

Fig. 2. Magnetic moment (continuous curve) and inverse of the magnetic susceptibility (broken curve) (both per one Mn atom) for $[\text{Mn}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4\text{O}_{12}] \cdot 2\text{CH}_3\text{COOH} \cdot 4\text{H}_2\text{O}$. [1 BM $\equiv 9.27 \times 10^{-24} \text{ J T}^{-1}$.]

and Cooper (1976) determined the temperature dependence of the magnetic susceptibility of $[\text{Mn}_2(2,2'\text{-bipyridine})_4\text{O}_2](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ and concluded that Mn^{3+} and Mn^{4+} are high spin and antiferromagnetically coupled.

The $\text{Mn}(1) \cdots \text{Mn}(1)$ symmetry-equivalent distances are 2.820 (3) (two) and 2.943 (3) Å. If exchange between all twelve $\text{Mn}(1)$, $\text{Mn}(2)$ and $\text{Mn}(3)$ high-spin atoms is assumed to be *via* O atoms, such a complicated dodecameric unit should have interesting magnetic properties. The magnetic measurements are given in Fig. 2. The magnetic moment increases from $30.9 \times 10^{-24} \text{ J T}^{-1}$ at 3.3 K to a maximum of $56.5 \times 10^{-24} \text{ J T}^{-1}$ in the range of 17–31 K and then decreases to $33.4 \times 10^{-24} \text{ J T}^{-1}$ at 280 K per Mn atom.

Since slow decomposition was sometimes observed at room temperature, to obtain more information about the stability of the compound thermogravimetric

measurements were made. It was found that decomposition started at 308 K. Above 308 K, up to 463 K, it follows the endothermic splitting off of water and acetic acid molecules of solvation. Next, at 468 K it follows the rapid exothermic decomposition of a complex.

The author thanks Mr Truong Xuân Mão (Vietnam) and Mr Edward Haraszkiwicz who participated in the early stage of this research for their MSc degrees.

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Acta Cryst. (1980). **B36**, 2046–2050

Tetrameric Methylzinc Methoxide

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(Received 5 March 1980; accepted 16 April 1980)

Abstract

Methylzinc methoxide is orthorhombic with $a = 7.481$ (15), $b = 7.673$ (15), $c = 29.42$ (5) Å, space

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0567-7408/80/092046-05\$01.00

group $P2_12_12_1$, $Z = 4$ units of $(\text{CH}_3\text{ZnOCH}_3)_4$. Final $R = 0.087$ for 1287 observed reflections. Methylzinc methoxide is tetrameric in the crystal, as was found in solution in benzene. The Zn and O atoms occupy the corners of two regular interpenetrating tetrahedra of different sizes, so that these atoms are four-coordinate and are situated on alternate corners of a distorted © 1980 International Union of Crystallography

cube. The distortion is such that the Zn—O—Zn angles are all $>90^\circ$. The average bond lengths are Zn—O 2.078, Zn—C 1.95, O—C 1.43 Å. The molecular symmetry approximates to $\bar{4}3m$, appreciable deviations from this being found for the C atoms attached to Zn.

Introduction

The reaction between a dialkylzinc compound and a ligand containing active hydrogen results in the evolution of hydrocarbons and the formation of a metal-containing product (Coates, Green & Wade, 1967). If this were monomeric, it would contain a coordinatively unsaturated Zn atom bound to a donor atom with pronounced donor properties. Association takes place: for example, methylzinc methoxide, *tert*-butoxide and phenoxide are tetrameric in benzene solution (Coates & Ridley, 1965), though the methoxide, ethoxide and *tert*-butoxide all form oligomers with more than four monomeric units in the gas phase (Adler, Lachowicz & Thiele, 1976).

