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A Combined X-Ray and Neutron Diffraction Investigation of Mercuric Cyanide

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The precise position of the Hg atom in $Hg(CN)_2$ was found by X-ray methods, while the CN group was localized by means of neutron data. The Hg-C distance is 1.986 ± 0.016 Å and the C-N triple bond is 1.186 ± 0.024 Å. The angle C-Hg-C is 171 ± 2°, while the Hg-C-N angle is 173 ± 2°. The distance between the Hg atom and two N atoms in neighbouring molecules is 2.70 Å. This indicates the existence of an interaction between them.

The space group and approximate Hg positions in $Hg(CN)_2$ were first established by Hassel[1] (1926). Although the light atoms were not detected, he concluded that the lattice must be built up of molecules, and not of separate Hg^{++} and CN^- ions. Later, Hanawolt *et al.*[2] confirmed the proposed structure, and in 1944, Zhdanov and Shugam[3] gave trial parameters for the light atoms, based upon the experimental data of Hanawolt. In a study by infrared spectra of solid $Hg(CN)_2$, Jones[4] was able to confirm the generally accepted opinion that the cyanide group was bound to the Hg atom through the C atom.

The structure was not, however, considered to be firmly established due to the uncertainty of the light atom positions. This uncertainty arises from the dominating influence of Hg *versus* C and N on the scattering of X-rays. For neutron diffraction no such difficulty occurs, as the coherent scattering amplitudes have the following values: $b_{Hg} = 1.30 \times 10^{-12}$ cm, $b_C = 0.66 \times 10^{-12}$ cm, $b_N = 0.94 \times 10^{-12}$ cm.

As no Hg-C distances have been accurately determined it seemed of interest to establish this distance with some precision by means of a neutron diffraction study.

EXPERIMENTAL

Mercuric cyanide crystallizes in the tetragonal space group No. 122 (International tables[5]) D_{2d}^{12}—$I\bar{4}2d$ with eight molecules in the unit cell. The CN groups are in the general 16-fold positions, while the Hg atoms are situated in the 8-fold position (*d*) with one degree of freedom only.

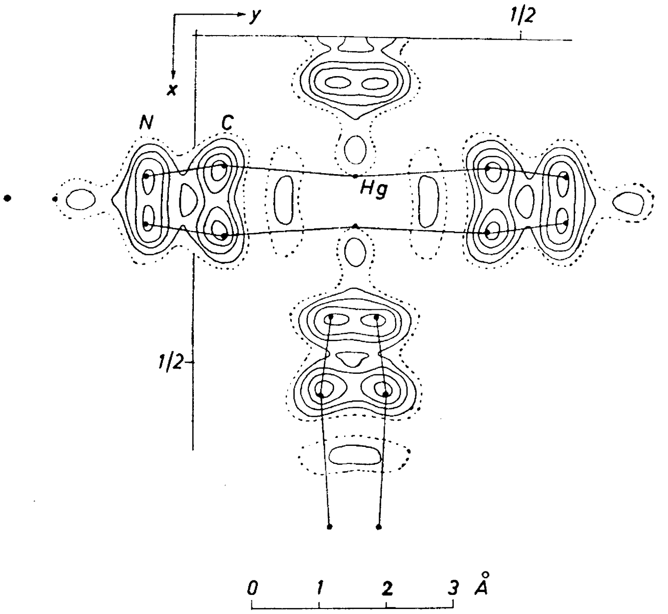

Fig. 1. Fourier projection on (001) of the electron density of the cyanide group in $Hg(CN)_2$, resulting from a synthesis of the coefficients $\{F_{obs} - F_c(Hg)\}$. Final coordinates are indicated by dots. Intervals at arbitrary scale.

The axial lengths were remeasured and found to be $a = 9.643$ Å and $c = 8.880$ Å. Hassel's values were 9.67 Å and 8.92 Å, respectively.

For the X-ray investigation a very small specimen was chosen. The data were recorded on Weissenberg diagrams, using Cu radiation. Multiple film technique and visual estimation was used to obtain the intensities in the *hk*0 zone. No 0*kl* data were recorded.

For the neutron work, a crystal with the dimensions 4.2 × 3.3 × 1.8 mm³ was grown from aqueous solution. The crystal was mounted on the goniometer

Table 1. Parameters found by X-rays and neutrons. Values for C and N atoms given for X-rays are found from $(F^X_{obs} - F^X_{calc})$ synthesis.

		Hg			C			N		
		x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Previous Work	Hassel	0.21	1/4	1/8	—	—	—	—	—	—
	Zhdanov and Shugam	0.21	1/4	1/8	0.21	0.03	0.18	0.21	−0.08	0.21
This invest.	X-ray data	0.2125	1/4	1/8	0.205	0.040	—	0.221	−0.068	—
	Neutron data	0.2125	1/4	1/8	0.197	0.047	0.159	0.212	−0.073	0.183

Table 2. Calculated and observed structure factors for X-rays, F^{X} and neutrons, F^{n}. Observed X-ray amplitudes believed to be suffering from extinction are marked with asterisks.

