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# THE CRYSTAL STRUCTURE OF METHYLMERCURY(II) CYANIDE

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## SUMMARY

The crystal structure of methylmercury(II) cyanide, $CH_3HgCN$, has been determined by three dimensional X-ray and neutron diffraction. The compound crystallises out in an orthorhombic unit cell, space group *Pnma*; cell dimensions (X-ray) $a=9.12(2)$, $b=6.14(2)$, $c=7.01(2)$ Å; cell dimensions (neutron), $a=9.11(2)$, $b=6.14(2)$, $c=7.01(2)$ Å. With four molecules of $CH_3HgCN$ per unit cell, all atoms, except the hydrogens, are on mirror planes at $y=\frac{1}{4}, \frac{3}{4}$. Interatomic distances are: Hg–C (cyanide) = 2.05(1), Hg–C (methyl) = 2.08(2), and C–N = 1.14(1) Å. Refinement indicates that the methyl group is rotating.

## INTRODUCTION

Recent studies of the vibrational spectrum of methylmercury(II) cyanide[1,2] have raised some doubt about the linearity of the C–Hg–C skeleton. The crystal structures of di-*p*-tolylmercury[3], diphenylmercury[4], and potassium iododicyanomercurate(II)[5] showed that the C–Hg–C skeletons were linear due to the mercury atoms being at centres of symmetry. However, in mercury(II) cyanide[6] and bis(pentafluorophenyl)mercury[7], where the mercury atoms do not lie at symmetry centres, the skeletons were non-linear with C–Hg–C angles of 171(2)° and 176(1)°, respectively. Consequently, the crystal structure determination of methylmercury(II) cyanide, a non-symmetrical molecule, was undertaken using both X-ray and neutron diffraction, in order to establish whether the C–Hg–C skeleton was linear. A preliminary communication of the X-ray structure has already been made[8].

## EXPERIMENTAL

Methylmercury(II) cyanide was prepared as previously reported[1]. Suitably needle shaped crystals were obtained from chloroform.

### *Crystal data*

$C_2H_3HgN$; mol.wt. = 241.6; orthorhombic; X-ray cell dimensions were obtained from oscillation and Weissenberg photographs calibrated with aluminium powder lines, $a=9.12(2)$, $b=6.14(2)$, $c=7.01(2)$ Å. Neutron cell dimensions were obtained using a neutron diffractometer, $a=9.11(2)$, $b=6.14(2)$, $c=7.01(2)$ Å; $d_m=3.97$ (by flotation in aqueous thallous formate/malonate solution); $Z=4$; $d_c=4.08$;

$F(000) = 408$; Space group, *Pnma* ($D_{2h}^{16}$), or $Pn2_1a$ ($D_{2v}^{9}$); *Pnma* selected; $\mu$ (measured for neutrons) $= 3.3\ cm^{-1}$; $\mu$ (X-ray, Cu-$K_\alpha$) $= 736\ cm^{-1}$.

*X-ray determination*

Cu-$K_\alpha$ radiation, nickel filtered; single crystal oscillation, and multiple film Weissenberg photographs. In the analysis, 271 non-zero reflections from four levels (*h*0*l* to *h*3*l*) were used. Cross levels (*hk*0, 0*kl*) were used for inter-layer scaling, and the structure amplitudes were put on an absolute basis by comparison with calculated structure factors. The visually estimated intensities were not corrected for either absorption or extinction. "Neutral Atom" atomic scattering factors given in International Tables[9] were used for mercury, carbon, and nitrogen. Least squares weights were assigned according to the Hughes' scheme[10].

*Neutron determination*

Data was collected using the A.I.N.S.E. single crystal diffractometer installed on the Australian Atomic Energy Commision's reactor HIFAR at Lucas Heights, N.S.W. A total of 293 independent reflections were collected up to $2\theta = 125°$, using a $2\theta/\theta$ step scan technique. The spectrometer was monitor controlled, and the monochromatic beam intensity at the specimen was approximately $10^5\ n \cdot cm^{-2} \cdot sec^{-1}$, at a wavelength of 1.19(1) Å. The step size was 0.03° of $2\theta$, and the scanning rate was one third of a degree of $2\theta$ per min. The neutron data was corrected for Lorentz factors and absorption effects. No corrections were made for extinction. For the calculation of structure factors, the following scattering lengths were used[11]: $b_{Hg} = 1.27 \times 10^{-12}$ cm, $b_C = 0.661 \times 10^{-12}$ cm, $b_N = 0.94 \times 10^{-12}$ cm, and $b_H = -0.375 \times 10^{-12}$ cm.

The observed structure factors were initially converted to absolute values by applying a scale factor, *K*, obtained from the intensity of the (200) reflection of a standard potassium bromide crystal. The final scaling of these observed structure factors was determined by least squares.