Methylzinc methoxide was prepared by the slow addition of methanol to an equimolar quantity of dimethylzinc in hexane at 203 K (Coates & Ridley, 1965). The infrared spectrum of a solution in cyclohexane is virtually identical to that of the solid examined as a Nujol mull and is relatively simple. The proton resonance spectrum of a freshly prepared solution of methylzinc methoxide in benzene at 318 K shows only one methoxy resonance (Allen, Bruce, Farren & Hutchinson, 1966), in agreement with the cubane structure reported in a preliminary account of this work (Shearer & Spencer, 1966). Since this report, a similar cubane structure has been reported for methyl(trimethylsilanolato)beryllium (Mootz, Zinnius & Böttcher, 1969) and a dicubane structure (Ziegler & Weiss, 1970) for $(\text{CH}_3)_6\text{Zn}_7(\text{OCH}_3)_8$, formed by controlled methanolysis of dimethylzinc (Eisenhuth & Van Wazer, 1968).

This paper reports in full the crystal structure of tetrameric methylzinc methoxide.

Experimental

The compound was recrystallized from hexane as needles elongated along *b* with well developed {100} and {001} faces. Crystals were sealed in Pyrex-glass capillary tubes in an atmosphere of dry nitrogen. In spite of these precautions the crystals acquired an opaque appearance which could only have been due to a surface layer of zinc oxide since the quality of the X-ray photographs did not seem affected. The cell dimensions were obtained from zero-level precession photographs.

Crystal data

$(\text{CH}_3\text{ZnOCH}_3)_4$, $M_r = 445.8$, orthorhombic, $P2_12_12_1$, $a = 7.481$ (15), $b = 7.673$ (15), $c = 29.42$ (5) Å, $U = 1688$ Å³, $D_m = 1.75$, $Z = 4$ units of $(\text{CH}_3\text{ZnOCH}_3)_4$, $D_c = 1.75$ Mg m⁻³, $\mu(\text{Cu } K\alpha) = 6.7$ mm⁻¹, $F(000) = 896$.

The layers *h0l-h7l* were recorded photographically by the equi-inclination Weissenberg method with Ni-filtered Cu $K\alpha$ radiation. The intensities were estimated visually and the layers placed on a common scale by comparison with photographs on which timed exposures of different nets had been made.

Lorentz and polarization factors were applied and, for the upper levels, the intensities were corrected for variation in spot length (Phillips, 1956). The dimensions of the crystal used for data collection were 0.26 × 0.90 × 0.19 mm along the three axial directions respectively and corrections for absorption were applied by the method of Busing & Levy (1957).

Structure determination and refinement

The positions of the four Zn atoms in the asymmetric unit were found by inspection of the Patterson function and those of the C and O atoms from an F_o synthesis phased on the heavy atoms. The atomic parameters were refined by least squares, with a block-diagonal approximation. With anisotropic thermal parameters for all the atoms R was 0.098. At this stage, an $F_o - F_c$ synthesis showed small peaks at the sites of the Zn, O and C atoms but no other pronounced features.

Refinement was then applied in which the individual scale factors for the reciprocal-lattice nets *h0l* to *h7l* were also refined. Half the scale factors increased while the remainder decreased. The maximum change in scale factor was 7.7%, the mean change being 4.3%. The treatment had no noticeable effect on the vibration-tensor elements U_{22} .

Finally, in order to obtain more precise information about the molecular symmetry, full-matrix refinement was applied, the layer scales now being held constant. These calculations reduced R to 0.087 for the 1287 observed reflections. Compared with the results from the block-diagonal treatment, the e.s.d.'s increased by about 12–13% but no noticeable change in atomic coordinates was observed. The U_{ii} values for Zn increased by 6–8% while the overall scale factor changed by 2%.

