

Structural Study of the System $\text{Hg}_2\text{O}-\text{N}_2\text{O}_5-\text{H}_2\text{O}$; Crystal Structures of Three Basic Mercury(I) Nitrates – Hydrolysis Products of Mercury(I) Nitrate Dihydrate

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Abstract. (1) $[(\text{Hg}_2)_2\text{O}(\text{NO}_3)]\text{NO}_3 \cdot \text{HNO}_3$, $M_r = 1005.4$, orthorhombic, *Aba*2, $a = 11.222$ (8), $b = 20.178$ (2), $c = 9.354$ (2) Å, $V = 2118$ (2) Å³, $Z = 8$, $D_m = 6.30$, $D_x = 6.306$ g cm⁻³, Mo *Kα*, $\lambda = 0.71069$ Å, $\mu = 558.1$ cm⁻¹, $F(000) = 3376$, room temperature. (2) $[(\text{Hg}_2)_5(\text{OH})_4(\text{NO}_3)_2](\text{NO}_3)_4$, $M_r = 2446.0$, triclinic, *P*1̄, $a = 9.990$ (3), $b = 9.091$ (4), $c = 7.657$ (3) Å, $\alpha = 94.05$ (3), $\beta = 101.25$ (3), $\gamma = 109.75$ (3)°, $V = 634.9$ (5) Å³, $Z = 1$, $D_m = 6.31$, $D_x = 6.398$ g cm⁻³, Mo *Kα*, $\lambda = 0.71069$ Å, $\mu = 581.8$ cm⁻¹, $F(000) = 1022$, room temperature. (3) $[\text{Hg}_2(\text{OHg})_2](\text{NO}_3)_2$, $M_r = 958.4$, monoclinic, *P*2₁/c, $a = 5.532$ (3), $b = 6.659$ (2), $c = 11.578$ (5) Å, $\beta = 98.84$ (3)°, $V = 421.4$ (3) Å³, $Z = 2$, $D_m = 7.52$, $D_x = 7.552$ g cm⁻³, Mo *Kα*, $\lambda = 0.71069$ Å, $\mu = 699.8$ cm⁻¹, $F(000) = 796$, room temperature. For structure solutions direct methods [*MULTAN*80, (1)] and Patterson methods [(2) and (3)] were used. Full-matrix least-squares refinements led to *R* values of 0.064 for (1), 0.067 for (2) and 0.060 for (3) using 1245, 2619 and 1071 unique reflections respectively [$I > 3\sigma(I)$]. Compound (1) is built up of mercurioxonium infinite chains with solvated HNO_3 molecules hydrogen-bonded to one of the nitrate ions, (2) of finite four-oxonium-link chains, and (3) of folded infinite oxonium layers containing Hg^I and Hg^{II} ions.

Introduction. As early as 1933, in their study of the ternary system $\text{Hg}_2\text{O}-\text{N}_2\text{O}_5-\text{H}_2\text{O}$, Denham & Fife (1933) concluded that more than thirty compounds had been described as phases of this system (see also Mellor, 1957). Forty-five years later, by the analysis of the vibrational spectra of mercurous nitrate dihydrate and its hydrolysis products, Tan & Taylor (1978)

confirmed the existence of only three 'basic' mercurous nitrates.*

Tan & Taylor were able to identify the functional groups but left solution of the structure to X-ray crystallography. In spite of the difficulties in the preparation of the single crystals, particularly the crystals of (3), we were successful in the structure determination of all three identified compounds.

Table 1 summarizes the previous results together with the correct formulae found in this investigation.

Experimental. The crystals of (1), (2) and (3) were prepared as described by Tan & Taylor (1978). Density was measured pycnometrically in CCl_4 . Unit-cell parameters were obtained from least-squares analysis of 20 reflections for (1) and (2) and 16 reflections for (3) on a Philips PW 1100 computer-controlled diffractometer. Intensity data were recorded on the same instrument using Mo *Kα* radiation ($\lambda = 0.71069$ Å; graphite-monochromatized), in the $\theta/2\theta$ scan mode and with a θ range of 2 to 30°. Data for all the compounds were corrected for Lorentz and polarization effects and (owing to the high absorption power of the crystals) also for absorption. Additional crystal data and experimental information are given in Table 2.

The structures of all three compounds were obtained using standard methods: Hg atoms were located either by three-dimensional Patterson synthesis or by means of *MULTAN*80 (Main *et al.*, 1980) [compound (1)], while the Fourier maps phased on the Hg-atom positions afforded the coordinates of all non-hydrogen

* We have noticed the existence of more than three products but they were unstable.