A standard deviation was assigned to each integrated intensity according to the expression:

$$\sigma^2(Qj) = Qj + 2\,Bj + (\alpha + \beta \cdot Qj)^2$$

Where $Qj$ = integrated intensity; $Bj$ = background count; $\alpha = Q$ min, the minimum observed intensity; and $\beta$ is the standard deviation of the standard reflection. A statistical test[12] applied to the neutron data indicated a centric space group. Therefore, the space group *Pnma* was chosen.

The X-ray structure was determined using locally written or modified FORTRAN programmes for data reduction (Mills and Kennard, GE 225), Fourier (Craven, IBM 7040, and 350/50) and least squares (Cox modified ORFLS, IBM 360/50). The absorption corrections to neutron intensities were made using an AAEC modified version of ORABS, and the structure was refined using Dr. J. Blount's version of ORFLS (CDC 3600).

STRUCTURE DETERMINATION

*X-ray data*

The atomic parameters for the mercury atoms were selected from an analysis of interatomic vectors in a three dimensional $F^2$ synthesis. Other non-hydrogen atoms were found from a Fourier synthesis using the heavy atom method. After four cycles of full matrix least squares with individual isotropic temperature factors, the variable parameters refined to give an $R$ of 0.133 compared to the initial $R$ of 0.218. Final fractional and thermal parameters are listed in Table 1, bond lengths and angles in Table 2, and the observed and calculated structure factors in Table 5.

TABLE 1

X-RAY ATOMIC PARAMETERS AND STANDARD DEVIATIONS FOR METHYLMERCURY(II) CYANIDE

| | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|
| Hg | 0.1156(2) | 0.25 | 0.0436(3) | 2.06(5) |
| C(methyl) | 0.488(5) | 0.25 | 0.198(7) | 2.2(7) |
| C(cyanide) | 0.235(5) | 0.25 | 0.802(8) | 2.9(8) |
| N | 0.311(6) | 0.25 | 0.666(8) | 3.0(1.1) |

TABLE 2

INTERATOMIC DISTANCES AND ANGLES

| | Neutrons | | X-rays | |
|---|---|---|---|---|
| | (Å) | (°) | (Å) | (°) |
| Hg–C(methyl) | 2.08(2) | | 2.15(5) | |
| Hg–C(cyanide) | 2.05(1) | | 2.01(5) | |
| C–N | 1.14(1) | | 1.18(7) | |
| C–H(1) | 1.03(6) | | | |
| C–H(2) | 1.00(8) | | | |
| C–H(3) | 0.91(6) | | | |
| C–Hg–C | | 180(2) | | 180(6) |
| Hg–C–N | | 180(3) | | 176(15) |
| Hg–C–H(1) | | 115(7) | | |
| Hg–C–H(2) | | 107(9) | | |
| Hg–C–H(3) | | 111(8) | | |
| H(1)–C–H(2) | | 123(13) | | |
| H(1)–C–H(3) | | 96(9) | | |
| H(2)–C–H(3) | | 108(12) | | |
| Hg···N′[a] | 3.15(1) | | 3.14(6) | |
| Hg···N″[b] | 3.26(1) | | 3.26(6) | |
| N′···Hg···N″ | | 108(1) | | 108(3) |
| N″···Hg···N″ | | 141(1) | | 141(4) |
| H(1)′···H(1)″ | 2.30(8) | | | |

[a] N′ is a nitrogen atom in the same mirror plane. [b] N″ is a nitrogen atom in another mirror plane.

TABLE 3

NEUTRON ATOMIC PARAMETERS AND STANDARD DEVIATIONS FOR METHYLMERCURY(II) CYANIDE[a]

| *Position parameters* | *x* | *y* | *z* |
|---|---|---|---|
| Hg | 0.1150(5) | 0.25 | 0.0453(6) |
| C(methyl) | 0.501(2) | 0.25 | 0.197(3) |
| C(cyanide) | 0.239(1) | 0.25 | 0.801(1) |
| N | 0.309(1) | 0.25 | 0.665(1) |
| H(1)[b] | 0.484(8) | 0.098(11) | 0.138(8) |
| H(2)[b] | 0.421(10) | 0.140(12) | 0.211(9) |
| H(3)[b] | 0.064(6) | 0.204(12) | 0.395(7) |

| *Thermal parameters* | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|
| Hg | 3.1(2) | 3.4(2) | 2.7(2) | | 0.3(2) | |
| C(methyl) | 4.6(8) | 4.5(1.0) | 5.3(9) | | −1.0(7) | |
| C(cyanide) | 4.0(6) | 4.8(6) | 3.9(4) | | 1.7(4) | |
| N | 5.7(5) | 6.6(5) | 4.8(3) | | 2.6(3) | |
| H(1) | 8(3) | 8(4) | 5(2) | −1(2) | −4(2) | −4(2) |
| H(2) | 23(11) | 5(2) | 8(3) | −6(5) | −8(5) | 0(3) |
| H(3) | 13(4) | 8(5) | 7(2) | −5(4) | 5(2) | 2(3) |

[a] Estimated standard deviations are given in parentheses. The temperature factor is defined by: $\exp\left[-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B_{ij}\cdot h_i\cdot h_j\cdot a_i^*\cdot a_j^*\right]$. [b] Multiplicity = 0.5.