In the final cycle the largest coordinate shift was less than one quarter of its e.s.d., whereas the U_{ii} values of the Zn atoms still showed shifts of one third of their e.s.d.'s. The structure factors were weighted by $w = 1/(p_1 + F_o + p_2 F_o^2)$ with $p_1 = 7.00$ and $p_2 = 0.02$. Unobserved reflections were given zero weight. The scattering factors are those listed in *International*

Table 1. Fractional atomic coordinates ($\times 10^5$ for Zn, $\times 10^4$ for O and C) with their e.s.d.'s in parentheses

	x	y	z
Zn(1)	6533 (46)	-13201 (40)	14028 (10)
Zn(2)	-11073 (43)	20657 (45)	17500 (10)
Zn(3)	7636 (41)	20216 (40)	8147 (9)
Zn(4)	-27923 (43)	408 (45)	9552 (11)
O(1)	-1897 (20)	-437 (22)	1609 (4)
O(2)	1366 (18)	1252 (19)	1483 (4)
O(3)	-1733 (20)	2517 (22)	1068 (4)
O(4)	-237 (18)	-507 (22)	761 (4)
C(1)	1854 (44)	-3553 (43)	1515 (11)
C(2)	-1880 (52)	3387 (39)	2275 (8)
C(3)	2120 (35)	3369 (36)	381 (8)
C(4)	-5029 (33)	-884 (42)	708 (7)
C(5)	-2893 (34)	-1482 (40)	1916 (8)
C(6)	2943 (30)	1763 (43)	1705 (9)
C(7)	-2770 (54)	4093 (40)	944 (9)
C(8)	146 (45)	-1533 (37)	367 (9)

Table 2. Interatomic distances (Å)

Zn(1)—Zn(2)	3.087 (5)	O(1)—C(5)	1.419 (30)
Zn(1)—Zn(3)	3.094 (4)	O(2)—C(6)	1.403 (28)
Zn(2)—Zn(3)	3.087 (4)	O(3)—C(7)	1.483 (37)
Zn(2)—Zn(4)	3.077 (5)	O(4)—C(8)	1.430 (31)
Zn(3)—Zn(4)	3.092 (5)	Zn(1)—O(1)	2.114 (15)
Zn(4)—Zn(1)	3.077 (5)	Zn(1)—O(2)	2.058 (15)
O(1)—O(2)	2.789 (20)	Zn(1)—O(4)	2.096 (13)
O(1)—O(3)	2.771 (22)	Zn(2)—O(1)	2.052 (17)
O(2)—O(3)	2.794 (20)	Zn(2)—O(2)	2.105 (14)
O(2)—O(4)	2.787 (19)	Zn(2)—O(3)	2.088 (13)
O(3)—O(4)	2.729 (23)	Zn(3)—O(2)	2.102 (13)
O(4)—O(1)	2.786 (18)	Zn(3)—O(3)	2.047 (15)
Zn(1)—C(1)	1.962 (33)	Zn(3)—O(4)	2.086 (16)
Zn(2)—C(2)	1.934 (27)	Zn(4)—O(1)	2.069 (13)
Zn(3)—C(3)	1.931 (25)	Zn(4)—O(3)	2.085 (17)
Zn(4)—C(4)	1.957 (26)	Zn(4)—O(4)	2.039 (14)

Tables for X-ray Crystallography (1962). The real part of the anomalous-dispersion correction was applied for Zn.

The final atomic parameters are given in Table 1.*

Description

The molecular arrangement is shown in Fig. 1, some interatomic distances in Table 2 and bond angles in Table 3. The Zn atoms lie at the corners of a tetrahedron and the O atoms at the corners of an interpenetrating but smaller tetrahedron. Thus, the Zn and O atoms are four-coordinate and are situated on alternate corners of a distorted cube. The arrangement is similar to that proposed for tetrameric thallium methoxide (Dahl, Davis, Wampler & West, 1962). The

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35341 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

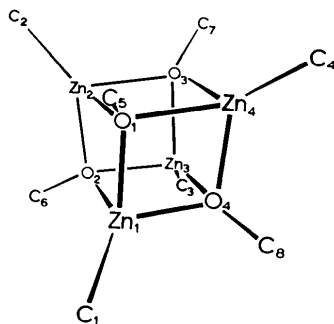


Fig. 1. Molecular structure of $(\text{CH}_3\text{ZnOCH}_3)_4$ showing atom numbering.