Table 1. Basic mercury(I) nitrates

| Phase (Denham & Fife, 1933) | Alternative formulation | Suggested on the basis of vibrational spectra (Tan & Taylor, 1978) | Formulae based on X-ray structure determination (this work) |
|--|--|---|--|
| (1) $4\text{Hg}_2\text{O} \cdot 3\text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}(\text{C})$ | $\text{Hg}_2(\text{OH})_2 \cdot 3\text{Hg}_2(\text{NO}_3)_2$ | $\text{Hg}_2(\text{NO}_3)_2 \cdot \text{Hg}_2\text{OH} \cdot \text{NO}_3$ | $[(\text{Hg}_2)_2\text{O}(\text{NO}_3)]\text{NO}_3 \cdot \text{HNO}_3$ |
| (2) $5\text{Hg}_2\text{O} \cdot 3\text{N}_2\text{O}_5 \cdot 3\text{H}_2\text{O}(\text{B})$ | $2\text{Hg}_2(\text{OH})_2 \cdot 3\text{Hg}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ | $2\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{Hg}_2(\text{OH})_2 \cdot \text{Hg}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O} \cdot \text{NO}_3$ | $[(\text{Hg}_2)_5(\text{OH})_4(\text{NO}_3)_2](\text{NO}_3)_4$ |
| (3) $2\text{Hg}_2\text{O} \cdot \text{N}_2\text{O}_5 \cdot \text{H}_2\text{O}(\text{A})$ | $\text{Hg}_2(\text{OH})_2 \cdot \text{Hg}_2(\text{NO}_3)_2$ | $\text{Hg}_2(\text{OH})(\text{NO}_3)$ (?) | $[\text{Hg}_2(\text{OHg})_2](\text{NO}_3)_2$ |

Table 2. Additional crystal data and experimental information

| | (1) | (2) | (3) |
|--|---|--|--|
| Crystal dimensions (mm from centroid) | (120), ($\bar{1}20$), ($1\bar{2}0$), ($\bar{1}20$) 0.040 (001), (00 $\bar{1}$) 0.109 | (010), (0 $\bar{1}0$) 0.079 (101), ($\bar{1}0\bar{1}$) 0.113 ($\bar{1}01$), ($10\bar{1}$) 0.075 (001), (00 $\bar{1}$) 0.101 | (010), (0 $\bar{1}0$) 0.050 (001), (00 $\bar{1}$) 0.013 ($\bar{5}12$), ($\bar{5}\bar{1}2$) 0.120 |
| Scan rate ($^{\circ}$ s $^{-1}$) | 0.03 | 0.04 | 0.04 |
| Scan width ($^{\circ}$) | 1.2 | 1.2 | 1.6 |
| Total unique data | 1308 | 2740 | 1104 |
| Least-squares parameters | 88 | 172 | 44 |
| ($\Delta\rho$) _{max} (e Å $^{-3}$) | ≤ 4.6 | ≤ 7.6 | ≤ 5.7 |
| Weights | $\cdot \{ \sigma^2(F_o) + 0.01594F_o^2 \}^{-1}$ | $\{ \sigma^2(F_o) + 0.01147F_o^2 \}^{-1}$ | $\{ \sigma^2(F_o) + 0.02875F_o^2 \}^{-1}$ |
| Largest Δ/σ in final cycle | 0.004 | 0.049 | 0.037 |

atoms. H atoms were not located. The structures were refined (on F) by full-matrix least-squares procedure assuming anisotropic thermal motion only for Hg atoms (1), Hg and oxonium O atoms (3) and for all atoms (2). The final R values are 0.064 ($wR = 0.067$) for (1), 0.067 ($wR = 0.067$) for (2) and 0.060 ($wR = 0.061$) for (3). The scattering factors for all atoms and correction for anomalous dispersion for the Hg atom were taken from *International Tables for X-ray Crystallography* (1974). No correction for secondary extinction. Calculations were made on the Univac 1110 computer of the University Computing Centre in Zagreb with the *SHELX76* system of programs (Sheldrick, 1976).*

Discussion. The atomic coordinates, equivalent isotropic thermal parameters and relevant interatomic distances and angles are listed in Tables 3 and 4 for (1), 5 and 6 for (2) and 7 and 8 for (3).

The mercurioxonium ion is the common feature in these three 'basic' mercury(I) nitrates (Fig. 1) (Kamenar, Matković-Čalogović & Nagl, 1981, 1985; Kamenar, Nagl & Matković-Čalogović, 1983). In the structure of (1) it is an infinite chain with the solvated HNO₃ molecule hydrogen-bonded to one nitrate ion,† in the structure of (2) a finite four-oxonium-link chain, and in the structure of (3) an infinite folded layer containing both Hg^I and Hg^{II} ions. Consequently, the best formulations of the compounds (1), (2) and (3) are [(Hg₂)₂O(NO₃)]NO₃.HNO₃, [(Hg₂)₅(OH)₄(NO₃)₂](NO₃)₄ and [Hg₂(OH)₂](NO₃)₂, respectively. All three structures are of interest because little is known about the structure of mercurioxonium compounds in the Hg^I series (Mereiter & Zemann, 1976; Stålhandske, Aurivillius & Bertinsson, 1985) compared with the Hg^{II} series

* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42539 (35 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† When this manuscript was completed we became acquainted with the paper by Brodersen, Liehr, Prochaska & Schottner (1985) in which a different interpretation of the structure of (1) was proposed. We agree with Professor Brodersen that the final answer should be left to the neutron diffraction analysis.

