The Molecular Structures of Bis-3-methoxypropyl zinc and Bis-4-methoxybutyl zinc, $Zn[(CH_2)_nOCH_3]_2$, $n=3$ and 4, by Gas Electron Diffraction. Intramolecular Oxygen−Zinc Coordination
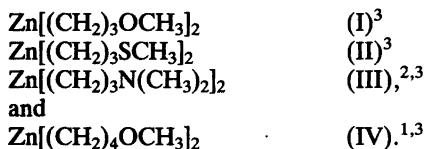
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The gas electron diffraction diagrams of $Zn[(CH_2)_nOCH_3]_2$, $n=3$ and 4, have been recorded with nozzle temperatures of about 80 °C. The chelating nature of the ligands is confirmed, and the Zn−O bond distances found to be 237(3) pm ($n=3$) and 238(5) pm ($n=4$).

Thiele and co-workers[1,2] and Hofstee and his co-workers[3] have synthesized and investigated a series of long chain organozinc compounds with a donor atom in the δ or ε position on the chain:

$Zn[(CH_2)_3OCH_3]_2$	(I)[3]
$Zn[(CH_2)_3SCH_3]_2$	(II)[3]
$Zn[(CH_2)_3N(CH_3)_2]_2$	(III),[2,3]
and	
$Zn[(CH_2)_4OCH_3]_2$	(IV).[1,3]

These compounds are all monomeric in benzene. In contrast to unsubstituted dialkylzinc compounds which can be separated from diethylether or tetrahydrofuran only by repeated fractional distillation,[4] they do not appear to interact with ethers. These observations suggest that the chains are coiled back to allow formation of donor-acceptor bonds between the donor atoms and zinc, as indicated for I and IV in Fig. 1.

Conclusive evidence for intramolecular coordination and the double chelate structure is provided by the ^{13}C NMR spectra, and the results of microwave titration with 2,2'-bipyridine indicate that the strength of the donor-acceptor bond decreases along the series

III > I > II > IV

The relation between III and I reflects the different strength of the interaction between dialkylzinc compounds with tertiary amines and ethers.[5,6] The weakness of the donor acceptor bond in IV is probably due to the strain imposed on a hydrocarbon chain of unfavorable length.

In this article we report the results of investigations of I and IV by means of gas electron diffraction. As far as we know these are the first dialkylzinc-ether complexes to be characterized structurally.

EXPERIMENTAL

Samples of $Zn[(CH_2)_3OCH_3]_2$ (I) and $[Zn(CH_2)_4OCH_3]_2$ (IV) were synthesized and characterized as described in Ref. 3.

The GED patterns were recorded on Balzers Eldigraph KDG-2 with nozzle temperatures of about 80 °C. Both compounds are stable below 100 °C[1]. Exposures were made with nozzle-to-plate distances of about 50 and 25 cm. Five plates from each set were photometered and the scattering data processed by standard procedures. The molecular intensity curves obtained for each nozzle-to-plate distance were averaged, but not connected. The curves extended from $s=25$ to
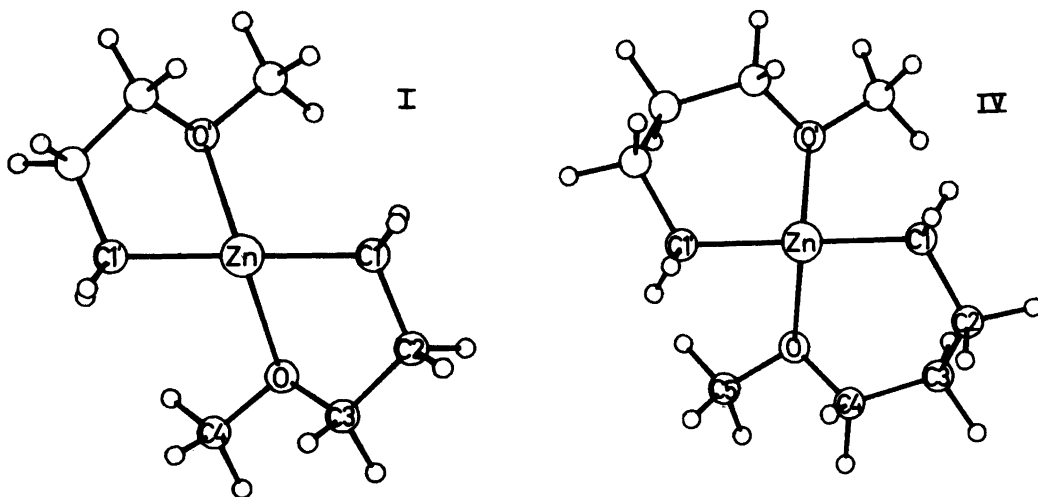
Fig. 1. Molecular models of $\overline{Zn[(CH_2)_3OCH_3]_2}$ (I) and $\overline{Zn[(CH_2)_4OCH_3]_2}$ (IV). Both models have C_2 symmetry with the symmetry axis through Zn and perpendicular to the plane of the paper.