Table 3. Bond angles ($^\circ$)

Zn(1)—O(1)—Zn(2)	95.6 (6)	O(1)—Zn(1)—C(1)	130.1 (11)
Zn(1)—O(1)—Zn(4)	94.7 (5)	O(2)—Zn(1)—C(1)	134.4 (10)
Zn(2)—O(1)—Zn(4)	96.6 (7)	O(4)—Zn(1)—C(1)	123.8 (10)
Zn(1)—O(2)—Zn(2)	95.7 (6)	O(1)—Zn(2)—C(2)	124.5 (10)
Zn(1)—O(2)—Zn(3)	96.1 (5)	O(2)—Zn(2)—C(2)	135.7 (12)
Zn(2)—O(2)—Zn(3)	94.4 (6)	O(3)—Zn(2)—C(2)	127.7 (10)
Zn(2)—O(3)—Zn(3)	96.6 (6)	O(2)—Zn(3)—C(3)	131.0 (8)
Zn(2)—O(3)—Zn(4)	95.0 (7)	O(3)—Zn(3)—C(3)	128.4 (9)
Zn(3)—O(3)—Zn(4)	96.9 (7)	O(4)—Zn(3)—C(3)	129.6 (9)
Zn(3)—O(4)—Zn(4)	97.1 (7)	O(1)—Zn(4)—C(4)	123.9 (8)
Zn(3)—O(4)—Zn(1)	95.5 (6)	O(3)—Zn(4)—C(4)	135.6 (10)
Zn(4)—O(1)—Zn(1)	96.2 (5)	O(4)—Zn(4)—C(4)	128.5 (9)
O(1)—Zn(1)—O(2)	83.9 (6)	Zn(1)—O(1)—C(5)	118.4 (15)
O(1)—Zn(1)—O(4)	82.9 (5)	Zn(2)—O(1)—C(5)	123.5 (14)
O(2)—Zn(1)—O(4)	84.3 (6)	Zn(4)—O(1)—C(5)	121.5 (13)
O(1)—Zn(2)—O(2)	84.3 (6)	Zn(1)—O(2)—C(6)	122.6 (16)
O(1)—Zn(2)—O(3)	84.1 (6)	Zn(2)—O(2)—C(6)	118.9 (13)
O(2)—Zn(2)—O(3)	83.6 (5)	Zn(3)—O(2)—C(6)	122.4 (14)
O(2)—Zn(3)—O(3)	84.7 (5)	Zn(2)—O(3)—C(7)	119.4 (13)
O(2)—Zn(3)—O(4)	83.5 (5)	Zn(3)—O(3)—C(7)	122.6 (16)
O(3)—Zn(3)—O(4)	82.7 (6)	Zn(4)—O(3)—C(7)	120.3 (16)
O(3)—Zn(4)—O(4)	82.9 (6)	Zn(1)—O(4)—C(8)	120.1 (15)
O(3)—Zn(4)—O(1)	83.7 (6)	Zn(3)—O(4)—C(8)	120.1 (14)
O(4)—Zn(4)—O(1)	85.4 (5)	Zn(4)—O(4)—C(8)	121.9 (16)

distortion can be described in terms of an inward movement of the O atoms along the threefold axes of the cube, resulting in Zn—O—Zn angles $>90^\circ$. The largest deviations from the tetrahedral value are found for the angles at Zn.

The Zn...Zn distances range from 3.077 to 3.094, mean 3.086 Å. None of the individual distances differs significantly from this mean. The O...O distances are all equal within experimental error and have a mean of 2.776 Å. The interpenetrating tetrahedra of Zn and O atoms are thus regular, within the limits of experimental error.

The twelve Zn—O bonds have lengths varying from 2.039 to 2.114 Å. None of the individual values differs from the mean of 2.078 Å at the 0.1% probability level and only one at the 1% probability level so that these differences do not appear to be significant. In phenylaluminium anilide (MacDonald & MacDonald, 1963), which also possesses the cubane-type arrangement, the corresponding bonds were found to be of equal length and indeed many were required to be so by the space-group symmetry.