Table 3. [(Hg₂)₂O(NO₃)]NO₃.HNO₃: atomic coordinates, equivalent isotropic thermal parameters for mercury atoms and isotropic thermal parameters for the other atoms with e.s.d.'s in parentheses

Here and in Table 5 and 7 the anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameters defined as: $U_{eq} = \sum_i \sum_j b_{ij}(\mathbf{a}_i, \mathbf{a}_j) / 6\pi^2$.

| | x | y | z | U_{eq} or U_{iso} (Å ²) |
|-------|------------|------------|-------------|---|
| Hg(1) | 0.0766 (1) | 0.4546 (1) | 0. | 0.0330 (4) |
| Hg(2) | 0.4045 (1) | 0.4680 (1) | -0.0164 (2) | 0.0283 (4) |
| Hg(3) | 0.2873 (2) | 0.2970 (1) | 0.0017 (3) | 0.0417 (5) |
| Hg(4) | 0.2495 (2) | 0.1807 (1) | -0.0811 (3) | 0.0387 (5) |
| O | 0.250 (2) | 0.408 (1) | -0.038 (2) | 0.018 (4) |
| N(1) | 0.280 (2) | 0.054 (1) | -0.240 (3) | 0.014 (5) |
| O(11) | 0.253 (3) | 0.071 (2) | -0.118 (5) | 0.047 (9) |
| O(12) | 0.265 (2) | 0.000 (1) | -0.281 (3) | 0.025 (5) |
| O(13) | 0.326 (2) | 0.103 (1) | -0.320 (4) | 0.033 (6) |
| N(2) | 0.462 (3) | 0.328 (2) | 0.262 (3) | 0.027 (6) |
| O(21) | 0.510 (3) | 0.286 (2) | 0.193 (4) | 0.038 (6) |
| O(22) | 0.492 (3) | 0.344 (2) | 0.376 (4) | 0.039 (7) |
| O(23) | 0.366 (3) | 0.359 (2) | 0.208 (4) | 0.047 (8) |
| N(3) | 0.501 (3) | 0.142 (2) | 0.267 (3) | 0.027 (7) |
| O(31) | 0.500 (3) | 0.162 (1) | 0.392 (3) | 0.032 (6) |
| O(32) | 0.413 (2) | 0.144 (2) | 0.193 (3) | 0.032 (6) |
| O(33) | 0.606 (3) | 0.128 (2) | 0.213 (4) | 0.043 (7) |

Table 4. [(Hg₂)₂O(NO₃)]NO₃.HNO₃: selected interatomic distances and angles

| (a) Bond lengths (Å) and angles ($^{\circ}$) | | | |
|--|-----------|--------------------------------|------------|
| Hg(1)–Hg(1) | 2.513 (3) | O–Hg(1)–Hg(1) | 157.1 (5) |
| Hg(2)–Hg(2 ^b) | 2.502 (2) | O–Hg(2)–Hg(2 ^b) | 173.3 (5) |
| Hg(3)–Hg(4) | 2.507 (3) | O–Hg(3)–Hg(4) | 145.9 (5) |
| Hg(1)–O | 2.19 (2) | O(23)–Hg(3)–Hg(4) | 141.1 (9) |
| Hg(2)–O | 2.12 (2) | O(11)–Hg(4)–Hg(3) | 165.8 (10) |
| Hg(3)–O | 2.31 (2) | Hg(1)–O–Hg(2) | 117.7 (9) |
| Hg(4)–O(11) | 2.24 (4) | Hg(1)–O–Hg(3) | 123.5 (10) |
| N(1)–O(11) | 1.23 (5) | Hg(2)–O–Hg(3) | 112.9 (10) |
| N(1)–O(12) | 1.17 (3) | O(11)–N(1)–O(12) | 122 (3) |
| N(1)–O(13) | 1.34 (4) | O(11)–N(1)–O(13) | 114 (3) |
| N(2)–O(21) | 1.19 (5) | O(12)–N(1)–O(13) | 124 (3) |
| N(2)–O(22) | 1.16 (5) | O(21)–N(2)–O(22) | 124 (4) |
| N(2)–O(23) | 1.34 (5) | O(21)–N(2)–O(23) | 119 (3) |
| N(3)–O(31) | 1.24 (4) | O(22)–N(2)–O(23) | 117 (4) |
| N(3)–O(32) | 1.21 (4) | O(31)–N(3)–O(32) | 122 (3) |
| N(3)–O(33) | 1.31 (5) | O(31)–N(3)–O(33) | 116 (3) |
| | | O(32)–N(3)–O(33) | 121 (3) |
| (b) Interatomic contacts (Å) | | | |
| Hg(1)···O(22 ⁱⁱⁱ) | 2.63 (4) | Hg(4)···O(13) | 2.86 (3) |
| Hg(1)···O(33 ^{iv}) | 2.62 (4) | Hg(4)···O(22 ^{vi}) | 2.97 (3) |
| Hg(2)···O(12 ^v) | 2.78 (3) | Hg(4)···O(31 ^{vii}) | 2.84 (3) |
| Hg(2)···O(31 ^{viii}) | 2.96 (2) | Hg(4)···O(32 ^{viii}) | 2.89 (3) |
| Hg(2)···O(11 ^{ix}) | 2.89 (4) | Hg(1)···Hg(2) | 3.693 (3) |
| Hg(3)···O(31 ^x) | 2.73 (3) | Hg(1)···Hg(3) | 3.963 (3) |
| Hg(3)···O(23) | 2.46 (4) | Hg(2)···Hg(3) | 3.697 (3) |
| | | O(32)···O(13 ^{xiii}) | 2.81 (3) |