TABLE 4

COMPARABLE BOND LENGTHS AND ANGLES IN OTHER COMPOUNDS

| Compound | C–N (Å) | Hg–C(cyanide)[a] (Å) | Hg–C(methyl)[a] (Å) | Ref. |
|---|---|---|---|---|
| $CH_3As(CN)_2$ | 1.09(4), 1.15(4) | | | 14 |
| $(CH_3)_2AsCN$ | 1.16(7) | | | 15 |
| $As(CN)_3$ | 1.13(7), 1.19(7), 1.14(7) | | | 16 |
| $S(CN)_2$ | 1.12(2), 1.13(2) | | | 17 |
| $HgO{\cdot}Hg(CN)_2$ | 1.18(6), 1.28(6) | 1.97(4), 2.02(4) | | 18 |
| $KI{\cdot}Hg(CN)_2$ | 1.19(2)[b], 1.05(14) | 2.08(10) | | 5, 10 |
| $(CH_3)_2Hg$ | | | 2.2(1)[c], 2.23(4)[c] | 19,20 |
| $CH_3HgCl$ | | | 2.06(2)[d], 2.06(3) | 21,22 |
| $CH_3HgBr$ | | | 2.07(2)[d] | 21 |
| $Hg(CN)_2$ | | 1.99(2)[b] | | |

| Compound | C–Hg–C[a] (°) | Ref. |
|---|---|---|
| $Hg(CN)_2$ | 171(2)[b] | 5 |
| $(C_6F_5)_2Hg$ | 176(1) | 6 |

[a] Only structures where the Hg atom does not lie at a centre of symmetry have been included. [b] Neutron diffraction. [c] Electron diffraction. [d] Microwave spectroscopy.

*Neutron data*

Possible hydrogen atom positions were indicated from Fourier and difference Fourier synthesis, when the final X-ray co-ordinates were used with neutron data. Least squares calculation based on these parameters failed to refine.

With four molecules of methylmercury(II) cyanide per unit cell in the space group *Pnma*, all the non-hydrogen atoms must be in the mirror planes at $y=\frac{1}{4}, \frac{3}{4}$. However, the hydrogen atoms need not be on the mirror plane. Because of this, four models were considered for the hydrogen atoms and are shown in Fig. 1. In models (A) and (B) one hydrogen is in the mirror plane and the other two are straddling it. Model (C) (disordered) is a combination of (A) + (B). Model (D) is an approximation to a rotating methyl group.

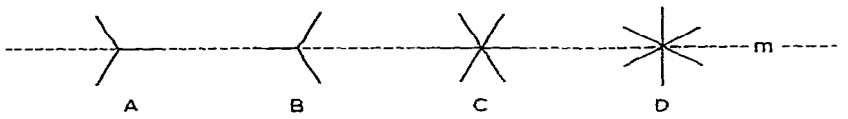


Fig. 1. Models considered for the hydrogen atom positions.

Using hydrogen atom co-ordinates calculated for a C–H bond length of 1.0 Å, and the usual tetrahedral angle, each model was tried, but refinement proved difficult, resulting mostly in high values for $R$, large standard deviations, and sometimes negative temperature factors. Model (B) refined more quickly than (A) to give $R=0.25$ after three cycles (isotropic temperature factors), and with two additional cycles, $R=0.16$ (anisotropic temperature factors). However, at this stage, the temperature factor of the in-plane hydrogen atom went negative. Two cycles of refinement using the disordered model (C) gave $R=0.21$ (isotropic temperature factors), the temperature factors for the in-plane hydrogen atoms being 28.2 and 5.9 Å$^2$, and for the out-of-plane hydrogens, 1.5 and $-2.9$ Å$^2$.

The best results were obtained when an approximate methyl group (D) was considered. In this model consisting of six fractional hydrogens lying on a ring 1.0 Å from the carbon atom, all the positional co-ordinates of the hydrogen atoms could be varied. Two cycles of least squares refinement reduced $R$ to 0.21, with isotropic temperature factors of 3.8, 4.5 and 9.6 Å$^2$ for the hydrogen atoms. Anisotropic refinement reduced $R$ to 0.114 after four cycles. Final positional and thermal parameters for the anisotropic refinement are listed in Table 3, bond lengths and angles in Table 2, and the observed and calculated structure factors in Table 6.