The Zn—O distances are greater than the 1.97 Å obtained from the sum of the tetrahedral covalent radii and the 1.98 Å observed in zinc oxyacetate (Koyama & Saito, 1954) where Zn has a tetrahedral environment. In methylzinc methoxide, the Zn and O atoms have three valence angles near 90° so that the atomic orbitals used in forming bonds to O will have increased *p* character. There is indeed better agreement with Zn—O distances in complexes where Zn is octahedrally coordinated, namely with the 2.04 Å in biuret zinc chloride (Nardelli, Fava & Giraldi, 1963) and the 2.05 Å in zinc 8-quinolinolate (Merritt, Cady & Mundy, 1954).

The Zn—C distances are equal within experimental error and have a mean of 1.95 Å. This is less than the sum (2.08 Å) of the covalent radii (Pauling, 1960) but agrees closely with the 1.94 Å in dimethylzinc (Rundle, 1963), where the shortening was explained by invoking hyperconjugation involving unoccupied 4*p* orbitals on Zn. Similarly, the O—C distances may be regarded as the same with a mean of 1.43 Å. This is in good agreement with the 1.427 Å in methanol (Venkateswarlu & Gordy, 1955) in spite of the change in coordination number of oxygen.

The twelve Zn—O—Zn angles average 95.9° and the O—Zn—O angles 83.8°. One of the O—Zn—O angles differs from its mean at the 1% probability level but the Zn—O—C angles are the same within experimental error with a mean of 121.0°. However, the O—Zn—C angles vary between 123.8 and 135.7°. The three such angles associated with each Zn atom show a tendency for one to fall at the lower end of this range, one at the upper end and one with an intermediate value.

The variation in the O—Zn—C angles can be related to some extent to the short intermolecular contacts. The positions of the C atoms involved in these angles appear to be displaced so as to alleviate the strain arising from short non-bonding contacts. Fig. 2 shows the packing of the tetramers viewed in projection along *a* and the non-bonding intermolecular contacts <4 Å are shown in Table 4.

The distance of 3.86 Å between C(2) and C(1¹) is the only short contact involving C(2). Displacement of C(2) in a direction away from C(1) makes O(2)—Zn(2)—C(2) the largest of the three angles at Zn(2). Similarly, the short contacts involving C(1) and C(4) are consistent with the observed order of the angles at

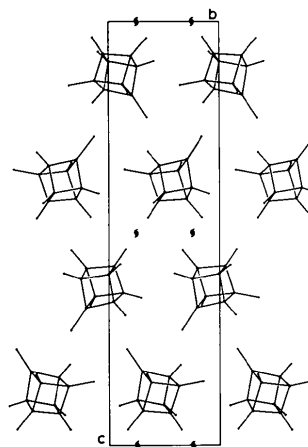


Fig. 2. Packing of the molecules in the (100) projection.

Table 4. Non-bonding intermolecular contacts <4 Å

E.s.d.'s 0.02–0.03 Å.

Symmetry code

None	<i>x</i> , <i>y</i> , <i>z</i>	(iv)	$\frac{1}{2} + x$, $\frac{1}{2} - y$, $-z$
(i)	$-x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$	(v)	$-1 + x$, <i>y</i> , <i>z</i>
(ii)	$1 + x$, <i>y</i> , <i>z</i>	(vi)	$-\frac{1}{2} + x$, $-\frac{1}{2} - y$, $-z$
(iii)	<i>x</i> , $1 - y$, <i>z</i>		
C(1)—C(4 ⁱⁱ)	3.91	C(4)—O(2 ^v)	3.89
C(1)—C(6 ⁱⁱⁱ)	3.73	C(4)—O(4 ^v)	3.91
C(2)—C(1 ⁱ)	3.86	C(4)—C(6 ^v)	3.88
C(3)—C(8 ^{vi})	3.98	C(4)—C(8 ^v)	3.78
C(4)—Zn(1 ^v)	3.84	C(4)—C(8 ^{vi})	3.74
C(4)—Zn(3 ^v)	3.87		

Zn(1) and Zn(4). C(3) is involved in only one contact <4 Å and that at a distance of 3.98 Å. Consistently, the range of angles at Zn(3) is only 3.5° whereas it is >10° at the other three Zn atoms. All the non-bonding intramolecular distances between peripheral C atoms are >3.9 Å and with two exceptions are all >4 Å.

