

SHORT COMMUNICATION

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Acta Cryst. (1975). B31, 2174

A redetermination of the crystal structure of mercury(I) nitrate dihydrate. By D. GRĐENIĆ, M. ŠIKIRICA and I. VICKOVIĆ, *Laboratory of General and Inorganic Chemistry, Faculty of Science, University of Zagreb, P.O. Box 153, 41001 Zagreb, Yugoslavia*

(Received 12 February 1975; accepted 12 March 1975)

The crystal structure of $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ was redetermined on the basis of three-dimensional X-ray diffraction data and refined to a final R of 0.054. The new light-atom coordinates differ essentially from those proposed previously. The hydrogen bonds, with lengths 2.68 and 2.70 Å, which interconnect the centrosymmetric cations $[\text{H}_2\text{O}-\text{Hg}-\text{Hg}-\text{OH}_2]^{2+}$ through the nitrate oxygen atoms form a helix about every other twofold screw axis. The bond lengths are Hg–Hg 2.508 Å, Hg–OH₂ 2.13 Å, with a Hg–Hg–OH₂ bond angle of 167.5°.

The redetermination of the crystal structure of mercury(I) nitrate dihydrate was desirable because the reported light-atom coordinates (Grđenić, 1956) did not satisfy the currently required reliability criteria. The disagreement between the proposed orientation of the water molecules in the crystal structure and that determined by El Saffar (1973) using proton magnetic resonance prompted the redetermination of the structure, the results of which are here reported.

The previous crystallographic data (space group $P2_1/n$, two formula units in the unit cell) were confirmed and the following more accurate unit-cell dimensions were obtained: $a = 8.633$ (3), $b = 7.506$ (4), $c = 6.256$ (3) Å, $\beta = 103.8$ (1)°, giving $V = 393.7$ Å³ and $D_x = 4.733$ g cm⁻³ ($D_m = 4.785$ g cm⁻³). The crystal used was ground to a sphere of 0.025 cm in diameter and protected from the atmosphere by a thin polystyrene coating. The three-dimensional diffraction data were recorded on a Philips PW 1100 four-circle automatic diffractometer using graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). The intensities of 736 independent reflexions with $I \geq 3\sigma(I)$ were recorded (all reflexions having $\theta \leq 30^\circ$), the usual Lorentz, polarization and absorption corrections [$\mu(\text{Mo } K\alpha) = 402.7$ cm⁻¹] were applied and the three-dimensional Fourier synthesis calculated from the previous mercury atom coordinates. The structure was then refined by two cycles of full-matrix least-squares refinement with isotropic thermal parameters to $R = 0.107$. Four cycles of refinement were then computed assuming anisotropic thermal parameters. Unit weight was used for all observations. The final reliability index was $R = 0.054$. Table 1 gives the final atomic coordinates together with the thermal

parameters. The atomic scattering factors according to Cromer & Mann (1968) with corrections for the anomalous scattering for the non-hydrogen atoms according to Cromer & Liberman (1970) were used.*

The structure is built up of the complex aquo-cation $[\text{H}_2\text{O}-\text{Hg}-\text{Hg}-\text{OH}_2]$ and nitrate anions. The interatomic distances of Hg–Hg 2.508 Å and Hg–OH₂ 2.13 Å with the bond angle Hg–Hg–OH₂ of 167.5° (Table 2) are in perfect agreement with the values reported for the crystal structure of the analogous mercurous compounds (Johansson, 1966; Dorm, 1971). The interatomic distances and bond angles in the nitrate ion also agree well with the known data (Addison, Logan, Walwork & Garner, 1971).

Each water molecule in the cation is linked to two oxygen atoms O(2) from two nitrate ions related to each other by the 2₁ symmetry operation so that two water molecules have one common nitrate oxygen atom O(2). In this way the hydrogen bonds, with the length of 2.68 and 2.70 Å originating from each water molecule form a helix about every other twofold screw axis (Fig. 1). A comparatively large hydrogen-bond angle of 115.0° at O(H₂O) explains the large proton–proton separation of 1.66 Å determined by El Saffar (1973). The line connecting the nitrate oxygen atoms

* The table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31007 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional atomic coordinates ($\times 10^4$) and thermal parameters ($\times 10^4$).

	x	y	z	β_{11}	β_{12}	β_{13}	β_{22}	β_{23}	β_{33}
Hg	858 (1)	−367 (2)	1866 (2)	65 (1)	12 (4)	−26 (2)	100 (2)	13 (5)	135 (2)
O(H ₂ O)	1829 (30)	−1118 (34)	5195 (41)	184 (44)	−318 (79)	−175 (95)	143 (45)	164 (105)	370 (83)
O(1)	4014 (25)	615 (27)	2757 (34)	105 (29)	77 (60)	157 (72)	91 (42)	1 (77)	243 (65)
O(2)	5995 (23)	−1027 (27)	2280 (29)	71 (25)	54 (52)	103 (62)	112 (33)	−33 (71)	180 (56)
O(3)	3504 (22)	−1955 (26)	1300 (33)	60 (25)	21 (48)	−83 (61)	105 (34)	−45 (76)	219 (60)
N	4513 (24)	−791 (28)	2041 (33)	66 (28)	40 (49)	−48 (60)	67 (38)	27 (64)	126 (50)

