Alkylzinc Compounds. Part I. Crystal Structure of Ethylzinc Iodide

By **P. T. Moseley** and **H. M. M. Shearer**,* Department of Chemistry, Durham University, South Road, Durham

The title compound crystallises in an orthorhombic cell with $a = 21{\cdot}17$, $b = 4{\cdot}33$, $c = 5{\cdot}38$ Å, $Z = 4$, space group *Pnma*. The structure was solved from photographic data by the heavy-atom method and refined by the method of least-squares to R 0·11 for the 335 observed reflections. The four units of EtZnI in the unit cell lie on the mirror planes at $y = 0{\cdot}25$ and 0·75. In the co-ordination polymer, each zinc atom is 2·64 Å from an iodine on the same mirror plane and 2·91 Å from iodines on mirror planes half-a-cell translation above and below. Zn–C is 1·95 Å and I–Zn–C, the angle formed by atoms on the same mirror plane, is 144·4°.

Molecular-weight measurements have indicated that monomeric ethylzinc iodide species are present in solution in ethyl iodide.

ETHYLZINC iodide was first prepared[1] over a hundred years ago. Subsequently there has been considerable interest in the nature of the alkylzinc halides and in compounds of the type RMX (M = Group II element, X = Cl, Br, or I).

At one time it was claimed[2] that, apart from the compounds of mercury, the Group II organometal halides exist as R_2M,MX_2 complexes rather than as RMX. Since then molecular-weight[3] and crystallographic[4] studies have shown the existence of monomeric solvated alkylmagnesium halides. More significant perhaps has been the demonstration of the centrosymmetric structure[5] of the dimeric triethylamine adduct of ethylmagnesium bromide, $[EtMgBr(NEt_3)]_2$. There is also evidence for the existence of solvated monomeric alkylzinc halides[6] and it has been suggested that the tetrameric unsolvated ethylzinc chloride and bromide[7] have cubane-type structures similar to that found[8] in tetrameric methylzinc methoxide. Significantly, differences were found in the properties, *e.g.* solubility in hydrocarbons, of ethylzinc chloride and bromide on the one hand and ethylzinc iodide on the other. These results are consistent with the crystal structure of the iodide now reported.

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EXPERIMENTAL

Crystals of ethylzinc iodide were obtained from solution in ethyl iodide as reported in ref. 9. Suitable specimens were sealed into thin-walled capillary tubes in an atmosphere of dry nitrogen. Repeated attempts were made to obtain a well-formed single crystal but the best specimen still gave rise to two separate diffraction patterns indicating that it consisted of two sections, aligned along the [100] direction, *i.e.* perpendicular to the plane of the plate. It was possible to proceed with this since the diffraction pattern from one portion of the crystal had intensities much greater than the other.

Crystal Data.—C_2H_5IZn, $M = 221{\cdot}3$, Orthorhombic, $a = 21{\cdot}17(5)$, $b = 4{\cdot}33(3)$, $c = 5{\cdot}38(3)$ Å, $U = 493{\cdot}2$ Å^3, $D_m = 2{\cdot}3$—$3{\cdot}1$, $Z = 4$, $D_c = 2{\cdot}98$. Space group $Pnma$ (D_{2h}^{16}) or $Pn2_1a$ (C_{2v}^{9}), from systematic absences; the former centrosymmetric alternative being chosen on the basis of structure analysis. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) $= 112{\cdot}5$ cm^{-1}.

The nets $h0$—$3l$ were recorded by the equi-inclination Weissenberg method with Zn-filtered Mo radiation, the films being interleaved with sheets of 0·0008 in nickel foil. Intensities were estimated visually by comparison with a scale and the different nets placed on a common scale by use of photographs of which timed exposures of several nets had been made. In certain cases overlapping occurred between the desired diffraction pattern and that from the second portion of the crystal. These reflections, which had small values of h, were excluded from the calculations. The usual Lorentz and polarisation factors were applied and in the case of the upper-level reflections the intensities were also corrected for variation in spot-length. Corrections for absorption were not applied.

Structure Determination and Refinement.—The iodine and zinc atoms were located by examination of the Patterson function and the carbon atom positions were obtained by Fourier methods. These atoms lie on the mirror planes at $y = 0{\cdot}25$ and $0{\cdot}75$ in accordance with the requirements of sub-set $4c$ of the space group $Pnma$. Atomic parameters were refined by the method of least squares using the full-matrix of the normal equations and in the later stages anisotropic temperature factors were employed. Only the overall scale factor was refined, since an attempt to refine individual scale factors for each net, in this way, would be expected to lead to a singular matrix. For the 335 observed reflections the final R was 0·11.

