266. *The* Hg–Hg *Bond Length in the Mercurous Ion. Part I. The Crystal Structure of Mercurous Nitrate Dihydrate.*

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Crystals of mercurous nitrate dihydrate, $Hg_2(NO_3)_2,2H_2O$, are monoclinic with space group C_{2h}^5-$P2_1/n$. The unit cell, of dimensions $a = 8·64$ Å, $b = 7·52$ Å, $c = 6·30$ Å, $\beta = 103°48'$, contains two formula units. The structure was determined with the aid of Patterson and Fourier–Bragg [010] and [100] projections, and by trial-and-error methods. The termination-of-series effect was quite large, so that the positions of the water molecules and nitrate ions could not be obtained accurately. The mercury atoms are linked in pairs across centres of symmetry, the distance between them being 2·54 ± 0·01 Å. Each mercury atom has three oxygen atoms as nearest neighbours, two belonging to the nitrate ion and the third to the water molecule at distances of 2·42, 2·40, and 2·15 Å, respectively. The close approach of 2·15 Å of the water molecule to the mercury atom gives evidence for a co-ordination link, resulting in the formation of an oxonium ion $[H_2O\cdot Hg\cdot Hg\cdot OH_2]^{2+}$.

Little is known about the crystal chemistry of mercurous compounds, the only crystal structures so far determined being those of mercurous chloride, bromide, and iodide.[1] These structures consist of linear X–Hg–Hg–X molecules with Hg–Hg distances of 2·53 Å in the chloride, 2·58 Å in the bromide, and 2·69 Å in the iodide. This apparent dependence of the Hg–Hg distance on the nature of the anion deserved further investigation and we have examined the mercurous nitrate dihydrate and fluoride. In the present communication the results of the crystal analysis of the former are reported and Part II (following paper) deals with the structure of mercurous fluoride.

Experimental

Crystallographic and X-*Ray Data.*—The crystals were prepared from a warm saturated solution of mercurous nitrate dihydrate in dilute nitric acid. When the solution was slowly cooled to room temperature the crystals obtained were usually prismatic, elongated in the [100] direction. By rapid cooling crystals in the form of plates parallel to (010) with well-developed (101) faces were formed. Crystals of both these habits had already been described and examined crystallographically by Marignac.[2] Another form, not described by Marignac, was also very occasionally obtained: these were prisms elongated along [010].

In the present paper all crystallographic data are referred to the axes chosen by Marignac. The unit cell as determined from oscillation photographs and goniometer measurements has the dimensions: $a = 8·64$ Å, $b = 7·52$ Å, $c = 6·30$ Å, $\beta = 103°48'$. The axial ratios $a : b : c = 1·149 : 1 : 0·838$ agree well with the values $a : b : c = 1·1503 : 1 : 0·8334$ and $\beta = 103°47·5'$ given by Marignac. Systematic extinctions were observed only for $h0l$ spectra with $h + l$ odd and for $0k0$ with k odd. The space group is therefore C_{2h}^5-$P2_1/n$. Two formula units being assumed in the unit cell, the calculated density is 4·683 in agreement with the value of 4·785 given by Playfair and Joule.[3]

Intensity Measurements.—In view of the large absorption power ($\mu = 750$ cm.$^{-1}$ for Cu-$K\alpha$ radiation) it was very important to choose a crystal whose shape was suitable for easy evaluation of the absorption correction. For recording $0kl$ spectra a plate-shaped crystal of convenient size was cut with a razor-blade parallel to the b axis. The crystal specimens were preserved from decomposition during photography by a thin coating of nitrocellulose laquer. Nickel-filtered Cu-K radiation was used, and all possible ($0kl$) and ($h0l$) spectra were recorded on double-film Weissenberg photographs. The relative intensities of the reflexions were determined from the optical densities of the spots measured with a microdensitometer and corrected by means of the characteristic curve of the film. The correction for absorption was made very carefully by applying formulæ described previously.[4] The ratios of the smallest absorption factor to the

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[1] Havighurst, *J. Amer. Chem. Soc.*, 1926, **48**, 2113.

[2] Marignac, *Ann. Chim. Phys.*, 1849, [iii], **27**, 332.

[3] Playfair and Joule, *Mem. Chem. Soc.*, 1845, **2**, 401.

[4] Grdenić, *Acta Cryst.*, 1952, **5**, 283.

largest were 1 : 60 and 1 : 29 for the *h*0*l* and 0*kl* reflexions, respectively. The corrections for polarization and Lorentz factors were made in the usual way. The number of *h*0*l* and 0*kl* reflexions observed was 64 and 49 respectively.

