Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE STEREOCHEMISTRY OF ORGANOMERCURY COMPOUNDS II. A REDETERMINATION OF THE STRUCTURE OF MERCURY(II) CYANIDE BY NEUTRON DIFFRACTION*

R. C. SECCOMBE AND C. H. L. KENNARD
Department of Chemistry, University of Queensland, Brisbane, Queensland 4067 (Australia)
(Received April 21st, 1969)

SUMMARY

The crystal structure of mercury(II) cyanide, $Hg(CN)_2$, has been determined using three dimensional neutron diffraction data. The compound crystallizes out in a tetragonal unit cell, space group $I\bar{4}2d$; cell dimensions, $a=9.643$, $c=8.88$ Å. There are eight molecules per unit cell. Interatomic distances and angles are: Hg–C, 2.015(3); C–N, 1.137(3); non bonding Hg–N, 2.742(3) Å; C–Hg–C, 175.0(2)°; Hg–C–N, 177.0(3)°.

INTRODUCTION

The crystal structure determinations of di-*p*-tolylmercury[1], diphenylmercury[2], potassium iododicyanomercurate(II)[3], and methylmercury(II) cyanide[4] showed that the C–Hg–C skeletons were linear due to mercury atoms being at centres of symmetry. However in mercury(II) cyanide[5], and bis(pentafluorophenyl)mercury[6], 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. From chemical consideration this anomalous behaviour could not be explained. Because of the limited two dimensional data used in the neutron determination of mercury(II) cyanide[5], (13 *hk*0, 22 0*kl* reflections, 5 positional and 3 thermal parameters), a redetermination using three dimensional neutron data was carried out to confirm whether the C–Hg–C skeleton was non linear.

CRYSTAL DATA

Mercury(II) cyanide, C_2HgN_2, mol.wt.=252.5; tetragonal, (previous cell dimensions used)[5] $a=9.643$, $c=8.88$ Å; $Z=8$, $d_c=4.06$; Space Group used, $I\bar{4}2d$ (D_{2d}^{12}, No. 122). Data were collected on a goniostat using the A.I.N.S.E. single crystal diffractometer installed at the 2TAN window of the Australian Atomic Energy Commission's reactor HIFAR at Lucas Heights, N.S.W. A total of 261 independent reflections were collected up to $2\theta=140°$, using a $2\theta/\theta$ step scan technique. The spectrometer was monitor controlled, and the monochromatic beam intensity at the

* For Part I see ref. 4.

TABLE 1

ATOMIC AND THERMAL PARAMETERS OF MERCURY(II) CYANIDE[a]

Atom	x/a		y/b		z/c		B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{iso} (ref. 5)
	This work	Ref. 5	This work	Ref. 5	This work	Ref. 5							
Hg	0.2117(1)	0.2125	0.25	0.25	0.125	0.125	2.95(9)	2.11(8)	2.83(7)	0	0	0	2.8
C	0.2026(9)	0.197	0.0447(7)	0.047	0.1630(1)	0.159	4.1(1)	2.1(1)	3.0(1)	0.1(1)	0.3(1)	0.2(1)	3.3
N	0.2039(9)	0.212	−0.0726(7)	−0.073	0.1805(8)	0.183	6.5(2)	2.2(1)	4.7(1)	0.3(1)	0.3(1)	0.5(1)	3.3

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

specimen was approximately $5 \times 10^5 n \cdot cm^{-2} \cdot sec^{-1}$ at a wavelength of 1.24(1) Å. Data was corrected for Lorentz factor and absorption but not for extinction. For the calculation of structure factors, the following scattering lengths were used[7] $b_{Hg} = 1.27 \times 10^{-12}$ cm, $b_C = 0.661 \times 10^{-12}$ cm, $b_N = 0.94 \times 10^{-12}$ cm. Absorption corrections to the neutron intensities were made using an A. A.E.C. modified version of ORABS, and the structure was refined using an A.A.E.C. version of ORFLS (COXFLS, IBM360/50) and Dr. J. Blount's version of ORFLS (CDC 3600).