In the final cycle, the parameter shifts were all $<0{\cdot}3\sigma$. The weighting was given by: $\sqrt{w} = \left\{1 - e^{-p_1\left(\frac{\sin\theta}{\lambda}\right)^2}\right\}^{\frac{1}{2}} \Big/ \{1 + p_2|F_o| + p_3|F_o|^2\}^{\frac{1}{2}}$, with $p_1 = 10$, $p_2 = 0{\cdot}1$, and $p_3 = 0{\cdot}00222$. The unobserved reflections were given zero weight in the refinement. The scattering factors were those given in ref. 10, the real parts of the dispersion correction being applied in the cases of iodine and zinc.

The final positional and thermal parameters are given in Table 1. The physically meaningless value of the tensor component U_{11} for C(1) and the very small value for C(2) are thought to arise from imperfections in the intensity data, particularly the lack of correction for the considerable absorption effects. However, the order of the magnitudes of the U_{ii} terms for these atoms seems reasonable and the use of anisotropic rather than isotropic thermal parameters permits a more satisfactory description of the bond distances. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20536 (2 pp., 1 microfiche).*

TABLE 1

Final positional parameters (fractional) and thermal vibration tensor components, U_{ij} (Å^2), with standard deviations in parentheses

Atom	x	y	z
I	0·19522(12)	0·25	0·04920(53)
Zn	0·31473(25)	0·25	0·18947(131)
C(1)	0·4020(16)	0·25	0·0710(109)
C(2)	0·4477(15)	0·25	0·2663(151)

Atom	10^4U_{11}	10^4U_{22}	10^4U_{33}	10^4U_{23}	10^4U_{31}	10^4U_{12}
I	408(15)	341(28)	190(13)	0	−5(11)	0
Zn	391(27)	383(49)	477(36)	0	15(21)	0
	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{23}	10^3U_{31}	10^3U_{12}
C(1)	−5(12)	215(79)	50(29)	0	19(17)	0
C(2)	0(14)	328(159)	79(51)	0	8(20)	0

RESULTS

Description.—A perspective view of part of the ethylzinc iodide co-ordination polymer is shown in Figure 1 and the bond distances and angles are given in Table 2. The iodine atom is at a distance of 2·64 Å from the zinc atom lying on the same mirror plane at $y = 0{\cdot}25$ and at distances of 2·91 Å

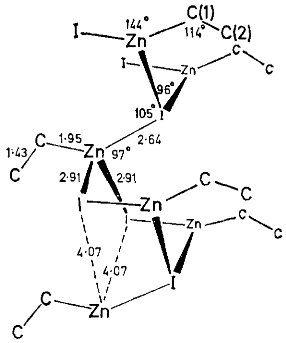

FIGURE 1 Part of the ethylzinc iodide co-ordination polymer

TABLE 2

(*a*) Bond lengths (Å) and their standard deviations

Zn–I	2·640(6)	Zn–C(1)	1·95(4)
Zn–I$^{\text{I}}$	2·911(6)	C(1)–C(2)	1·43(8)

(*b*) Bond angles (°) and their standard deviations

I–Zn–C(1)	144·4(1·7)	Zn$^{\text{II}}$–I–Zn$^{\text{III}}$	96·1(8)
Zn–C(1)–C(2)	113·6(4·1)	I–Zn–I$^{\text{I}}$	96·9(8)
Zn–I–Zn$^{\text{II}}$	105·0(8)	C(1)–Zn–I$^{\text{I}}$	106·6(1·7)

(*c*) Non-bonding contacts (Å) $<4{\cdot}33$ Å

I · · · I$^{\text{I}}$	4·16	I · · · C(2$^{\text{II}}$)	4·02
I · · · Zn$^{\text{I}}$	4·07	C(1) · · · C(2$^{\text{IV}}$)	4·26
I · · · C(1$^{\text{I}}$)	4·10	C(2) · · · C(2$^{\text{IV}}$)	4·22
I · · · C(1$^{\text{II}}$)	3·94	C(2) · · · C(2$^{\text{V}}$)	3·99

Superscripts in Roman numerals refer to the following positions relative to the reference molecule at x, y, z:

I	$\frac{1}{2} - x, -y, \frac{1}{2} + z$	IV	$1 - x, -y, -z$
II	$\frac{1}{2} - x, -y, -\frac{1}{2} + z$	V	$1 - x, -y, 1 - z$
III	$\frac{1}{2} - x, 1 - y, -\frac{1}{2} + z$		

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970 Issue No. 20 (items less than 10 pp. are sent as full size copies).

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from two other zinc atoms on adjacent mirror planes at $y = 0{\cdot}75$ and $-0{\cdot}25$. The sum of the tetrahedral covalent radii [11] is 2·59 Å and a length of 2·62 Å is found in zinc iodide [12] itself, in good agreement with the shorter Zn–I distance in ethylzinc iodide.