Superscripts refer to the following equivalent positions relative to atom x, y, z : (i) $-x, 1-y, z$; (ii) $1-x, 1-y, z$; (iii) $0.5-x, y, z-0.5$; (iv) $x-0.5, 0.5-y, z$; (v) $x, y+0.5, z+0.5$; (vi) $1-x, 0.5-y, z-0.5$; (vii) $0.5-x, y+0.5, z$; (viii) $0.5-x, y, 0.5+z$.

Table 5. $[(\text{Hg}_2)_5(\text{OH})_4(\text{NO}_3)_2](\text{NO}_3)_4$: coordinates and equivalent isotropic thermal parameters with *e.s.d.*'s in parentheses

| | x | y | z | $U_{eq}(\text{Å}^2)$ |
|-------|------------|------------|------------|----------------------|
| Hg(1) | 0.2508 (1) | 0.7665 (1) | 0.6373 (1) | 0.0320 (3) |
| Hg(2) | 0.2890 (1) | 0.0514 (1) | 0.7176 (1) | 0.0326 (3) |
| Hg(3) | 0.4377 (1) | 0.4315 (1) | 0.6135 (1) | 0.0299 (3) |
| Hg(4) | 0.0779 (1) | 0.3640 (1) | 0.7380 (1) | 0.0362 (3) |
| Hg(5) | 0.8869 (1) | 0.1540 (1) | 0.8440 (1) | 0.0357 (3) |
| O(1) | 0.316 (1) | 0.291 (2) | 0.781 (2) | 0.027 (4) |
| O(2) | 0.204 (2) | 0.523 (2) | 0.585 (2) | 0.032 (5) |
| N(1) | 0.070 (2) | 0.205 (2) | 0.278 (2) | 0.030 (6) |
| O(11) | 0.989 (2) | 0.089 (2) | 0.157 (2) | 0.042 (7) |
| O(12) | 0.145 (3) | 0.185 (3) | 0.415 (3) | 0.071 (9) |
| O(13) | 0.065 (3) | 0.334 (2) | 0.256 (3) | 0.065 (8) |
| N(2) | 0.686 (2) | 0.368 (3) | 0.911 (3) | 0.044 (9) |
| O(21) | 0.639 (3) | 0.475 (3) | 0.931 (3) | 0.062 (9) |
| O(22) | 0.787 (2) | 0.360 (2) | 0.035 (2) | 0.039 (6) |
| O(23) | 0.630 (2) | 0.260 (3) | 0.783 (3) | 0.055 (8) |
| N(3) | 0.394 (2) | 0.130 (2) | 0.203 (3) | 0.029 (5) |
| O(31) | 0.278 (2) | 0.049 (2) | 0.080 (2) | 0.038 (5) |
| O(32) | 0.413 (2) | 0.095 (2) | 0.356 (2) | 0.044 (6) |
| O(33) | 0.487 (2) | 0.240 (2) | 0.153 (3) | 0.053 (7) |