STRUCTURE DETERMINATION

Starting with the original parameters[5], three cycles of full matrix least squares refinement with individual isotropic temperature factors reduced the conventional $R_1[=\Sigma||F_{obs}|-|F_{calc}||/\Sigma|F_{obs}|]$ to 0.086. After four cycles of anisotropic refinement R_1 reduced to 0.036 and a weighted $R_2[=\Sigma w \cdot (|F_{obs}|-|F_{calc}|)^2/\Sigma w \cdot |F_{obs}|^2]$ to 0.033.

TABLE 2

INTERATOMIC DISTANCES AND ANGLES

		Corrected for thermal motion	Ref. 5
Hg–C	2.015(3)	2.019(3)	1.99(2)
C–N	1.137(3)	1.160(3)	1.18(2)
Hg–N[1]	2.742(3)		2.70
C–Hg–C	175.0(2)		171(2)
Hg–C–N	177.0(3)		173(2)

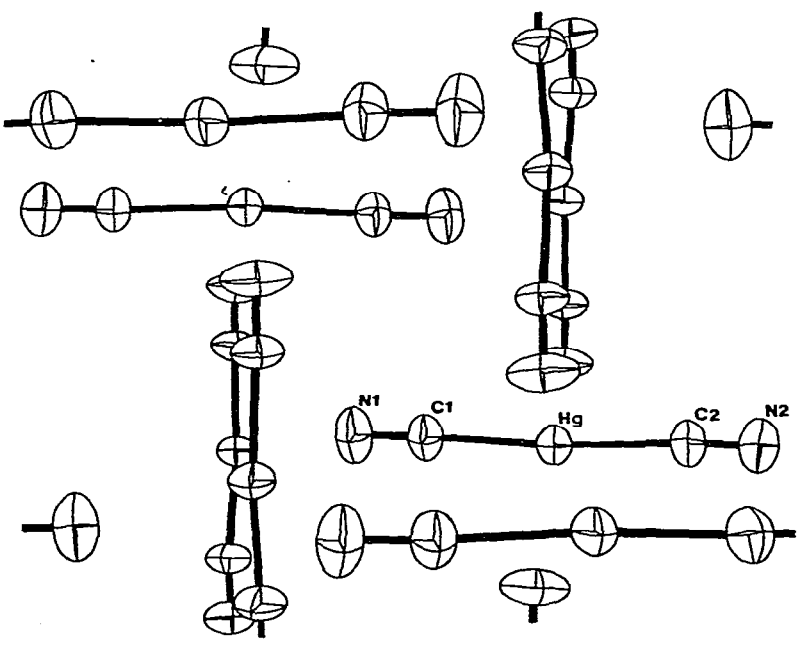

Fig. 1. Atomic arrangement in the unit cell of mercury(II) cyanide: projection on the (001) plane.

TABLE 3

OBSERVED STRUCTURE AMPLITUDES AND CALCULATED STRUCTURE FACTORS (SCALE: 100× ABSOLUTE)