(*hkl*)	F^{X}_{calc}	F^{X}_{obs}	F^{n}_{calc}	F^{n}_{obs}
200	565	317 *	11.6	11.3
400	422	341	13.1	12.6
600	255	260	11.3	12.0
800	78	88	10.0	9.9
1 000	32	46		
1 200	6	0		
310	80	62	5.8	5.4
510	140	141	3.7	4.3
710	181	209	1.5	0
910	228	295		
1 110	202	202		
220	400	240 *	5.5	5.8
420	338	229	3.8	5.4
620	230	211	11.7	11.1
820	86	95	0.2	0
1 020	41	47		
530	67	67	2.0	1.9
730	133	138	0	0
930	183	198		
1 130	175	185		
440	248	209 *	4.5	4.4
640	140	121	5.9	6.3
840	31	0		
1 040	13	0		
750	77	68		
950	120	115		
1 150	125	106		
660	51	44	2.1	2.2
860	22	0		
1 060	68	57		
970	40	37		
880	56	53		

(*hkl*)	F^{n}_{calc}	F^{n}_{obs}
004	16.4	15.0
008	2.3	2.1
011	1.1	1.5
013	11.2	11.3
015	7.1	7.4
017	5.2	5.2
022	14.5	14.8
024	8.4	8.9
026	3.1	2.6
031	12.4	14.2
033	5.1	5.9
035	6.3	7.1
037	2.3	0
042	1.5	0
044	8.1	7.3
046	3.7	0
051	14.5	13.9
053	6.1	7.3
055	6.4	5.7
057	1.1	0.9
062	8.3	10.8
064	4.1	3.6
066	1.2	0
071	8.4	7.1
073	11.9	12.1
075	1.8	0
082	2.9	2.0
084	1.2	0

described by Barstad and Andresen[6]. The neutron source was the Kjeller reactor JEEP, using monochromatic beam with wavelength 1.132 Å. Data for the *hk*0 and 0*kl* zones were recorded.

X-RAY WORK

A very accurate value for the parameter of Hg was derived from the X-ray data by means of Fourier methods. Due to the dominating influence of this atom in the X-ray spectra, a temperature parameter $B_{\text{Hg}} = 1.1$ Å^2 could be

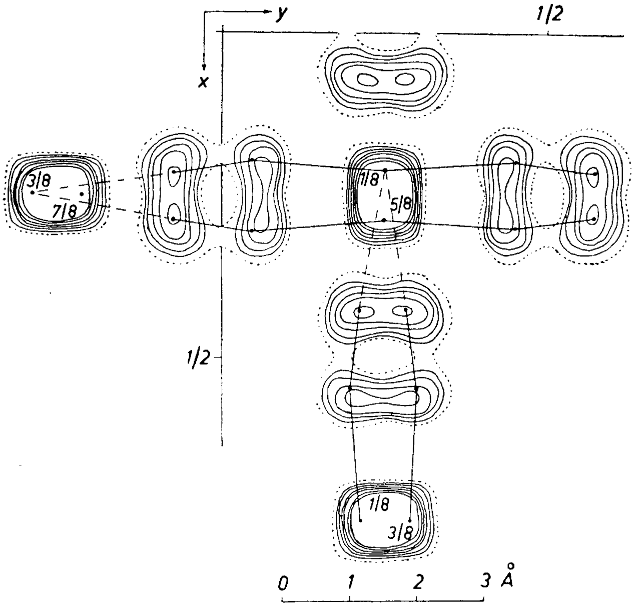

Fig. 2. Fourier projection on (001) by neutron data. Final coordinates are indicated by dots, and z-parameters of Hg are given as fractions of the cell edge. Broken lines indicate the Hg..N interactions. Contours are drawn at intervals of 0.33×10^{-12} cm/Å^2. The zero level is dotted.

assigned to this atom without knowledge of the precise light atom positions. Hence a difference synthesis with the coefficients ($F_{\rm obs}$—$F({\rm Hg})_{\rm calc}$) could be made. In the Fourier map (Fig. 1) the light atoms show up, indicating a slight deviation from linearity in the molecule. The parameters are listed in Table 1, and observed and calculated absolute values of the amplitudes are given in Table 2. The R index for the X-ray data with final parameters was 8.1 % when reflexions believed to be seriously affected by extinction were omitted.

Significant deviation from linearity in the molecule could, however, not be claimed from the X-ray data.

TREATMENT OF NEUTRON DATA

The approximate light atom positions formed the basis for further work with the neutron data. From the $hk0$ data it became evident that the linear model must be rejected. The Fourier map in Fig. 2 also indicates this, although it suffers severely from series termination errors. Successive (F_o—F_c) syntheses finally lead to the parameters given in Table 2. The B value for C and N in this zone was 1.7 Å^2.