Table 6. $[(\text{Hg}_2)_5(\text{OH})_4(\text{NO}_3)_2](\text{NO}_3)_4$: selected interatomic distances and angles

| (a) Bond lengths (Å) and angles (°) | | | |
|-------------------------------------|-----------|---|-----------|
| Hg(1)—Hg(2 ⁱⁱ) | 2.500 (2) | O(2)—Hg(1)—Hg(2 ⁱⁱⁱ) | 174.5 (5) |
| Hg(3)—Hg(3 ⁱⁱ) | 2.495 (1) | O(1)—Hg(2)—Hg(1 ^{iv}) | 178.5 (3) |
| Hg(4)—Hg(5 ^{iv}) | 2.511 (1) | O(1)—Hg(3)—Hg(3 ^v) | 172.9 (4) |
| Hg(1)—O(2) | 2.09 (2) | O(2)—Hg(4)—Hg(5 ^{vi}) | 166.1 (4) |
| Hg(2)—O(1) | 2.11 (2) | Hg(4 ^{vii})—Hg(5)—O(3 ^{ix}) | 174.3 (5) |
| Hg(3)—O(1) | 2.13 (2) | Hg(2)—O(1)—Hg(3) | 110.6 (7) |
| Hg(4)—O(2) | 2.15 (2) | Hg(1)—O(2)—Hg(4) | 120.7 (9) |
| Hg(5)—O(3 ^{ix}) | 2.22 (2) | O(12)—N(1)—O(13) | 122 (2) |
| N(1)—O(11 ^{ix}) | 1.27 (2) | O(12)—N(1)—O(11 ^{ix}) | 121 (2) |
| N(1)—O(12) | 1.23 (3) | O(13)—N(1)—O(11 ^{ix}) | 117 (2) |
| N(1)—O(13) | 1.21 (3) | O(21)—N(2)—O(23) | 122 (2) |
| N(2)—O(21) | 1.23 (4) | O(21)—N(2)—O(22 ^{ix}) | 119 (2) |
| N(2)—O(22 ^{ix}) | 1.27 (3) | O(23)—N(2)—O(22 ^{ix}) | 118 (3) |
| N(2)—O(23) | 1.23 (3) | O(31)—N(3)—O(32) | 121 (2) |
| N(3)—O(31) | 1.29 (2) | O(31)—N(3)—O(33) | 116 (2) |
| N(3)—O(32) | 1.23 (3) | O(32)—N(3)—O(33) | 123 (2) |
| N(3)—O(33) | 1.25 (3) | N(3)—O(31)—Hg(5 ^x) | 117 (1) |

| (b) Interatomic contacts (Å) | | | |
|------------------------------|----------|------------------------------|-----------|
| Hg(5)···O(22 ^{ix}) | 2.84 (2) | Hg(5)···O(11 ^{ix}) | 2.87 (2) |
| Hg(5)···O(11 ^{ix}) | 2.61 (2) | Hg(1)···O(22 ^{ix}) | 2.87 (2) |
| Hg(2)···O(31 ^{ix}) | 2.80 (2) | Hg(4)···O(22 ^{ix}) | 2.71 (2) |
| Hg(4)···O(1) | 2.65 (1) | Hg(1)···O(33 ^{ix}) | 2.81 (2) |
| Hg(3)···O(2) | 2.71 (2) | Hg(1)···Hg(4) | 3.690 (2) |
| Hg(3)···O(21) | 2.74 (2) | Hg(2)···Hg(3) | 3.488 (2) |

Superscripts refer to the following equivalent positions relative to atom *x, y, z*: (i) 1 - *x, 1 - y, 1 - z*; (ii) *x - 1, y, z*; (iii) *x, 1 + y, z*; (iv) *x, y - 1, z*; (v) 1 - *x, -y, 1 - z*; (vi) *x, y, 1 + z*; (vii) 2 - *x, -y, 1 - z*; (viii) 1 + *x, y, z*.

Table 7. $[\text{Hg}_2(\text{OHg})_2](\text{NO}_3)_2$: coordinates, equivalent isotropic thermal parameters for Hg(1), Hg(2) and O and isotropic thermal parameters for the nitrate atoms with *e.s.d.*'s in parentheses

| | x | y | z | U_{eq} or $U_{iso}(\text{Å}^2)$ |
|-------|------------|------------|------------|-----------------------------------|
| Hg(1) | 0.0001 (1) | 0.3054 (1) | 0.2404 (1) | 0.0155 (2) |
| Hg(2) | 0.3231 (1) | 0.0126 (1) | 0.0557 (1) | 0.0174 (2) |
| O | 0.015 (2) | 0.044 (2) | 0.148 (1) | 0.013 (3) |
| N | 0.457 (3) | 0.519 (2) | 0.136 (1) | 0.021 (3) |
| O(1) | 0.637 (2) | 0.587 (2) | 0.104 (1) | 0.019 (2) |
| O(2) | 0.476 (2) | 0.365 (2) | 0.205 (2) | 0.036 (3) |
| O(3) | 0.247 (2) | 0.590 (2) | 0.107 (1) | 0.021 (2) |

in which the occurrence of the oxonium ions has been well established (Grdenić, 1965, 1981).