## DISCUSSION

Methylmercury(II) cyanide exists in the solid state as discrete monomeric molecules with the C–Hg–C–N skeleton linear (Fig. 2). Of the related molecules, dimethylmercury and mercury(II) cyanide, the former[13] has been shown to have a linear skeleton in the liquid phase by vibrational spectroscopy, while the latter[6] is non-linear in the solid state. Each mercury atom in solid mercury(II) cyanide is surrounded by two bonding cyanide groups, and four equidistant non-bonded nitrogen atoms from neighbouring molecules. The non-bonded distance of 2.70 Å is significantly less than the Van der Waals contact distance (3.1 Å), but greater than

TABLE 5

OBSERVED STRUCTURE AMPLITUDES AND CALCULATED STRUCTURE FACTORS; X-RAY DIFFRACTION
(scale: 5 × absolute)

| 0,0,1 | | | 4,0,1 | | | 8,0,1 | | | 2,1,1 | | | 6 1 1 | | | 0 2 1 | | | 5 2 1 | | | 10 2 1 | | | 4 3 1 | | | 9 3 1 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 846 | 992 | 0 | 820 | 1041 | 0 | 494 | 615 | 0 | 960 | -1314 | 0 | 763 | 866 | 2 | 827 | -887 | 1 | 697 | 769 | 0 | 232 | -261 | 0 | 208 | 235 | 1 | 109 | 126 |
| 4 | 407 | 462 | 2 | 919 | -970 | 2 | 461 | 467 | 1 | 223 | -256 | 2 | 641 | 652 | 4 | 397 | -416 | 2 | 245 | -234 | 1 | 76 | 73 | 1 | 223 | -235 | 2 | 224 | 217 |
| 8 | 342 | -290 | 3 | 223 | -165 | 3 | 228 | 195 | 2 | 1304 | -1081 | 3 | 265 | 217 | 8 | 282 | 267 | | 1 2 1 | | 2 | 168 | -191 | 2 | 185 | 167 | 4 | 315 | 337 |
| | | | 4 | 482 | -362 | 4 | 257 | 228 | 4 | 550 | -446 | 4 | 309 | 278 | | | | 4 | 342 | -274 | 3 | 236 | 246 | 3 | 602 | -553 | | 10 3 1 | |
| 1,0,1 | | | 5 | 268 | -188 | 5 | 199 | 202 | 5 | 129 | -68 | 5 | 237 | 187 | 1 | 737 | -912 | 5 | 138 | 108 | 4 | 72 | -87 | 4 | 86 | 57 | 0 | 302 | 341 |
| 1 | 773 | 1069 | 6 | 86 | 57 | 9,0,1 | | | 6 | 130 | 63 | 7 | 156 | 122 | 2 | 419 | 434 | 6 | 312 | -243 | | 11 2 1 | | 5 | 610 | -561 | 2 | 233 | 266 |
| 2 | 421 | -504 | 1 | 108 | -94 | 1 | 419 | 522 | 7 | 123 | -91 | | 7 1 1 | | 3 | 537 | -548 | 7 | 155 | -136 | 2 | 121 | 192 | 7 | 384 | -370 | 3 | 100 | 136 |
| 3 | 551 | 620 | 8 | 235 | 199 | 3 | 366 | 336 | 8 | 259 | 239 | 1 | 593 | 697 | | 6 2 1 | | | 0 3 1 | | | 5 3 1 | | | | | | | |
| 4 | 569 | -590 | 5,0,1 | | | 4 | 119 | -110 | | 3,1,1 | | 2 | 141 | -141 | 5 | 112 | -95 | 0 | 246 | 260 | 1 | 201 | 245 | 1 | 386 | -352 | | | |
| 5 | 89 | 104 | 1 | 849 | -854 | 5 | 63 | 71 | 1 | 702 | -984 | 3 | 452 | 394 | 6 | 447 | 403 | 1 | 205 | -211 | 3 | 681 | 677 | 2 | 474 | -402 | | | |
| 6 | 509 | -440 | 2 | 247 | 262 | 10,0,1 | | | 2 | 363 | 312 | 4 | 249 | -190 | 7 | 142 | 115 | 2 | 272 | 242 | 5 | 670 | 698 | 3 | 269 | -259 | | | |
| 7 | 151 | -125 | 3 | 694 | -546 | 0 | 218 | 283 | 3 | 699 | -580 | 5 | 147 | 105 | 8 | 236 | 235 | 3 | 594 | -472 | 7 | 467 | 431 | 4 | 447 | -446 | | | |
| 8 | 247 | -255 | 4 | 380 | 299 | 1 | 75 | -78 | 4 | 610 | 461 | 6 | 172 | -151 | | 2 2 1 | | 4 | 119 | 106 | | 1 3 1 | | 6 | 456 | -420 | | | |
| 9 | 198 | -206 | 5 | 165 | -118 | 2 | 181 | 207 | 5 | 176 | -112 | 7 | 126 | -109 | 1 | 309 | 354 | 5 | 627 | -508 | 1 | 637 | 681 | | 6 3 1 | | | | |