FIG. 1. *Electron-density projection of mercurous nitrate dihydrate along* (*a*) [010], (*b*) [100], *with superimposed atomic positions. The contacts, water–mercury, nitrate–nitrate ion, water–nitrate ion, are represented by broken lines with distances in* Å. *Contours are drawn on an arbitrary scale. Only alternate levels are drawn on the mercury-atom peaks.*

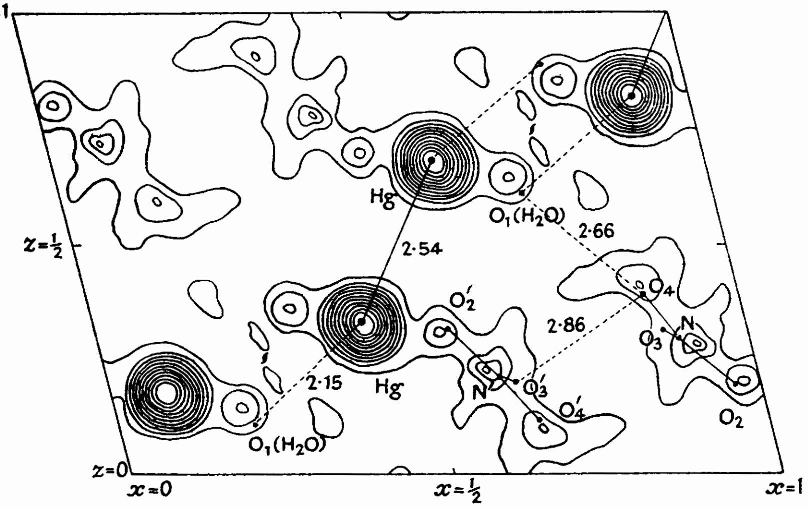
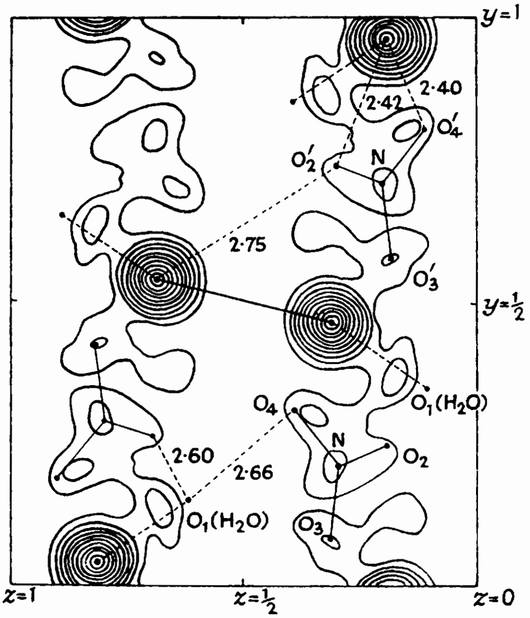


FIG. 2.



Determination of the Structure.—By using the mercury parameters $x_{Hg} = 0{\cdot}085$ and $z_{Hg} = 0{\cdot}189$, evaluated from the (*x*, *z*) Patterson projection, the signs for observed F(*h*0*l*) were calculated, with neglect of the contributions of light atoms. The Fourier projection on (010) is shown in Fig. 1. The water molecule and nitrate ion peaks are also, though badly, resolved. The parameter y_{Hg} was easily obtained by trial-and-error methods, the best agreement between observed and calculated intensities being obtained by taking $y_{Hg} = 0{\cdot}04$. By means of these y_{Hg} and z_{Hg} parameters, the signs of the observed F(0*kl*) were computed and the Fourier projection along [100] evaluated (Fig. 2). The water-molecule peak did not appear at the same position in both projections, the difference being about 0·2 Å in the *z* co-ordinate. The nitrate-ion peaks were also resolved, but not as clearly as in the [010] projection. The oxygen peak near to the mercury peak was accompanied by a broad, low, spurious peak.