$[(\text{Hg}_2)_2\text{O}(\text{NO}_3)]\text{NO}_3 \cdot \text{HNO}_3$ (1)

In the structure of (1) there are four crystallographically independent Hg atoms in general positions forming three Hg_2^{2+} pairs; two of these, Hg(1)—Hg(1ⁱ) [2.513 (3) Å] and Hg(2)—Hg(2ⁱⁱ) [2.502 (2) Å], are related by diad axes, while Hg(3) and Hg(4) are linked together in the third pair [2.507 (3) Å] (Fig. 2). All three Hg—Hg pairs surround the oxonium O atom at Hg—O distances of 2.19 (2), 2.12 (2) and 2.31 (2) Å, respectively. The longest bond Hg(3)—O can be easily explained by the interaction of Hg(3) with nitrate O(23) at 2.46 (4) Å. The OHg_3 unit is in the form of a very flattened trigonal pyramid with angles at the O atom of

Table 8. $[\text{Hg}_2(\text{OHg})_2](\text{NO}_3)_2$: selected distances and angles

| (a) Bond lengths (Å) and angles (°) | | | |
|-------------------------------------|-----------|-------------------------------|-----------|
| Hg(2)—Hg(2 ⁱⁱ) | 2.510 (2) | O—Hg(1)—O ⁱⁱⁱ | 172.5 (5) |
| Hg(1)—O | 2.05 (1) | O—Hg(2)—Hg(2 ⁱⁱ) | 177.9 (3) |
| Hg(1)—O ⁱⁱⁱ | 2.06 (1) | Hg(1)—O—Hg(1 ⁱⁱⁱ) | 108.6 (5) |
| Hg(2)—O | 2.16 (1) | Hg(1)—O—Hg(2) | 116.0 (6) |
| | | Hg(2)—O—Hg(1 ⁱⁱⁱ) | 110.4 (6) |
| N—O(1) | 1.20 (2) | O(1)—N—O(2) | 120 (1) |
| N—O(2) | 1.29 (2) | O(1)—N—O(3) | 124 (1) |
| N—O(3) | 1.25 (2) | O(2)—N—O(3) | 117 (1) |

| (b) Interatomic contacts (Å) | | | |
|------------------------------|----------|-------------------------------|-----------|
| Hg(1)···O(2) | 2.75 (1) | Hg(2)···O ⁱⁱⁱ | 2.80 (1) |
| Hg(1)···O(3) | 2.91 (1) | Hg(2)···O(3 ^{vi}) | 2.92 (1) |
| Hg(1)···O(2 ^{iv}) | 2.89 (1) | Hg(1)···Hg(2) | 3.570 (2) |
| Hg(1)···O(3 ⁱⁱⁱ) | 2.79 (1) | Hg(1)···Hg(2 ⁱⁱ) | 3.460 (2) |
| Hg(1)···O(1 ^v) | 2.88 (1) | Hg(1)···Hg(1 ⁱⁱⁱ) | 3.337 (2) |

Superscripts refer to the following equivalent positions relative to atom *x, y, z*: (i) 1 - *x, -y, -z*; (ii) -*x, 0.5 + y, 0.5 - z*; (iii) -*x, y - 0.5, 0.5 - z*; (iv) *x - 1, y, z*; (v) 1 - *x, y - 0.5, 0.5 - z*; (vi) *x, y - 1, z*; (vii) -*x, -y, -z*.

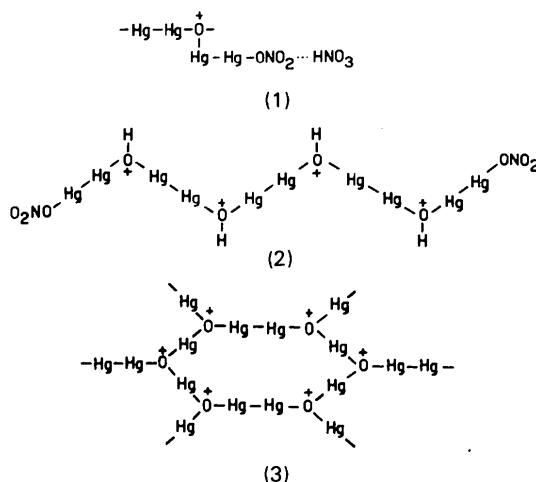


Fig. 1. Different oxonium cations: (1) infinite chain with the hydrogen-bonded solvated HNO_3 molecule; (2) a finite four-oxonium-link chain; (3) an infinite folded layer containing both Hg_2^{2+} and Hg_2^{2+} ions.