| 2,0,1 | | | 6 | 368 | 264 | 3 | 260 | -266 | 6 | 490 | 371 | | 8 1 1 | | 2 | 137 | -135 | 7 | 291 | -332 | 2 | 335 | 349 | 0 | 588 | -711 | | | |
| 1 | 343 | -416 | 7 | 164 | 147 | 4 | 84 | 93 | 7 | 135 | 130 | 0 | 324 | 327 | 3 | 907 | 741 | | 7 2 1 | | 3 | 407 | 424 | 2 | 602 | -542 | | | |
| 2 | 185 | 160 | 8 | 119 | 138 | 11,0,1 | | | 8 | 187 | 173 | 1 | 147 | -181 | 4 | 81 | -62 | 1 | 191 | -231 | 4 | 550 | 574 | 3 | 206 | -181 | | | |
| 3 | 981 | -834 | 6,0,1 | | | 2 | 176 | -207 | 4,1,1 | | | 2 | 225 | 222 | 5 | 839 | 705 | 2 | 296 | -290 | 5 | 122 | 102 | 4 | 245 | -235 | | | |
| 4 | 114 | 71 | 0 | 270 | -285 | 0,1,1 | | | 0 | 280 | -303 | 3 | 390 | -370 | 7 | 457 | 473 | 3 | 227 | -187 | 6 | 457 | 405 | 5 | 196 | -159 | | | |
| 5 | 938 | -774 | 1 | 236 | 232 | 1 | 269 | -294 | 1 | 272 | 294 | 4 | 128 | 112 | | 3 2 1 | | 4 | 601 | -493 | 7 | 129 | -122 | 7 | 56 | -105 | | | |
| 7 | 586 | -513 | 2 | 267 | -267 | 3 | 724 | -850 | 2 | 213 | -205 | 5 | 418 | -377 | 1 | 539 | 673 | 6 | 385 | -363 | 8 | 221 | 229 | | 7 3 1 | | | | |
| 3,0,1 | | | 3 | 603 | 517 | 5 | 765 | -846 | 3 | 852 | 675 | | 9 1 1 | | 2 | 499 | 463 | | 8 2 1 | | | 2 3 1 | | 1 | 544 | -581 | | | |
| 1 | 667 | -780 | 4 | 165 | -116 | 7 | 613 | -505 | 4 | 91 | -66 | 1 | 120 | -150 | 3 | 329 | 288 | 0 | 473 | -564 | 0 | 985 | 1018 | 2 | 124 | 117 | | | |
| 2 | 524 | -526 | 5 | 649 | 552 | 1,1,1 | | | 5 | 869 | 668 | 2 | 268 | -255 | 4 | 657 | 584 | 1 | 84 | -76 | 1 | 150 | 151 | 3 | 323 | -334 | | | |
| 3 | 389 | -311 | 7 | 363 | 358 | 1 | 684 | -894 | 7 | 457 | 433 | 3 | 78 | -53 | 5 | 150 | 123 | 2 | 442 | -428 | 2 | 864 | 845 | 4 | 172 | 162 | | | |
| 4 | 781 | -644 | 7,0,1 | | | 2 | 358 | -428 | 5,1,1 | | | 4 | 406 | -394 | 6 | 534 | 499 | 3 | 187 | -179 | 4 | 406 | 364 | 5 | 80 | -89 | | | |
| 5 | 184 | -136 | 1 | 209 | 253 | 3 | 523 | -534 | 1 | 371 | 427 | | 10 1 1 | | 7 | 104 | -100 | 4 | 224 | -210 | 5 | 99 | 59 | 6 | 100 | 129 | | | |
| 6 | 695 | -544 | 2 | 313 | 316 | 4 | 709 | -711 | 2 | 496 | 499 | 0 | 395 | -401 | 8 | 225 | 244 | 5 | 213 | -187 | 6 | 201 | -205 | | 8 3 1 | | | | |
| 7 | 135 | 109 | 3 | 243 | 206 | 5 | 151 | -124 | 3 | 399 | 318 | 1 | 74 | -80 | 4 | 2 | 1 | 6 | 41 | 26 | | 3 3 1 | | 0 | 247 | -275 | | | |
| 8 | 274 | -264 | 4 | 610 | 538 | 6 | 541 | -481 | 4 | 660 | 529 | 2 | 284 | -311 | 0 | 828 | 935 | 9 | 2 | 1 | 1 | 654 | 774 | 1 | 141 | 151 | | | |
| | | | 6 | 422 | 393 | 7 | 169 | 144 | 6 | 552 | 494 | 3 | 159 | -158 | 2 | 974 | 860 | 1 | 421 | -481 | 2 | 297 | -256 | 2 | 178 | -188 | | | |
| | | | | | | 8 | 276 | -267 | 7 | 79 | -60 | 4 | 125 | -138 | 3 | 164 | 149 | 2 | 76 | 53 | 3 | 520 | 470 | 3 | 353 | 314 | | | |
| | | | | | | | | | 8 | 191 | 253 | | 11 1 1 | | 4 | 383 | 329 | 3 | 304 | -310 | 4 | 420 | -377 | 4 | 70 | -95 | | | |
| | | | | | | | | | | | | 1 | 322 | -367 | 5 | 231 | 171 | 4 | 111 | 101 | 5 | 88 | 94 | 5 | 334 | 323 | | | |
| | | | | | | | | | | | | 3 | 144 | -233 | 7 | 97 | 87 | | | | 6 | 344 | -314 | | | | | | |
| | | | | | | | | | | | | | | | 8 | 196 | -184 | | | | 7 | 114 | -112 | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | 8 | 95 | -149 | | | | | | |

