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The Crystal and Molecular Structure of Octameric Methylzinc Isopropylsulphide

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Summary In the crystal of dimethylzinc isopropylsulphide, the molecules are octamers with each zinc bonded to three sulphur atoms and one carbon atom, and each sulphur to three zinc atoms and one carbon atom.

THE determination of the crystal structure of octameric methylzinc isopropylsulphide shows that the molecules possess an unusual polyhedral arrangement of eight zinc and eight sulphur atoms. The compound belongs to the large group of substances formed by the reaction of a dialkylzinc or dialkylcadmium compound with donor molecules containing an active hydrogen atom. It is prepared by the reaction of dimethylzinc with an equimolar quantity of propane-2-thiol. Molecular-weight measurements indicated that the compound is hexameric in benzene solution.¹

An X-ray examination has shown that the sulphide crystallises in a tetragonal cell with $a = b = 13.61$, $c = 15.16$ Å, $Z = 2$ units of $(\text{CH}_3\text{ZnSC}_3\text{H}_7)_8$ and space group $P4_2/nmm$. The crystals are air-sensitive and deteriorate rapidly on exposure to X-radiation, so that three crystals were employed for data collection. The nets $0kl-6kl$ were recorded photographically by the equi-inclination Weissenberg technique and the intensities estimated visually. On well-exposed photographs, the very strong reflections appeared diffuse and in one or two cases such reflections seemed to be linked by very weak diffuse streaks.

The Patterson function could be interpreted on the basis that the unit cell contained twice the expected number of zinc and sulphur atoms, each with a statistical weight of one-half, and that zinc and sulphur atoms were situated at virtually identical sites. A difference map then revealed a similar increase in the number of carbon atoms. The positional and anisotropic thermal parameters of these atoms were refined using the full-matrix least-squares

method. There were no indications of any differences in the co-ordinates of the zinc and sulphur atoms and so averaged scattering factors were used for these atoms. The present value of R is 0.11 for the 606 independent observed reflections.

Despite these features, only one molecular arrangement is possible, if it is assumed that the molecule contains no Zn-Zn bonds and that no interchange of organic groups has taken place between the zinc and sulphur atoms. These assumptions are consistent with the properties of this compound. A perspective drawing of the central portion of the molecule, viewed down the c axis, is shown in the Figure together with the independent bond distances (in Å).

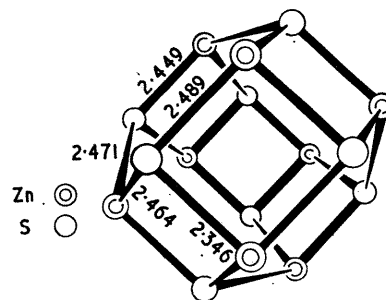


FIGURE. The polyhedral arrangement of zinc and sulphur atoms.

In the crystal, the molecules are octamers with each zinc atom bonded to three sulphur atoms and to one carbon atom and each sulphur to three zinc and one carbon atom. The e.s.d.s in the lengths of the Zn-S bonds are *ca* 0.005 Å, if no allowance is made for the additional uncertainty in position arising from the superposition of atoms. Some of the Zn-S bonds seem appreciably longer than in zinc sulphide (2.35 Å) but all lie within the range found in methylzinc *t*-butylsulphide.²

The molecule described above has $\bar{4}$ symmetry whereas the site symmetry in the crystal is $\bar{4}2m$. If the higher site symmetry arises from twinning and the true space group is $P\bar{4}n2$ then a satisfactory account has to be devised for the systematic absences amongst the $hk0$ reflections. An explanation in terms of disorder seems in better agreement with the experimental observations.

The zinc and sulphur atoms lie near the corners of a truncated bisphenoid giving rise to four-, six-, and eight-membered rings. This is in contrast to the structure of

pentameric methylzinc t-butylsulphide which is based on a distorted square-based pyramid of zinc atoms and contains only four- and six-membered rings. The octameric isopropylsulphide arrangement can however be related to the cubane-type structure found in tetrameric methylzinc methoxide³ since the upper and lower parts of the polyhedra can each be obtained by opening out the cubane arrangement.

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- ¹ G. E. Coates and D. Ridley, *J. Chem. Soc.*, 1965, 1870; *J. Chem. Soc. (A)*, 1966, 1064. G. E. Coates and A. Lauder, *ibid.*, p. 264.
² G. W. Adamson, H. M. M. Shearer and C. B. Spencer, *Acta Cryst., Suppl.*, 1966, **21**, A135.
³ H. M. M. Shearer and C. B. Spencer, *Chem. Comm.*, 1966, 194.