The Crystal Structure of Methylmercury(II) Cyanide determined by X-Ray Diffraction

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IN structural studies of di-*p*-tolylmercury[1] and diphenylmercury,[2] the mercury atoms are at a centre of symmetry, and consequently the C–Hg–C bonds are colinear. Non-linear C–Hg–C skeletons have been reported for mercury(II) cyanide[3] (171 ± 2°), and bispentafluorophenylmercury[4] (176·2 ± 1·2°). Because the vibrational spectrum of methylmercury(II) cyanide[5] leaves some doubt about the linearity of the C–Hg–C–N skeleton, the structure of this compound has been determined using *X*-rays. A neutron-diffraction analysis is currently being carried out.

Needle-shaped crystals of methylmercury(II) cyanide were crystallised from chloroform. Crystal data: C_2H_3HgN; $M = 241{\cdot}6$; orthorhombic; $a = 9{\cdot}12 \pm 0{\cdot}02$; $b = 6{\cdot}14 \pm 0{\cdot}02$; $c = 7{\cdot}01 \pm 0{\cdot}02$ Å; $U = 393$Å^3; $D_m = 3{\cdot}97$ (by flotation); $Z = 4$; $D_c = 4{\cdot}08$; $F(000) = 408$; Space group, *Pnma* (D_{2h}^{16}, No. 62), or $Pn2_1a$ (C_{2v}^9, No. 33); Cu-K_α radiation, nickel filtered; single crystal oscillation and multiple film Weissenberg photographs. In the analysis, 272 non-zero reflections from four levels (*h*0*l* to *h*3*l*) were used. The visually estimated intensities were not corrected for absorption. An intensity-distribution curve using neutron-diffraction data indicated a centre of symmetry, confirming the space group *Pnma*. Thus, all atoms, except two of the three hydrogens, lie in the mirror planes at $y = \frac{1}{4}, \frac{3}{4}$. This would be responsible for the ease with which the crystals may be cleaved perpendicular to the needle *b* axis.

The structure was solved using three-dimensional Patterson and Fourier syntheses. Four cycles of full matrix least-squares refinement, using individual isotropic temperature factors, reduced *R* from 0·218 to 0·133. However, structure factors calculated from only the final mercury parameters gave $R = 0{\cdot}155$. When the final carbon and nitrogen positions in the cyanide group were interchanged, *R* refined to 0·133 after two cycles.

Bond lengths are: Hg–C (methyl) = 2·15 ± 0·05, Hg–C (cyanide) = 2·01 ± 0·05, and C–N = 1·18 ± 0·07 Å. Although the mercury atom is not at a centre of symmetry, the C–Hg–C angle is 180° ± 2°. In mercury(II) cyanide[3] because of intermolecular interaction, this angle is 171° ± 2°, with two nitrogen atoms of neighbouring molecules situated at 2·70 Å from the mercury atom. There is no corresponding intermolecular interaction in methylmercury(II) cyanide. Of three neighbouring nitrogen atoms, one is at 3·14 Å (in the same plane), and two are at 3·26 Å from the mercury atom.

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