TABLE 6

OBSERVED STRUCTURE AMPLITUDES AND CALCULATED STRUCTURE FACTORS; NEUTRON DIFFRACTION
(scale: 100 × absolute)

| | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 0 1 | | | 6 0 1 | | | 4 | 263 | 272 | 4 | 262 | 244 | 2 | 107 | 81 | 0 4 1 | | | 1 5 1 | | | 4 44 33 |
| 2 45 | -43 | | 1 67 | 22 | | 5 | 187 | 177 | 5 | 126 | 77 | 3 | 231 | 208 | 0 999 | 973 | | 1 166 | -159 | | 5 80 54 |
| 4 331 | 263 | | 2 206 | -201 | | 6 | 256 | 244 | 9 | 108 | 90 | 4 | 511 | 496 | 2 94 | -108 | | 3 114 | -120 | | 5 6 1 |
| 6 212 | 200 | | 3 94 | 129 | | 7 | 81 | 33 | 2 | 2 | 1 | 5 | 149 | 95 | 4 146 | 96 | | 4 252 | -282 | | 1 123 119 |
| 8 273 | -304 | | 5 406 | 434 | | 9 | 89 | 117 | 1 | 274 | 258 | 6 | 81 | 114 | 6 109 | 112 | | 5 109 | -72 | | 2 88 -86 |
| 1 0 1 | | | 7 0 1 | | | 4 | 1 | 1 | 2 | 100 | -98 | 7 | 199 | -158 | 1 4 1 | | | 2 5 1 | | | 5 67 40 |
| 1 565 | 563 | | 3 302 | 234 | | 0 | 284 | -306 | 3 | 264 | 261 | 2 | 3 | 1 | 1 217 | 199 | 0 | 202 | -171 | | 6 64 -87 |
| 2 322 | -318 | | 4 426 | 406 | | 1 | 107 | 146 | 4 | 158 | -144 | 1 | 563 | 590 | 2 220 | -179 | 1 | 308 | -300 | | 7 59 -58 |
| 3 106 | 70 | | 5 127 | -118 | | 3 | 386 | 376 | 5 | 186 | 187 | 2 | 402 | 390 | 3 279 | 272 | 2 | 255 | -279 | | |
| 4 301 | -294 | | 6 89 | 93 | | 4 | 93 | 76 | 6 | 96 | 56 | 3 | 184 | -148 | 4 206 | -176 | 3 | 85 | 80 | | h71 |
| 5 90 | -67 | | 8 0 1 | | | 5 | 164 | 178 | 3 | 2 | 1 | 4 | 215 | 178 | 2 4 1 | | | 3 5 1 | | | |
| 6 61 | -48 | | 0 371 | 326 | | 6 | 93 | -218 | 1 | 396 | 406 | 5 | 97 | -121 | 1 144 | -121 | 1 | 206 | -219 | 270 | 134 146 |
| 7 84 | 3 | | 2 134 | 104 | | 7 | 202 | 178 | 2 | 216 | 219 | 3 | 247 | -264 | 2 71 | 48 | 2 | 59 | 46 | 670 | 97 -106 |
| 8 223 | -201 | | 3 150 | 169 | | 8 | 67 | 66 | 3 | 239 | -231 | 1 | 328 | 341 | 3 247 | -264 | 3 | 161 | -159 | 171 | 92 98 |
| 9 129 | -108 | | 4 202 | 158 | | 9 | 105 | 98 | 4 | 200 | 199 | 2 | 102 | -191 | 5 142 | -151 | 4 | 102 | 117 | 271 | 106 110 |
| 2 0 1 | | | 5 53 | 53 | | 5 | 1 | 1 | 5 | 266 | 270 | 3 | 207 | 213 | 3 4 1 | | | 4 5 1 | | | |
| 0 451 | -480 | | 8 56 | -126 | | 1 | 93 | 86 | 6 | 344 | 354 | 4 | 140 | -144 | 1 310 | -310 | 0 | 89 | -99 | 572 | 87 -83 |
| 1 390 | -372 | | 9 0 1 | | | 2 | 455 | 463 | 4 | 2 | 1 | 5 | 63 | -64 | 2 176 | -183 | 1 | 91 | 108 | 573 | 77 -42 |
| 2 225 | 208 | | 1 227 | 218 | | 3 | 264 | 255 | 0 | 81 | -41 | 4 | 3 | 1 | 3 138 | 156 | 3 | 161 | 170 | 475 | 71 89 |
| 3 207 | -205 | | 2 91 | 128 | | 4 | 65 | -17 | 1 | 161 | -167 | 0 | 147 | 151 | 4 92 | -114 | 5 | 135 | 150 | 476 | 72 33 |
| 4 316 | 276 | | 3 196 | 187 | | 5 | 105 | -140 | 2 | 520 | 571 | 1 | 62 | -66 | | | | | | | h81 |
| 5 256 | -203 | | 4 156 | -191 | | 5 | 1 | 1 | 4 | 71 | 104 | 3 | 259 | -248 | 5 109 | -160 | 6 | 71 | -78 | 080 | 180 208 |
| 6 173 | -141 | | 10 0 1 | | | 6 | 297 | 347 | 5 | 173 | 193 | 4 | 84 | -66 | 4 4 1 | | 7 | 106 | 107 | 482 | 112 -127 |