The shapes and positions of the light-atom peaks appeared to be considerably influenced by diffraction effects from the mercury atoms. These effects were especially pronounced in the [100] projection, owing to the smaller number of terms used in the summation. Models of possible structures were projected on to both electron-density maps by means of a mirror and a parallel source of light, and the atomic positions adjusted to give the most reasonable fit. In this way, it was possible to establish the positions of the light atom with an accuracy of about ±0·1 Å. Table 1 contains the final atomic co-ordinates given in fractions of the unit-cell edges. Figs. 1 and 2 show the atomic positions superimposed on the Fourier projections. Because all the signs of the reflexions are defined by the contribution of the mercury atom alone, the Fourier projections could not be improved with the data available and the further refinement of the structure was therefore not possible.

TABLE 1. *Final atomic co-ordinates.*

	x	*y*	*z*		*x*	*y*	*z*
Hg	0·087	−0·038	0·188	O_3	−0·13	0·08	0·31
O_1 (H_2O)	0·21	0·34	0·10	O_4	−0·15	0·31	0·39
O_2	−0·04	0·25	0·19	N	−0·11	0·22	0·29

TABLE 2. *Observed and calculated values of the structure factors.*

*h*0*l*	$F_{obs.}$	$F_{calc.}$	*h*0*l*	$F_{obs.}$	$F_{calc.}$	0*kl*	$F_{obs.}$	$F_{calc.}$	0*kl*	$F_{obs.}$	$F_{calc.}$
200	26	30	$\bar{4}08$	2	5	002	48	−45	073	0	0
400	38	−34	501	16	−26	004	0	−2	083	2	4
600	26	−31	503	23	20	006	15	11	093	1	4
800	6	−5	505	15	−8	020	37	44	014	9	8
10,0,0	5	6	$\bar{5}01$	0	6	040	22	28	024	0	2
101	14	−4	$\bar{5}03$	15	22	060	0	2	034	22	16
103	30	−37	$\bar{5}05$	18	−21	080	6	−5	044	3	3
105	42	24	$\bar{5}07$	8	6	011	20	23	054	27	17
107	10	−7	602	17	20	021	21	−27	064	2	0
$\bar{1}01$	55	49	604	5	−4	031	12	16	074	16	12
$\bar{1}03$	30	−47	$\bar{6}02$	23	18	041	28	−37	084	0	0
$\bar{1}05$	15	18	$\bar{6}04$	3	6	051	5	6	015	22	21
$\bar{1}07$	2	1	$\bar{6}06$	9	−12	061	24	24	025	6	4
202	59	−63	701	0	4	071	0	−1	035	16	15
204	35	30	703	8	8	081	10	−10	045	6	6
206	5	−4	705	0	7	091	0	−2	055	5	4
$\bar{2}02$	17	24	$\bar{7}01$	24	−26	012	16	−17	065	8	4
$\bar{2}04$	27	−36	$\bar{7}03$	18	23	022	33	−33	075	0	1
$\bar{2}06$	16	19	$\bar{7}05$	5	−7	032	23	−17	016	5	−3
$\bar{2}08$	4	−7	$\bar{7}07$	4	−4	042	16	−19	026	13	10
301	37	−37	802	13	11	052	23	−18	036	12	7
303	14	11	804	15	−7	062	0	0	046	8	5
305	7	6	$\bar{8}02$	10	−10	072	14	−11	056	10	−7
307	10	−7	$\bar{8}04$	16	16	082	2	3	066	2	0
$\bar{3}01$	38	45	$\bar{8}06$	12	−9	092	1	−5	017	4	−4
$\bar{3}03$	11	8	901	11	13	013	39	−40	027	5	−5
$\bar{3}05$	10	−11	903	4	−4	023	10	14	037	4	−3
$\bar{3}07$	11	11	$\bar{9}01$	10	−13	033	32	−27	047	8	−5
402	4	−1	$\bar{9}03$	2	3	043	15	−6			
404	20	18	$\bar{9}05$	6	5	053	12	−9			
406	17	−10	$\overline{10},0,2$	11	−10	063	5	8			
$\bar{4}02$	46	46	$\overline{10},0,4$	12	7						
$\bar{4}04$	36	−27	$\overline{11},0,1$	0	1						
$\bar{4}06$	2	3	$\overline{11},0,3$	5	−5						

Structure factors were calculated by using values for the atomic scattering factors given in "Internationale Tabellen,"[5] multiplied by an average temperature factor with $B = 4$ Å^2.