117.7 (9), 123.5 (10) and 112.9 (10)° and the distance between the apical O atom and the plane through three Hg atoms of 0.31 (4) Å. The O—Hg—Hg angles are very different depending upon the different contacts of the Hg atoms with the neighbouring atoms, *i.e.* upon the effective coordination around each Hg atom. Hg(1), apart from being bonded to another Hg atom and an oxonium O atom, is approached by two other adjacent nitrate O atoms [O(22ⁱⁱⁱ) and O(33^{iv})] at distances of 2.63 (4) and 2.62 (4) Å. Owing to such close approaches of the neighbouring O atoms the bonds O—Hg(1)—Hg(1') significantly deviate from collinearity with the angle at Hg(1) only 157.1 (5)°. In contrast, the interactions of Hg(2) with the neighbouring nitrate O atoms O(11^{vii}), O(12^v) and O(31^{vi}) are very weak [2.89 (4), 2.78 (3) and 2.96 (2) Å] so that the bonds O—Hg(2)—Hg(2'') are almost collinear with the angle at Hg(2) 173.3 (5)°. Following such behaviour the bonds Hg(4)—Hg(3)—O deviate most from collinearity [145.9 (5)°] owing to the very close approach of the nitrate O(23) atom to Hg(3) [2.46 (4) Å] exhibiting thus an almost trigonal characteristic coordination of the Hg(3) atom. Again, the angle at Hg(4) increases to 165.8 (10)° owing to the weak interactions of Hg(4) with the neighbouring nitrate O atoms O(13), O(31ⁱⁱⁱ) and O(32ⁱⁱⁱ) at 2.86 (3), 2.84 (3) and 2.89 (3) Å, respectively. The characteristic coordination of Hg(4) is digonal being bonded to Hg(3) and O(11) [2.24 (4) Å].

Though the H atoms could not be located in a difference Fourier synthesis, according to the known data on the mercurioxonium salts (Grdenić, Sikirića, Matković-Čalogović & Nagl, 1983; Matković-Čalogović, 1985) we assume that HNO₃ exists in the structure as a solvate molecule hydrogen-bonded to one of the nitrate ions [O(32)—H...O(13^{viii})], 2.81 (3) Å].

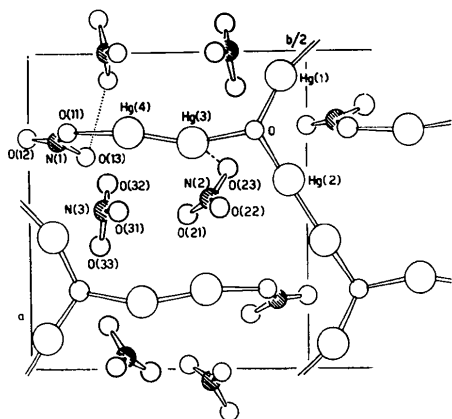


Fig. 2. The crystal structure of $[(\text{Hg}_2)_2\text{O}(\text{NO}_3)_3]\text{NO}_3 \cdot \text{HNO}_3$ projected in the ab plane. The hydrogen bond between solvated HNO₃ and the NO₃⁻ ion is shown by a dotted line, the closest contact between Hg(3) and O(23) by a broken line.

The N—O bond lengths and O—N—O angles in the nitrate ions as well as in the HNO₃ solvate molecule are within expected values.



The structure of (2) is similar to that of trimercury(II) dihydroxide bis(sulfate) monohydrate, Hg₃(OH)₂(SO₄)₂·H₂O (Bonefačić, 1962; Björnlund, 1974; Aurivillius & Stålhandske, 1976), in which the dimercurated oxonium chains contain Hg^{II} ions, in (2) the Hg—Hg pairs. In the structure there are five crystallographically independent Hg atoms forming three Hg₂²⁺ pairs; one of them is related by the symmetry centre [Hg(3)—Hg(3')], while Hg(1) and Hg(2), and Hg(4) and Hg(5) are linked in two separate pairs (Fig. 3). The corresponding Hg—Hg bond lengths are 2.495 (1), 2.500 (2) and 2.511 (1) Å, respectively. In comparison with (1), in the structure of (2) the oxonium O atoms are surrounded by two Hg₂²⁺ ions and one H atom. The Hg—O distances to the oxonium O(1) atom are 2.11 (2) and 2.13 (2) Å, and those to O(2) 2.09 (2) and 2.15 (2) Å. The Hg—O—Hg angles at the oxonium O atoms are 110.6 (7) [at O(1)] and 120.7 (9)° [at O(2)], respectively. The O—Hg—Hg angles range from 166.1 to 178.5° depending also upon the effective coordination around each particular Hg atom. For example, the O(1)—Hg(2)—Hg(1^{iv}) bonds are almost collinear due to very weak interactions of Hg(2) with the neighbouring atoms. The only significant approach to Hg(2) is that of O(31^{vi}) at 2.80 (2) Å. All other Hg atoms are approached by more than one neighbouring O atom: Hg(1) by the nitrate O atoms O(22ⁱ) and O(33^j) [2.87 (2) and 2.81 (2) Å], Hg(3) by the oxonium O(2) and nitrate O(21) atoms [2.71 (2) and 2.74 (2) Å], Hg(4) by the oxonium O(1) and