| 7 335 | -341 | | 0 163 | 177 | | 7 | 69 | 50 | 6 | 312 | -124 | 5 | 215 | -243 | 1 120 | 122 | 5 | 5 1 | | 583 | 68 -52 |
| 9 105 | -88 | | 2 78 | 70 | | 8 | 77 | 114 | 5 | 2 | 1 | 6 | 100 | 124 | 2 402 | -388 | 1 | 85 | 44 | 484 | 86 -17 |
| 3 0 1 | | | 0 1 1 | | | 9 | 59 | -70 | 1 | 274 | 280 | 7 | 162 | -147 | 4 84 | -109 | 2 | 207 | 197 | | |
| 1 354 | -354 | | 1 396 | 410 | | 6 | 1 | 1 | 2 | 209 | -187 | 8 | 35 | -30 | 5 116 | -133 | 3 | 143 | 139 | | |
| 2 216 | -209 | | 3 251 | -259 | | 0 | 439 | 419 | 3 | 285 | 263 | 9 | 54 | -51 | 8 30 | 49 | 6 | 106 | 181 | | |
| 3 175 | 125 | | 5 539 | -546 | | 2 | 250 | 276 | 4 | 67 | 64 | 5 | 3 | 1 | 5 4 1 | | 6 | 5 1 | | | |
| 4 309 | -293 | | 7 161 | -163 | | 3 | 211 | 174 | 5 | 81 | 55 | 1 | 84 | -50 | 1 214 | -222 | 0 | 212 | 230 | | |
| 5 314 | -300 | | 1 1 1 | | | 8 | 1 | 1 | 6 | 200 | -223 | 2 | 410 | -415 | 2 135 | 108 | 7 | 5 1 | | | |
| 6 331 | -349 | | 1 238 | -248 | | 0 | 206 | 162 | 7 | 123 | -116 | 3 | 248 | -259 | 3 206 | -200 | 1 | 124 | 193 | | |
| 7 141 | 160 | | 2 143 | -163 | | 1 | 172 | -180 | 6 | 2 | 1 | 5 | 122 | 144 | 4 88 | -18 | 0 | 6 1 | | | |
| 4 0 1 | | | 3 359 | -306 | | 9 | 1 | 1 | 1 | 103 | -72 | 6 | 198 | -236 | 5 39 | -22 | 0 | 485 | -487 | | |
| 1 118 | 125 | | 4 504 | -504 | | 1 | 132 | -110 | 2 | 159 | 171 | 8 | 91 | -114 | 6 120 | 162 | 4 | 117 | -98 | | |
| 2 569 | -612 | | 5 112 | 67 | | 10 | 1 | 1 | 3 | 78 | -113 | 6 | 3 | 1 | 7 80 | 75 | 1 | 6 1 | | | |
| 3 91 | 63 | | 6 36 | -68 | | 0 | 262 | -255 | 8 | 2 | 1 | 0 | 378 | -385 | 8 72 | 24 | 1 | 154 | -153 | | |
| 5 203 | -210 | | 7 245 | 215 | | 1 | 127 | -98 | 0 | 312 | -326 | 1 | 141 | 131 | 6 4 1 | | 2 | 75 | 86 | | |
| 6 49 | 74 | | 8 151 | 118 | | 0 | 2 | 1 | 9 | 2 | 1 | 2 | 207 | -213 | 1 98 | 73 | 3 | 116 | -127 | | |
| 9 53 | -27 | | 2 1 1 | | | 0 | 1114 | -1162 | 1 | 213 | -184 | 3 | 135 | -95 | 2 97 | -94 | 2 | 6 1 | | | |
| 10 125 | 140 | | 1 510 | -526 | | 2 | 158 | 141 | 10 | 2 | 1 | 7 | 3 | 1 | 8 4 1 | | 0 | 72 | 49 | | |
| 5 0 1 | | | 2 373 | -365 | | 4 | 187 | -153 | 0 | 144 | -168 | 1 | 303 | -298 | 1 96 | 2 | 1 | 98 | 77 | | |
| 1 262 | -243 | | 3 265 | 241 | | 6 | 202 | -222 | 0 | 3 | 1 | 8 | 3 | 1 | 9 4 1 | | 2 | 62 | -47 | | |
| 2 258 | 258 | | 4 336 | -290 | | 8 | 198 | 252 | 3 | 243 | 240 | 0 | 157 | -164 | 1 119 | 138 | 3 | 6 1 | | | |
| 4 160 | -148 | | 6 96 | 111 | | 1 | 2 | 1 | 5 | 332 | 348 | 1 | 98 | 146 | 0 5 1 | | 1 | 94 | 143 | | |
| 5 90 | -76 | | 3 1 1 | | | 1 | 376 | -365 | 7 | 132 | 133 | 9 | 3 | 1 | 1 74 | -30 | 2 | 71 | 99 | | |
| 6 258 | 283 | | 1 435 | -410 | | 2 | 293 | 278 | 1 | 3 | 1 | 1 | 191 | 95 | 3 201 | -172 | 4 | 6 1 | | | |
| 7 183 | 186 | | 2 92 | -78 | | 3 | 319 | -264 | 1 | 221 | 216 | 10 | 3 | 1 | 5 286 | -286 | 2 | 228 | 225 | | |
| 9 47 | 74 | | 3 304 | -319 | | | | | | | | | | | | | | | | | |