Molecular symmetry

The molecular symmetry approximates to 43*m*. The directions of the molecular axes were calculated from the coordinates of the Zn and O atoms, with averaged weights for each type of atom, derived from the coordinate e.s.d.'s. The atomic coordinates referred to these axes and to the molecular centre at -0.06209 , 0.07022 , 0.12307 (in fractional coordinates) are given in Table 5.

For the Zn, O and methoxy C atoms C(5) to C(8), the values agree closely amongst themselves. The mean Zn parameter is 1.091 Å and the average deviation from this mean is 0.002 Å. For the O atoms, the

Table 5. Direction cosines of the molecular axes and atomic coordinates referred to these axes (Å)

	0.91145	-0.24905	-0.32743
	0.30868	0.94018	0.14414
	0.27355	-0.22758	0.93455
Zn(1)	1.089	-1.092	1.087
Zn(2)	-1.093	1.092	1.090
Zn(3)	1.093	1.095	-1.091
Zn(4)	-1.089	-1.095	-1.086
O(1)	-1.017	-0.956	0.978
O(2)	1.007	0.963	1.005
O(3)	-0.949	0.983	-0.991
O(4)	0.945	-0.983	-1.001
C(1)	2.226	-2.378	2.031
C(2)	-2.377	2.089	2.143
C(3)	2.178	2.196	-2.242
C(4)	-2.200	-2.383	-2.062
C(5)	-1.792	-1.180	1.801
C(6)	1.770	1.789	1.847
C(7)	-1.837	1.828	-1.822
C(8)	1.782	-1.802	-1.827

corresponding values are 0.981 and 0.020 Å and for the methoxy C atoms 1.809 and 0.020 Å respectively. For these twelve atoms, only one parameter, belonging to O(4), differs from its mean value at the 1% probability level, so that these atoms appear to conform to the requirements of $\bar{4}3m$ symmetry. C(1) to C(4) attached to Zn show much greater differences. Their mean coordinate is 2.209 Å; the average deviation from this mean is 0.094 Å and four of the individual differences exceed 0.15 Å.

Similar information about the symmetry is provided by other tests. The Zn...Zn distances will be distributed like χ^2 and a value of 12.0 is obtained for this quantity when the distances are all taken as independent. With five degrees of freedom, the proposition that these are all equal is acceptable at the 1% probability level. For the O...O distances, χ^2 is 6.3 and these may be taken as the same at the 5% probability level.

For the Zn-O lengths, again taking these as independent, χ^2 has a value of 32.3 which, with eleven degrees of freedom, is not acceptable at the 1% probability level. On the other hand, the use of the 24 coordinates of the Zn and O atoms, transformed with respect to the molecular axes and shown in Table 5, results in a value of χ^2 of 39.6. These coordinates may be taken as related by the elements of symmetry $\bar{4}3m$ at the 1% probability level. In view of all these circumstances, it does not seem possible to maintain

that the coordinates of the Zn, the O and also the C atoms attached to the O atoms depart significantly from the requirements of this symmetry.

Thus, the only large deviations occur for the C atoms bound to Zn. These atoms are the furthest from the molecular centre and are exposed to the intermolecular forces on the periphery of the molecule, leading to the variation in the O-Zn-C angles already discussed.

The authors thank Dr D. Ridley for preparing the compound, Professor D. W. J. Cruickshank, Dr J. Sime and their colleagues for the use of programs and Professor G. E. Coates for his interest throughout the work. CBS thanks Drs N. A. Bell and I. W. Nowell for helpful discussions.

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