The Crystal Structure of Tetrameric Methylzinc Methoxide

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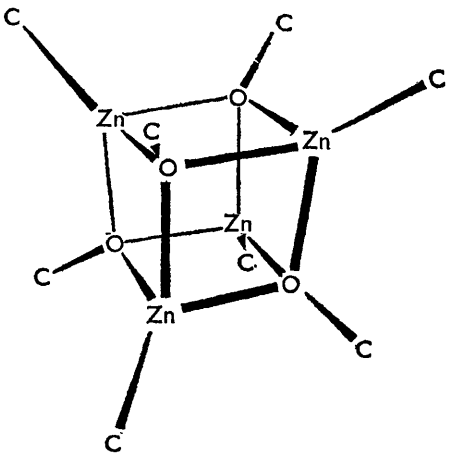
METHYLZINC METHOXIDE is prepared by the slow addition of methanol to dimethylzinc in hexane at −70°, one mole of methane being evolved. Cryoscopic measurements in benzene have shown that the molecule is tetrameric.[1] The infrared spectrum of a solution in cyclohexane is the same as that of the solid examined as a Nujol mull.

An *X*-ray examination has shown that methylzinc methoxide crystallises in an orthorhombic cell with $a = 7{\cdot}48$, $b = 7{\cdot}67$, $c = 29{\cdot}41$Å, space group $P2_12_12_1$. The unit cell contains four units of $(CH_3ZnOCH_3)_4$. Three-dimensional intensity data were recorded using equi-inclination Weissenberg techniques and were estimated visually. The structure was determined by the heavy-atom method and is being refined by least-squares techniques. At the present stage of refinement, using anisotropic temperature parameters, the reliability index R for the 1269 independent reflections is 0·12.

The structure is as shown in the Figure. The zinc atoms occupy the corners of a regular tetrahedron and the oxygen atoms the corners of an interpenetrating but smaller tetrahedron. Thus, four-co-ordinate zinc and oxygen atoms occupy alternate corners of a distorted cube and the molecular symmetry approximates to $\bar{4}3m$. The arrangement is similar to that proposed[2] for $(TlOCH_3)_4$. The distortion can be described in terms of an inward movement of the oxygens along the threefold axes of the cube and results in the Zn–O–Zn angles being greater than 90°. As expected, the deviation of the angles at zinc from the tetrahedral are greater than those at oxygen. At the present stage of refinement the mean lengths and angles are: Zn–C 1·94, Zn–O 2·09, O–C 1·44Å, Zn–O–Zn 96°, O–Zn–O 83°. The shortest contact between peripheral methyl carbons is almost 4Å.



A similar cubane-type structure has recently been assumed[3] for $[CH_3CdOSi(CH_3)_3]_4$, the report of which prompts this Communication.

(*Received, February 18th*, 1966; *Com.* 099.)

[1] G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1965, 1870.
[2] L. F. Dahl, G. L. Davis, D. L. Wampler, and R. West, *J. Inorg. Nuclear Chem.*, 1962, **24**, 357.
[3] F. Schindler, H. Schmidbaur, and U. Krüger, *Angew. Chem. Internat. Edn.*, 1965, **4**, 876.