the normal covalent bond length of 2.1–2.2 Å. Likewise in potassium iododicyanomercurate(II)[4], each mercury atom is surrounded by four equidistant iodine atoms at 3.38 (1) Å. This distance lies between the covalent Hg–I bond length of 2.75 Å, and the Van der Waals contact distance of 3.70 Å. The mercury atom in methylmercury(II) cyanide shows no similar tendency to increase its co-ordination number beyond two by non-bonded interaction with the surrounding atoms. Its intermolecular Hg···N approaches are 3.15 (1) Å in the same mirror plane, and 3.26 (1) Å in the planes above and below. Therefore, the molecules of methylmercury(II) cyanide seem to be held together in the crystal only by Van der Waals forces.

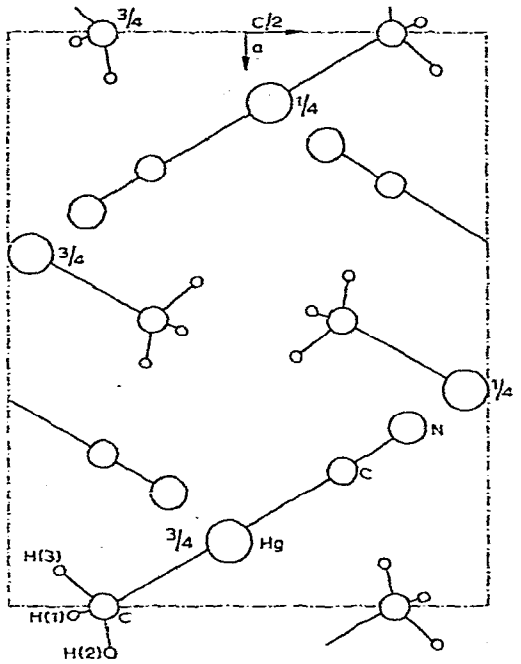


Fig. 2. Atomic arrangement in the unit cell of methylmercury(II) cyanide: projection on the (010) plane (hydrogen atoms are representational only).

Bond lengths in similar compounds are given in Table 4. Bond length differences with methylmercury(II) cyanide are generally smaller than the significance level of three times the standard deviation. The length of the Hg–C(methyl) bond compares well with the Hg–C bond lengths in methylmercury(II) chloride (2.06 Å)[22]. However, it is shorter than the length of the Hg–C bond in dimethylmercury (2.23 Å, electron diffraction)[20].

It was confirmed that the cyanide group is bonded to mercury through the carbon atom. This was done by attempting to refine the neutron data with the carbon and nitrogen co-ordinates interchanged. After one cycle of least squares, the temperature factor of the interchanged carbon atom went negative.

The neutron structure could only be refined by considering that the hydrogen atoms about the methyl group are rotating. No spectroscopic data is at present available to indicate whether this is a correct interpretation. No other similar structures have been fully determined using neutron diffraction, so there is little evidence to show whether it is common for methyl groups, attached to metal atoms to rotate. It does not appear to be the case in tetrameric trimethylplatinum hydroxide[23].

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