Estimated standard deviations are in parentheses.
Thermal parameters are in the form $\exp[-(\beta_{11}h^2 + \dots + 2\beta_{23}kl)]$

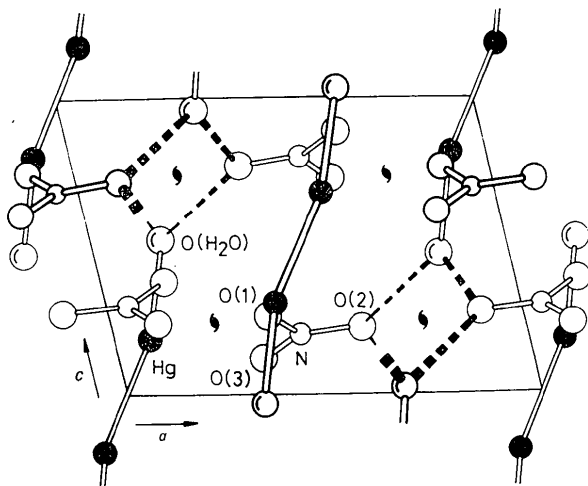


Fig. 1. Projection of the crystal structure on the *ac* plane.

O(2ⁱⁱⁱ) and O(2), which are linked to the water molecule by the hydrogen bonds, is defined by a polar angle of 94.2° from [001] and an azimuthal angle of ±34.7° from [010]. This is in good agreement with the values of 98° and ±42°, respectively, determined by El Saffar (1973) for the proton-proton direction if it is assumed parallel to the O(2ⁱⁱⁱ)-O(2) direction. All atoms apart from the mercury atom at a distance less than the sum of the van der Waals radii are considered to belong to the effective coordination about mercury (Grdenić, 1965). There are three nitrate oxygen atoms at the distances of 2.68, 2.75 and 2.81 Å in addition to one mercury and one water oxygen atom at 2.508 and 2.13 Å, respectively, in an irregular square pyramid.

The authors thank Professor A. Coda, University of Pavia, for help in collecting the automatic diffractometer

Table 2. Interatomic distances (Å) and bond angles (°) with their estimated standard deviations in the last figure (in parentheses)

Hg-Hg ^I	2.508 (2)	O(2 ⁱⁱ)...O(H ₂ O ⁱⁱⁱ)	2.70 (3)
Hg-O(H ₂ O)	2.13 (2)	Hg...O(3)	2.68 (2)
N-O(1)	1.26 (3)	Hg...O(1)	2.75 (2)
N-O(2)	1.26 (3)	Hg...O(1')	3.03 (2)
N-O(3)	1.24 (3)	Hg...O(3')	2.81 (2)
O(2 ⁱⁱ)...O(H ₂ O)	2.68 (3)	O(1)...O(3')	3.00 (3)
Hg ^I -Hg-O(H ₂ O)			167.5 (7)
O(1)-N-O(2)			119.8 (20)
O(2)-N-O(3)			123.0 (21)
O(3)-N-O(1)			116.9 (21)
O(H ₂ O)...O(2 ⁱⁱ)...O(H ₂ O ⁱⁱⁱ)			122.1 (15)
O(2 ⁱⁱ)...O(H ₂ O ⁱⁱⁱ)...O(2 ^{iv})			115.0 (15)

The positions without a label are given by *x, y, z*, as in Table 1. The labels are as follows: (i) $-x, -y, -z$; (ii) $1-x, -y, 1-z$; (iii) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (iv) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

data, and the Scientific Research Council, Zagreb, for financial support.

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Book Review

Works intended for notice in this column should be sent direct to the Book-Review Editor (M. M. Woolfson, Physics Department, University of York, Heslington, York YO1 5DD, England). As far as practicable books will be reviewed in a country different from that of publication.

The chemistry of imperfect crystals. By F. A. KRÖGER.

Vol. 1: pp.xiii+313, Figs. 58, Tables 10. Price £70.00 (about U.S. \$25.50). Vol. 2: pp. 1000. Price £275.00 (about U.S. \$105.75). Vol. 3: pp.xiv+306, Figs. 42, Tables 15. Price £100.00 (about U.S. \$38.50). Amsterdam: North Holland, 1974.

This is a book primarily for research workers already in, or about to enter, the field of solid-state physics, chemistry or materials science; it is a book for the working specialist rather than the amateur. It concedes little to a user unfamiliar with crystal structures or to one who does not already know the context and priorities of the subject.

The first edition was published in 1964; the second is a thoroughly up-dated and somewhat expanded version. The

book has the characteristics both of a textbook, with its detailed didactic presentation of theory, and of a review with its numerous references to the literature. This dual objective is the main difficulty of the book, for with so large a subject the material has become so bulky that its practical usefulness is jeopardized. The author is aware of the size of the field and of the existence of many smaller works dealing with specialized areas, but he is also aware of the value of a coherent presentation of a subject by a single author. He consciously offers his book, therefore, as giving, 'as before, a one-man view of solid-state chemistry'.

The new edition has essentially the same structure as the first but the three parts of the original book have become three separately bound volumes. The first volume (which appeared ahead of the other two, about six months ago)