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	0	0	1050	1042	5	4	3	504	498	7	3	6	206	218
4	0	0	1136	1133	7	4	3	493	488	9	3	6	263	261
6	0	0	903	895	9	4	3	494	481	6	4	6	202	204
8	0	0	796	792	6	5	3	656	651	8	4	6	349	361
10	0	0	134	159	8	5	3	315	309	10	4	6	312	305
3	1	0	517	507	10	5	3	407	408	5	5	6	322	301
5	1	0	260	243	7	6	3	353	324	7	5	6	215	201
2	2	0	572	537	9	6	3	523	509	9	5	6	240	255
4	2	0	446	425	11	6	3	148	143	8	6	6	285	290
6	2	0	987	975	10	7	3	238	257	10	6	6	167	163
10	2	0	559	578	9	8	3	2.)	242	7	7	6	298	304
5	3	0	172	147	10	9	3	260	304	1	0	7	518	513
9	3	0	690	693	0	0	4	1531	1612	3	0	7	248	239
4	4	0	537	526	2	0	4	806	816	7	0	7	366	343
6	4	0	436	417	4	0	4	782	777	9	0	7	138	148
7	5	0	183	177	6	0	4	465	426	2	1	7	587	573
9	5	0	318	298	3	1	4	686	690	4	1	7	449	444
11	5	0	248	260	5	1	4	797	790	6	1	7	143	127
10	6	0	237	247	9	1	4	648	628	8	1	7	520	488
9	7	0	217	212	11	1	4	308	320	10	1	7	147	138
1	0	1	197	125	13	1	4	238	244	5	2	7	337	359
3	0	1	1267	1267	2	2	4	410	422	7	2	7	529	510
5	0	1	1331	1339	4	2	4	556	551	11	2	7	169	213
9	0	1	531	547	6	2	4	503	481	4	3	7	192	186
2	1	1	421	396	8	2	4	290	296	10	3	7	139	149
4	1	1	387	366	10	2	4	300	314	5	4	7	410	412
6	1	1	452	432	5	3	4	271	264	7	4	7	342	318
10	1	1	366	379	7	3	4	542	543	11	4	7	144	176
3	2	1	363	341	9	3	4	432	422	6	5	7	273	295
5	2	1	231	224	11	3	4	216	240	8	5	7	378	387
7	2	1	208	212	13	3	4	151	184	10	5	7	144	135
9	2	1	500	512	4	4	4	502	512	7	6	7	256	263
4	3	1	687	689	6	4	4	285	279	9	6	7	193	207
6	3	1	778	773	8	4	4	290	291	8	7	7	145	177
8	3	1	319	324	10	4	4	265	264	10	7	7	126	140
10	3	1	421	422	7	5	4	496	487	9	8	7	147	210
5	4	1	558	553	9	5	4	350	372	0	0	8	157	162
7	4	1	280	296	11	5	4	240	259	2	0	8	458	476
9	4	1	677	685	6	6	4	193	182	4	0	8	303	309
6	5	1	695	758	8	6	4	188	188	8	0	8	448	449
8	5	1	320	339	10	6	4	240	251	3	1	8	359	336
10	5	1	430	460	9	7	4	242	265	5	1	8	369	364
7	6	1	502	509	10	8	4	153	174	7	1	8	339	327
9	6	1	578	575	1	0	5	693	700	2	2	8	867	868
10	9	1	160	169	3	0	5	672	655	6	2	8	145	164
2	0	2	1387	1411	5	0	5	632	614	8	2	8	255	253
10	0	2	982	953	7	0	5	182	183	5	3	8	189	180
12	0	2	459	459	9	0	5	567	556	7	3	8	252	252
1	1	2	812	804	2	1	5	581	575	4	4	8	353	346
3	1	2	983	976	4	1	5	492	479	8	4	8	264	261
5	1	2	712	696	6	1	5	519	514	7	5	8	145	153
7	1	2	383	384	8	1	5	315	330	0	5	8	166	174
9	1	2	590	593	10	1	5	538	522	6	6	8	263	285
4	2	2	475	469	3	2	5	424	457	1	0	9	271	234
6	2	2	574	554	5	2	5	497	506	2	1	9	207	231
8	2	2	233	241	7	2	5	183	168	6	1	9	411	383
10	2	2	458	464	9	2	5	520	505	8	1	9	164	179
12	2	2	219	223	4	3	5	427	435	10	1	9	137	135
5	3	2	582	562	6	3	5	311	296	3	2	9	424	414
9	3	2	410	402	10	3	5	288	301	5	2	9	367	363
6	4	2	302	282	5	4	5	557	564	9	2	9	149	218
8	4	2	284	265	7	4	5	177	173	4	3	9	200	177
10	4	2	484	468	9	4	5	390	384	6	3	9	232	233
12	4	2	244	263	11	4	5	179	198	8	3	9	157	194
8	5	2	395	373	6	5	5	429	433	5	4	9	240	227
7	5	2	198	197	8	5	5	273	295	7	4	9	301	291
9	5	2	249	243	10	5	5	202	210	6	5	9	162	167
8	6	2	353	339	7	6	5	248	271	8	5	9	280	294
10	6	2	242	265	9	6	5	145	174	7	6	9	154	167
7	7	2	357	367	8	7	5	390	406	2	0	10	490	479
9	9	2	444	457	10	7	5	277	272	4	0	10	220	169
1	0	3	1104	1129	9	8	5	265	278	8	0	10	291	265
3	0	3	465	456	2	0	6	270	275	1	1	10	486	455
5	0	3	603	577	4	0	6	283	279	3	1	10	318	309
7	0	3	1133	1128	8	0	6	448	457	5	1	10	224	218
11	0	3	148	143	10	0	6	305	282	7	1	10	233	239
2	1	3	734	740	12	0	6	152	197	4	2	10	176	169
4	1	3	378	373	1	1	6	975	983	3	3	10	277	273
6	1	3	296	291	3	1	6	582	582	5	3	10	159	173
8	1	3	621	645	5	1	6	741	750	7	3	10	173	179
10	1	3	201	203	7	1	6	451	441	6	4	10	179	220
3	2	3	496	486	4	2	6	136	134	4	1	11	273	259
5	2	3	336	328	6	2	6	142	159	5	2	11	269	293
7	2	3	500	494	8	2	6	445	455	6	3	11	211	99
11	2	3	181	179	10	2	6	312	312	4	4	12	200	182
4	3	3	305	302	12	2	6	182	211					
10	3	3	380	387	3	3	6	490	480					
12	3	3	171	195	5	3	6	548	545					