Thus the iodine atom forms two long and one more normal bond to zinc and has a nearly pyramidal environment, the bond angles at iodine of 105, 105, and 96° all being less than the tetrahedral value. On the other hand, the angles at zinc are distorted considerably from the tetrahedral. The I–Zn–C(1) angle of 144·4° may be regarded as arising from a situation intermediate between a polymer and discrete monomer units and the structure may be compared with that of mercury(II) cyanide [13] where almost linear $Hg(CN)_2$ units are linked by long Hg–N bonds.

The Zn–C(1) distance (1·95 Å) is less than the sum (2·08 Å) of the covalent radii but agrees closely with values in dimethylzinc (1·94 Å) [14] and tetrameric methylzinc methoxide (1·95 Å),[8] despite the differing co-ordination numbers at zinc. The C(1)–C(2) bond length [1·43(8) Å] does not differ significantly from the value found in diamond. The thermal tensor vibration components, U_{22}, of the carbon atoms, which lie in directions normal to the C–C bond, are very large and correction for the effect of the atomic librations would increase the length of this bond.

The non-bonding contacts, smaller than the shortest unit cell translation are also shown in Table 2. The closest distance of approach between carbon atoms in different layers is 3·99 Å so that neighbouring layers pack easily. Figure 2 shows the packing between layers in the projection along *b*.

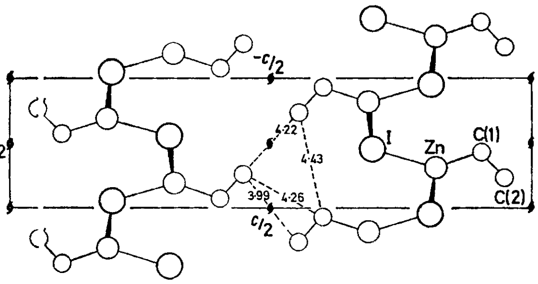

FIGURE 2 Arrangement of the molecules in the projection along *b*

DISCUSSION

Polymerisation in unsolvated alkyl Group IIB metal halides arises from the tendency of the metal to expand its covalency by co-ordination with more electronegative atoms. Entropy considerations of course favour the smallest degree of association but discrete monomeric units have only been found so far in compounds of mercury. Methylmercury chloride and bromide [15] in the vapour and both methylmercury chloride and ethylmercury bromide [16] in the solid state are monomeric with linear co-ordination at the metal. The same situation has also been found [17] in methylmercury cyanide.

Association in alkylzinc halides would be expected to be more pronounced than in compounds of the heavier metals. As mentioned earlier, ethylzinc chloride and bromide are tetrameric in benzene solution and a cubane-type structure has been suggested for them.

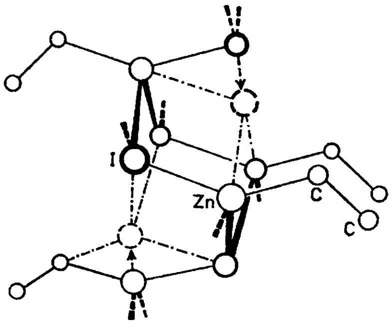

FIGURE 3 The relationship between the polymeric structure and the theoretical cubane-type arrangement

The cubane-type tetramer is the smallest reasonable structural unit which permits the zinc atom to be four-co-ordinate. The relationship between the polymer and the theoretical tetrameric alternative is shown in Figure 3, where it will be seen that, in a representative fragment of the polymer, only two atoms would be required to form two bonds each in an opposite direction in order to obtain the pseudo-cubane structure. However there are limitations in this form arising from the presence of four-membered rings. In related dimeric compounds, the main factor in determining the ring geometry appears [18] to be the halogen–halogen repulsions across the ring and increase in size of these atoms, along the series fluorine, chlorine, and bromine, leads to progressively smaller ring angles at the halogen. The polymeric structure of ethylzinc iodide may be related to the lower electronegativity of the halogen but the arrangement with quasi-monomeric units loosely linked by long bonds gives rise to six-membered zinc–iodine rings, with the ring angles all greater than 90°, so reducing the zinc–zinc and iodine–iodine repulsions across the rings.

Molecular Weight in Solution.—The establishment of the polymeric crystal structure of ethylzinc iodide led to an interest in the nature of the dissolved species. Molecular-weight measurements were therefore carried out on solutions of ethylzinc iodide in ethyl iodide by the Signer method of isothermal distillation [19] by use of an apparatus similar to that described in ref. 20.

Two bulbs, each with an attached pipette, contained solutions in ethyl iodide of ethylzinc iodide and of a

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standard (triphenylmethane) respectively. The mass of solute in each bulb was known and the solutions shared a common atmosphere of ethyl iodide. Solute distilled from the solution of lower molarity to the more concentrated one until equilibrium was reached. Measurements of the volumes of the two solutions (by transferring each to its attached pipette) showed that monomeric solvated ethylzinc iodide species were present in the ethyl iodide solution.

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