Sci., Part B, Polymer Letters*, in the press.