150 nm^{-1} with increment Δs=1.25 nm^{-1} (50 cm) and from s=40 to 285 nm^{-1} with increment Δs=2.50 nm^{-1} (25 cm).

The complex atomic scattering factors, $f'(s)$, were calculated from an analytical representation of the atomic potential,[7] using a program written by Yates.[8] The molecular intensities were modified by multiplication with $s/|f'_c||f'_{zn}|$.

Structure analysis. Structure refinements were based on the C_2 symmetry models shown in Fig. 1. In order to reduce the number of parameters to be refined, we made the following additional assumption for each molecule:

(i) All C−C bonds are equal
(ii) All C−O bonds are equal
(iii) All C−H bonds are equal
(iv) All ∠CCC angles are equal
(v) The OCH$_3$ fragments have C_{3v} symmetry with ∠OCH=110°.
(vi) The ∠HCH valence angles of the methylene groups were fixed at 106°, and the plane defined by the group was assumed to bisect the opposite angle.

After these assumptions have been made, the molecular structure of I is determined by thirteen independent parameters, *e.g.* the C−H, C−O, C−C and Zn−C bond distances, the valence angles ∠CZnC, ∠ZnCC, ∠CCC, ∠CCO and ∠COC, and the torsion angles τ[C(1')ZnC(1)C(2)], τ[ZnC(1)C(2)C(3)], τ[C(1)C(2)C(3)O] and τ[C(2)C(3)OC(4)].

The thirteen structure parameters, five r.m.s.

vibrational amplitudes (*l*) and two scale factors were refined by least-squares calculations on the modified molecular intensity curves under the constraints of a geometrically consistent r_a structure.[9] Those amplitudes that could not be refined were fixed at values that appeared reasonable in comparison with the published amplitudes of diethylzinc and dipropylzinc,[10] normal butane[11] and tetrahydrofurane.[12]

After the assumptions (i) through (vi) have been made, the molecular structure of IV is determined by fourteen independent structure parameters, *e.g.* the four bond distances and five valence angles listed for I plus the five torsion angles τ[C(1')ZnC(1)C(2)], τ[ZnC(1)C(2)C(3)], τ[C(1)C(2)C(3)C(4)], τ[C(2)C(3)C(4)O)] and τ[C(3)C(4)OC(5)]. The fourteen structure parameters, four vibrational amplitudes and two scale factors were refined by least-squares calculations in the same way as for I.

For both molecules we found that refinements with different start values led to stable least-squares minima with very different values for the dihedral angles determining the conformation of the chelate rings. The dihedral angles listed in Table 1 corresponds to the best model for each molecule, but since they are not unique, we do not list the standard deviations.

Fortunately the values obtained for bond distances and valence angles did not differ greatly between the various least-squares minima. The standard deviations listed in Table 1 have been

Table 1. Structure parameters of $\overline{Zn|(CH_2)_3OCH_3|_2}$ (I) and $\overline{Zn|(CH_2)_4OCH_3|_2}$ (IV). Estimated · standard deviations in parenthesis in units of the last digit.

	I	IV
Bond distances/pm		
Zn−C	197.4(4)	198.4(6)
Zn−O	237(3)	238(5)
C−C	152.8(4)	153.0(5)
C−O	142.8(3)	142.6(4)
C−H	110.8(3)	110.9(4)
Valence angles/deg		
∠CZnC	175(20)	158(13)
∠OZnO	111(20)	92(10)
∠OZnC(1)	77(3)	102(3)
∠OZnC(1′)	106(3)	93(7)
∠ZnCC	112(2)	116(2)
∠CCC	113(2)	117(2)
∠CCO	109(4)	116(4)
∠COC	114(6)	112(4)
∠ZnOC(3/4)	97(3)	95(4)
∠ZnOC(4/5)	117(3)	128(10)
Torsion angles [a]/deg		
τ(ZnC(1)C(2)C(3))	−12	−36
τ(C(1)C(2)C(3)C(4))		+57
τ(C(1/2)C(2/3)C(3/4)O)	−35	−88
τ(C(2/3)C(3/4)OZn)	+53	+70
τ(C(3/4)OZnC(1))	−48	−43
τ(OZnC(1)C(2))	+31	+30
τ(C(1′)ZnC(1)C(2))	−95	+104
τ(C(2/3)C(3/4)OC(4/5))	+177	−156
Vibrational amplitudes/pm		
Zn−C	6.0(5)	6.2(6)
Zn−O	16(3)	13(3)
C−C	(5.4)	(5.4)
C−O	(5.2)	(5.2)
C−H	8.1(4)	7.1(6)
Zn···C(2)	(10.0)	(10.0)
Zn···C(3)	20(7)	16(5)
Zn···C(4)		(24)
Zn···(C4/5)	22(10)	(27)

