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# The Structure and Reactivity of $[Zn(OMe)_2 \cdot (EtZnOMe)_6]$

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**Synopsis.** The molecular structure of $[Zn(OMe)_2 \cdot (EtZnOMe)_6]$, an enantiomorphic catalyst for the polymerisation of methyloxirane, has been determined.

It has been reported that zinc dialkoxide exhibits an excellent stereoselective behaviour as a catalyst for the polymerisation of methyloxirane. In the systematic studies of organozinc compounds as polymerisation catalysts, a complex, $[Zn(OMe)_2 \cdot (EtZnOMe)_6]$ has been isolated in colourless crystalline form.[1] All the stereochemical results so far obtained led to the conclusion that polymerisation of methyloxirane with a catalyst involving zinc dialkoxide proceeds by an enantiomorphic catalyst site control mechanism,[2] similar to the polymerisation of α-olefin to an isotactic polymer with Ziegler-Natta catalyst.[3] The structure of such catalyst sites, however, has not been studied in detail. Thus, elucidation of the structure of zinc dialkoxide complex, $[Zn(OMe)_2 \cdot (EtZnOMe)_6]$, is of particular interest.

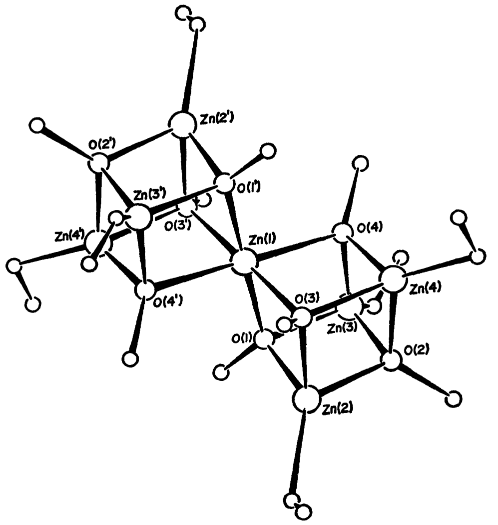
The complex was prepared by addition of 16 mmol of methanol to 14 mmol of diethylzinc in 10 ml of heptane under an argon atmosphere (a typical example). The complex has been formulated as $[Zn(OMe)_2 \cdot (EtZnOMe)_6]$, based on the cryoscopic measurement in benzene as well as analyses by EDTA titration for $Zn^{2+}$, by VPC for $CH_3OH$ and by ethane evolution after hydrolysis. The 100 MHz NMR spectra of the complex in benzene were recorded at 5 to 10 w/v %. The chemical shifts (δ) of $CH_2$ at 0.54 (relative intensity, 2), $CH_3$ at 1.46 (3) and $CH_3O$ at 3.51 (4) were observed at room temperature (23 °C). In contrast, the resonance of $CH_3O$ group was split into a doublet having the intensity ratio of 1 : 3 at 80 °C; 0.53 (2) for $CH_2$, 1.43 (3) for $CH_3$ and 3.56 (1) and 3.58 (3) for $CH_3O$. Coupling constants, $J_{CH_2-CH_3}$, were 8.0 Hz in both cases. There was no sign of dissociation for this complex by an equilibrium involving $ZnEt_2$, $(EtZnOMe)_4$, $[Zn(OMe)_2 \cdot (EtZnOMe)_6]$, *etc.* (*cf.* $Me_6Zn_7(OMe)_8$[4]).

In accord with the line split of methoxy groups, the complex showed catalytic activity for methyloxirane at 80 °C, whereas no catalytic activity was observed at room temperature; methyloxirane/complex=2.1 (mol/mol), methyloxirane/benzene(solvent) $=5.8 \times 10^{-2}$ (v/v), 3 days : methyloxirane converted=97% at 80 °C and 0% at 30 °C, $CH_3O$ group reacted per mol of the complex=0.58 mol at 80 °C and 0 mol at 30 °C. Under the conditions of methyloxirane/complex= 150 (mol/mol) at 80 °C for 4 days, high molecular weight poly(methyloxirane) was obtained in 56% yield.

The molecular structure of $[Zn(OMe)_2 \cdot (EtZnOMe)_6]$ was determined by maens of X-ray diffraction. In spite of very careful sealing in glass-capillary tubes in argon, most of the crystals decomposed after a few days, only one crystal being found useful to some extent for the X-ray analysis.

*Crystal Data*: $C_{20}H_{54}O_8Zn_7$, *M* 880.24, monoclinic, $P2_1/c$, $a=11.276(3)$, $b=15.741(3)$, $c=10.715(2)$ Å, $\beta=106.68(2)°$, $U=1821.9(7)$ Å$^3$, $1.59/D_m/1.63$ g·cm$^{-3}$. (floatation in cyclohexyl iodide and *n*-butyl iodide), $Z=2$, $D_c=1.604$ g·cm$^{-3}$.

The determination of unit-cell dimensions and collection of intensity data were carried out on a Rigaku automated, single crystal diffractometer using Nickel-filtered Cu*K*α radiation. A total of 1884 integrated intensities was measured by θ-2θ scan technique up to $(\sin\theta)/\lambda=0.50$, of which only 942 reflexions were above the background because of rapid decrease of diffraction intensity in high angle region. The structure was solved by the heavy-atom method and refined by the block-diagonal least squares procedure. Applying isotropic temperature factors for non-hydrogen atoms except zinc the *R* index converged to 0.142 for observed reflexions. The temperature factors were relatively large especially for the terminal methyl carbon atoms of ethyl groups.



The molecular structure is shown in the Figure. The centrosymmetric complex consists of two enantiomorphic distorted cubes which share a corner, the center of symmetry. Each distorted cube is similar to that of $(MeZnOMe)_4$; the zinc atoms occupy the corners of a tetrahedron and oxygen atoms the corners of an interpenetrating but smaller tetrahedron. The average bond distances and bond angles are : Zn–O 2.06, O–C 1.48, Zn–C 2.07 Å, O–Zn–O 82.5°, and Zn–O–Zn 97.0°. The largest distortions are observed in the geometry of the central zinc atom, Zn(1), Zn(1)–O(4) (2.18(3) Å) and Zn(1)–O(3) (2.12(3) Å) being longer and O–Zn(1)–O angles (average 80.2°) smaller than the average values of other zinc atoms.

The X-ray results suggest the cleavage of two zinc(1)–oxygen bonds involving Zn(1)–O(4) and/or Zn(1)–O(4') at elevated temperatures. This reasonably explains the results of NMR and reactivity of [Zn-$(OMe)_2 \cdot (EtZnOMe)_6$]. Namely, the zinc dialkoxide part has vacant seats for coordination of methyloxirane under the influence of chiral circumstance at 80 °C, by a process of dissociation of two methoxy groups.

## References

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