Final fractional and thermal parameters are compared with the original results[5] in Table 1. Table 2 lists interatomic distances and angles, while in Table 3 the observed and calculated structure factors are tabulated. The weighting scheme was based on the standard deviation of the integrated intensity.

DISCUSSION

This work showed that both the C–Hg–C and N–C–Hg angles are close to 180° and not as distorted as previously reported[5]. It is a moot point whether these links are not linear.

Mercury(II) cyanide exists in the solid state as discrete monomeric molecules arranged in a zig-zag pattern as shown in Fig. 1. Each mercury atom is surrounded by two bonding cyanide groups, (linked through the carbon), and two sets of two equidistant nitrogen atoms from neighbouring molecules. The shortest non-bonded distance of 2.74 Å is significantly less than the Van der Waals contact distance (3.1 Å) but greater than the covalent length (2.1–2.2 Å). Inspection of the figure shows the presence of a capillary of approximate diameter 3 Å running parallel to the c axis.

ACKNOWLEDGEMENTS

We wish to express our sincere thanks to the Australian Institute of Nuclear Science and Engineering (A.I.N.S.E.) for a grant, and for providing neutron diffraction facilities, and to the members of the A.I.N.S.E. Neutron Diffraction Group for their assistance. One of us (R.C.S.) is a recipient of a Commonwealth Postgraduate Scholarship.

REFERENCES

1 N. R. KUNCHUR AND M. MATHEW, *Proc. Chem. Soc.*, (1964) 414.
2 B. ZIOLKOWSKA, *Rocz. Chem.*, 36 (1962) 1341; B. ZIOLKOWSKA, R. M. MYASNIKOVA AND A. I. KITAIGORODSKII, *J. Struct. Chem. (Engl. Trans.)*, 5 (1964) 678.
3 F. H. KRUSE, *Acta Crystallogr.*, 16 (1963) 105.
4 J. C. MILLS, H. S. PRESTON AND C. H. L. KENNARD, *J. Organometal. Chem.*, 14 (1968) 33.
5 J. HVOSLEF, *Acta Chem. Scand.*, 12 (1958) 1568.
6 N. R. KUNCHUR AND M. MATHEW, *Chem. Commun.*, (1966) 71.
7 M. ELCOMBE, private communication from G. Bacon.