In the projection along the a axis, the z parameters are determined from the inclination of N—C—Hg—C—N with the c axis. For this angle, Zhdanov

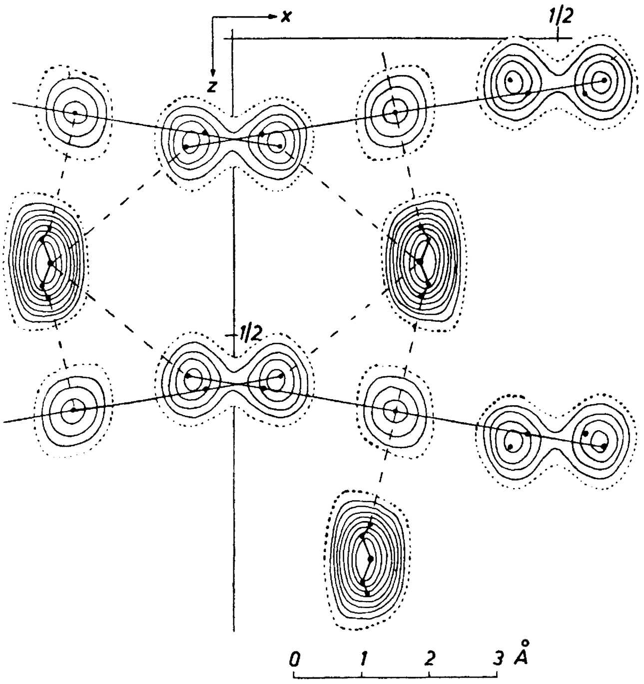

Fig. 3. Fourier projection on (100) by neutron data. Contour intervals are now drawn at intervals of 0.66 × 10^{-12} cm/Å^2. The interaction between Hg and neighbouring N atoms form zig-zag chains through the lattice, as shown by the broken lines.

and Shugam[3] suggest 76.5° while Jones[4] finds 73°. The treatment of the neutron data for this projection finally lead to the Fourier map shown in Fig. 3. It is unfortunate that most atoms overlap, but as the x and y parameters were known, the z parameters could be determined by a combination of trial-and-error methods and (F_o-F_c) syntheses. During this procedure, the parameters finally converged to the values listed in Table 1. It appeared from these values that the inclination of the molecule to the c axis was 81.2°.

Larger values for the temperature amplitudes were found in this projection. No attempt was made to correct for anisotropy, but it is believed that the higher B values ($B_{Hg} = 2.8$ Å^2, $B_{CN} = 3.3$ Å^2) are significant, indicating higher amplitudes along the c axis.

The over-all R index for the neutron data was 8.9 %, the zero observed reflexions omitted. Absolute values of the neutron amplitudes are listed in Table 2.

RESULTS AND DISCUSSION

The intramolecular distances and their estimated standard deviations (Cruickshank[7] 1949) are as follows: Hg—C = 1.986 ± 0.016 Å, C—N =

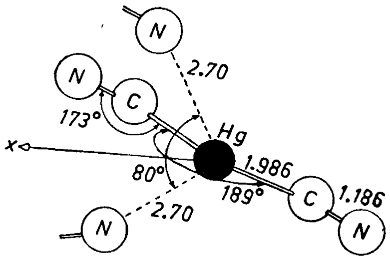

Fig. 4. The atomic arrangement around a Hg atom. The N...Hg...N plane is at an angle of 92° to the plane through the $Hg(CN)_2$ molecule, and the direction from a Hg atom along the x-direction bisects the N..Hg..N and C-Hg-C angles.

1.186 ± 0.024 Å. The angles are: C—Hg—C = 171 ± 2°, Hg—C—N = 173 ± 2°.

From the e.s.d. it must be concluded that the deviation from linearity in N—C—Hg—C—N is significant. In this connection, it is interesting to note that the distance from a mercury atom to two crystallographically equivalent N atoms in neighbouring molecules is 2.70 Å, *i. e.* 0.3—0.4 Å shorter than the van der Waals distance. The N...N distance is 3.44 Å, and the plane N...Hg...N is almost normal to C—Hg—C. Fig. 4 illustrates the atomic arrangement around a Hg atom. All other intermolecular distances have normal values.

These relationships indicate an interaction between Hg and the neighbouring cyanide groups which may be interpreted as due to electrostatic attraction. This attraction is thought to arise from the strong polar properties of the CN group, leaving a small positive charge at the Hg atom and a negative charge at the N atoms. This possibility has also been pointed out by Zhdanov and Shugam, but their N...Hg distance was only 2.52 Å, which would imply a stronger interaction.

Considering the N...Hg interaction as a bond, the $Hg(CN)_2$ molecules are linked together in endless zig-zag chains through the lattice. This is illustrated in Fig. 3.

This investigation was suggested by Dr. G. C. A. Schuit of the Koninklijke/Shell Laboratory, Amsterdam, in connection with the work in progress there in the structure of HgX_4^{--} ions.

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