[a] The dihedral angles are not unique. See text.

expanded to include systematic errors and the uncertainty introduced by non-refined parameters.

DISCUSSION

The best values for the structural parameters and their estimated standard deviations are listed in Table 1. The dihedral angles are not unique and are therefore listed without standard deviations.

In agreement with the conclusions reached by Hofstee and co-workers[3] we find that the hydrocarbon chains are coiled back to allow the oxygen to coordinate to the zinc atom. In I the Zn−O bond distance is 237(3) pm and the corresponding
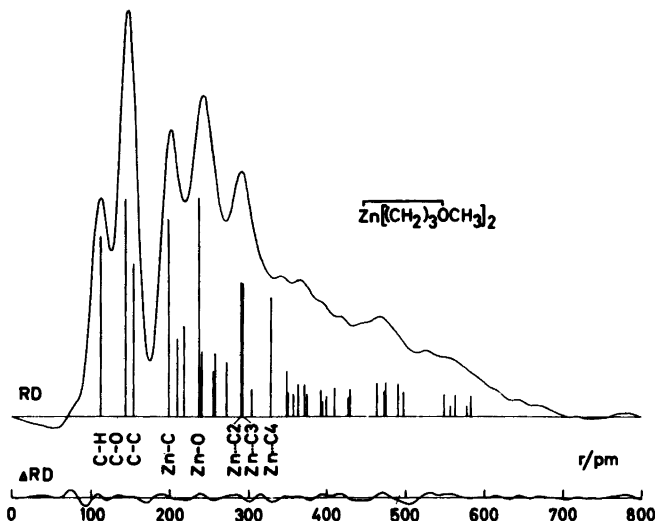
Fig. 2. Above: Experimental radial distribution (RD) curve for I. Artificial damping constant $k=0.2$ pm^2. Major interatomic distances are indicated by bars of height approximately proportional to the area under the corresponding peak. *Below:* Difference between the experimental curve and the theoretical curve calculated for the best model.
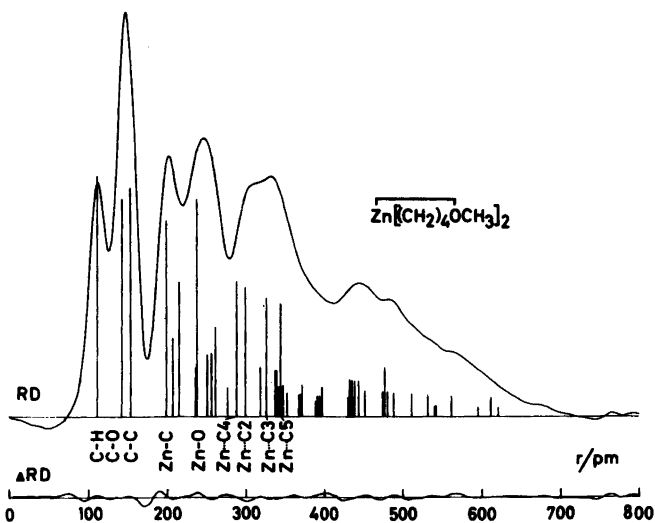

Fig. 3. Experimental RD curve and difference curve for IV. For further comments consult text below Fig. 2.

amplitude $l=16(3)$ pm. In IV the bond distance is 238(5) pm and the amplitude 13(3) pm.

The O→Zn interaction is not sufficiently strong to reduce the ∠CZnC angle to a tetrahedral value, ∠CZnC may in fact be close to 180° in both compounds. While the fivemembered chelate rings in I are fairly flat, the sixmembered chelate rings in IV are strongly buckled and the valence angles ∠ZnCC, ∠CCC and ∠CCO appear to be larger. Unfortunately, because of the large number of structural parameters that had to be refined, the error limits are

too wide to warrant a further discussion of these points.

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