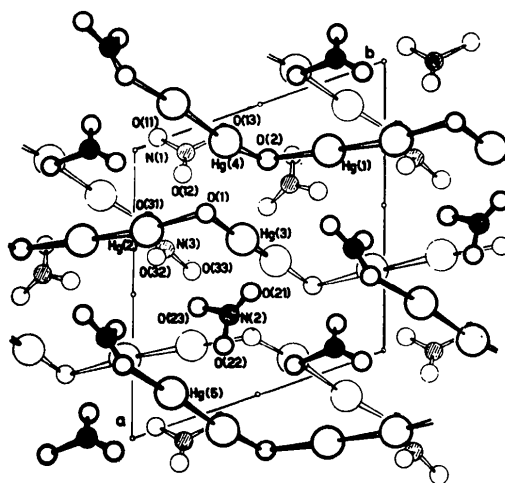


Fig. 3. The crystal structure of $[(\text{Hg}_2)_5(\text{OH})_4(\text{NO}_3)_2](\text{NO}_3)_4$ projected in the ab plane.

nitrate O(22ⁱ) atoms [2.65 (1) and 2.71 (2) Å], and Hg(5) by three nitrate atoms O(22^{vi}), O(11^{vi}) and O(11^{vii}) [2.84 (2), 2.61 (2) and 2.87 (2) Å].

The N—O bonds and O—N—O angles within nitrate ions are normal.

[Hg₂(OHg)₂](NO₃)₂ (3)

The yellow-coloured compound (3) is the oxidation product of Hg₂(NO₃)₂·2H₂O containing both Hg^I and Hg^{II} ions so that the usual yellowish colour of the laboratory chemical mercury(I) nitrate dihydrate actually comes from this compound. The structure of (3) is partially similar to the recently published structure of [Hg₂(OHg)₂]I₂ (Stålhandske, Aurivillius & Bertinsson, 1985). In contrast to the iodide structure, which has been described as a three-dimensional network, the nitrate one is built up of infinite zigzag —Hg^{II}—O—Hg^{II}— chains linked together in folded layers by Hg₂²⁺ pairs (Fig. 4). Each oxonium O atom within the layer is surrounded by two Hg^{II} atoms and by one Hg^I atom of the centrosymmetrical Hg₂²⁺ pair. The OHg₃ unit forms an irregular flattened trigonal pyramid of height 0.62 (2) Å. The angles at the apical O atom are 116.0 (6), 108.6 (5) and 110.4 (6)°, respectively.

The characteristic coordination of both Hg^{II} and Hg^I atoms, *i.e.* of Hg(1) and Hg(2), is digonal. The Hg(1) atom is bonded to two oxonium O atoms at almost the same distances of 2.05 (1) and 2.06 (1) Å, Hg(2) to its Hg(2ⁱ) pair at 2.510 (2) Å and to the oxonium O atom at 2.16 (1) Å. It is interesting that the Hg^I—O bond is significantly longer than the Hg^{II}—O bond. The same

lengthening of the Hg^I—O bond compared with the usual Hg^{II}—O bond has been noticed also in the structures of (1) and (2). The angles O—Hg(1)—Oⁱⁱ and O—Hg(2)—Hg(2ⁱ) of 172.5 (5) and 177.9 (3)° are not very far from 180° owing to the weak interactions of both Hg atoms with their neighbouring atoms. The significant Hg(1)···O and Hg(2)···O contacts to the adjacent nitrate and oxonium O atoms are given in Table 8.

The N—O bond lengths and O—N—O angles in the nitrate ion are usual.

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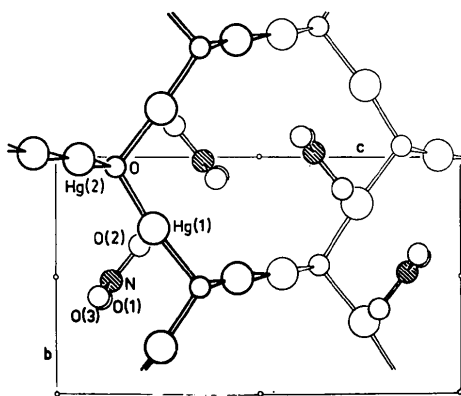


Fig. 4. The crystal structure of [Hg₂(OHg)₂](NO₃)₂ projected in the *bc* plane. The Hg^{II}—O—Hg^{II}— infinite zigzag chains running along *b* are interconnected in a layer by Hg^I—Hg^I pairs.