Nevertheless, a test of the reliability of the atomic co-ordinates may be obtained by comparing the observed and the calculated structure amplitude. This is done in Table 2. At the

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[5] "Internationale Tabellen zur Bestimmung der Kristallstrukturen," Borntraeger, Berlin, 1935, Vol. II, p. 571.

first stage of the analysis, when the structure amplitudes were calculated for the mercury atom alone, the reliability index $R = \sum||F_o| - |F_c||/\sum|F_o|$ was 0·26. For the complete structure $R = 0{\cdot}25$ for the $h0l$ terms and 0·22 for the $0kl$ terms. The large disagreement for some reflexions may have been caused by uncertainty in estimation of the absorption factor when the formulæ could not be applied, *e.g.*, when the incident angle of the *X*-ray beam to the crystal face was near zero, or when a rough edge caused by cutting of the crystal was reflecting. Further, for weak or very weak reflexions the calculated contributions of light atoms were generally of the opposite sign to that of the mercury atom; this incidentally proved the reliability of the co-ordinates for oxygen and nitrogen given in Table 1.

The accuracy of the co-ordinates of mercury was estimated by Cruickshank's formula[6] for the standard deviation $\sigma(x)$ and $\sigma(z)$ of a peak position in an electron-density map. The result obtained was $\sigma(x) = \sigma(z) = 0{\cdot}005$ Å. Owing to the centre-of-symmetry relation between mercury atoms the standard deviation for the value obtained for the Hg–Hg bond length is $\sigma(d_{\text{Hg-Hg}}) = 0{\cdot}01$ Å.

DISCUSSION

Determination of the Hg–Hg bond length in the mercurous ion was the main aim of this investigation. The value obtained, 2·54 ± 0·01 Å, is almost equal to that found previously[1] for the Hg–Hg distance in crystals of mercurous chloride. Further discussion of this value does not seem to be very profitable until more data on the Hg–Hg bond length in various mercurous compounds are collected.

The positions of the light atoms obtained define the structure in a satisfactory way. The distances and the co-ordination of the atoms are consistent with known crystallochemical facts. The length of the N–O bonds in the nitrate ion is 1·1 Å and the angle between them about 120°, which, within the estimated limits of error, correspond to recorded values (1·20 Å and 120°).

The light-atom part of the structure can be described in the following way: The nitrate ions related by a two-fold screw axis are arranged in infinite chains parallel to the *b* axis. The contact distance between each nitrate ion and a neighbour in the same chain, measured by the oxygen–oxygen distance (O_4–O_3'), is 2·86 Å. There is no direct contact between the nitrate-ion chains, but they are linked across by means of water molecules at rather short contact distances of 2·60 Å from each chain, probably by means of hydrogen bonds. From each water molecule two such bonds are directed to two different nitrate ions at an angle of 110°. Thus, the nitrate ions and water molecules together form a frame-work, in the holes of which the mercurous ions are located in such a way that each mercury atom is surrounded by four atoms, namely the next mercury atom at 2·54 Å, two oxygen atoms of the same nitrate ion at 2·40 and 2·42 Å, and one oxygen atom belonging to a water molecule at a distance of 2·15 Å. The short distance between the mercury atom and the water molecule suggests a polarisation effect of the mercurous ion on the water molecule, and that an oxonium ion, $[H_2O\text{–}Hg\text{–}Hg\text{–}OH_2]^{2+}$, probably exists in the crystal structure. The bond angle Hg–Hg–OH_2, which should be 180° if the bond were truly covalent, is about 160°. This departure indicates the remarkable influence of the neighbouring nitrate ion, resulting in the formation of the hydrogen bonds described above. It may be assumed that such an oxonium ion occurs also in a solution of mercurous nitrate. A short co-ordination bond of nearly the same length (2·21 Å) has been shown to exist in mercury diethylene oxide.[7] A much shorter, covalent Hg–O bond (2·03 Å) was found recently in the crystal structure of tri(chloromercury)oxonium chloride[8] and in trimercuric oxychloride.[9]

The values for the distances from mercury to the nitrate-oxygen atoms (2·40 and 2·42 Å) are in both cases less than the sum of corresponding van der Waals radii (1·50 Å for mercury and 1·40 Å for oxygen), so that they also suggest polarization caused by the mercurous ion. It is interesting that this distance is nearly equal to the sum of ionic

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[6] Cruickshank, *Acta Cryst.*, 1949, **2**, 65.

[7] Grdenić, *ibid.*, 1952, **5**, 367.

[8] Scavnicar and Grdenić, *ibid.*, 1955, **8**, 275.

[9] Scavnicar, *ibid.*, p. 379.

radii if the values of 1·10 Å, the generally accepted value for the radius of the mercuric ion, and 1·35 Å for the oxygen are used.

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