Acta Cryst. (1985). C**41**, 997–998

Structural Studies of Mercury(I) Compounds. I. Structure of Mercury(I) Nitrite, $Hg_2(NO_2)_2$

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(*Received* 17 *October* 1983; *accepted* 8 *March* 1985)

Abstract. $M_r = 493{\cdot}2$, monoclinic, $P2_1/c$, $a = 4{\cdot}4145\ (9)$, $b = 10{\cdot}3334\ (20)$, $c = 6{\cdot}2775\ (11)$ Å, $\beta = 108{\cdot}834\ (15)°$, $V = 271{\cdot}03$ Å^3, $Z = 2$, $D_m(298\text{ K}) = 6{\cdot}20\ (5)$, $D_x = 6{\cdot}04$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 544{\cdot}83$ cm^{-1}, $F(000) = 412$, $T = 298$ K, $R = 0{\cdot}067$ for 375 reflections. Discrete centrosymmetric planar $Hg_2(NO_2)_2$ units [Hg—Hg = 2·516 (2) Å] pack together to form the structure; the NO_2 ligand is monodentate through an oxygen atom [Hg—O = 2·24 (2) Å]. The N—O bond lengths are the same as in other nitrites. The molecules pack together compactly, with the Hg atom four-coordinated.

Introduction. To date no structural studies have been carried out on Hg^I nitrites. Groth (1906) noted light yellow triclinic crystals of $Hg_2(NO_2)_2.\frac{1}{2}H_2O$ produced by the reaction of Hg metal with dilute nitric acid, but Potts & Allred (1966) remark that mercury(I) nitrite is too unstable to isolate. As part of a study on the products of the reaction between dilute HNO_3 and excess Hg metal, we report here the crystal and molecular structure of $Hg_2(NO_2)_2$, a simple binary cluster complex with a remarkably high density and mass absorption coefficient (the crystals are 81·3% by mass Hg; 81·10% Hg by analysis).

Experimental. Clumps of large yellow monoclinic crystals of $Hg_2(NO_2)_2$ grew in beakers containing a lake of mercury covered with 20% nitric acid; the beakers were left undisturbed over periods of up to two weeks while crystals formed. Subsequent to the crystallization of yellow $Hg_2(NO_2)_2$, there appeared well-formed colourless needles of a second compound, also analysing approximately as $Hg_2(NO_2)_2$; in contrast to the yellow crystals, these were orthorhombic. Yellow $Hg_2(NO_2)_2$ is moisture and light sensitive, and many crystals contain occluded mercury. Yellow crystals were separated and dried rapidly without washing. D_m determined by loss of weight suspended in ethyl iodide (mean of several determinations on different crystals). Data collected from prismatic crystal (approx. 0·4 × 0·4 × 0·4 mm) with Enraf–Nonius CAD-4 diffractometer, ω–2θ scan, 25 reflections for refinement of cell parameters, variable scan speed with max. 2·06° min^{-1}, $2 < \theta < 27°$, 2·3% variation of standard reflections over 37 h radiation time, 1184 reflections ($0 \leq h \leq 5$, $-13 \leq k \leq 13$ and $-8 \leq l \leq 8$) collected for triclinic lattice to remove all doubt about space group for this strongly absorbing crystal, 554 unique reflections for $P2_1/c$, $R_{\text{int}} = 0{\cdot}128$, 375 with $I > 2\sigma(I)$ used to refine 22 parameters, data corrected for Lorentz and polarization effects and empirically for absorption by the ψ-scan method (North, Phillips & Mathews, 1968), absorption correction range 0·998 to 0·665. Structure solved by Patterson synthesis, refined by full-matrix least squares on F with Hg atoms refined anisotropically; final $R = 0{\cdot}0672$, $wR = 0{\cdot}0682$, $w = 1{\cdot}2065/[\sigma^2(F) + 0{\cdot}0045F^2]$, $(\Delta/\sigma)_{\max}$ in final cycle = 0·013, several difference electron-density peaks with heights between 1 and 3 e Å^{-3} closely associated with Hg_2^{2+} cluster; these peaks not refinable as alternative atomic positions and not investigated further; f, f' and f'' from *International Tables for X-ray Crystallography* (1974); program *SHELX* (Sheldrick, 1976). Atomic coordinates and thermal parameters are listed in Table 1.‡

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and temperature factors* (Å$^2 \times 10^3$) *with e.s.d.'s in parentheses*

For Hg, $U_{\text{eq}} = \frac{1}{3}$ trace $\tilde{\mathbf{U}}$.

	x	y	z	U
Hg	1534 (3)	−809 (1)	1443 (2)	31*
O(1)	3801 (57)	−2365 (25)	3943 (42)	36 (6)
O(2)	7384 (65)	−1012 (25)	4254 (49)	40 (6)
N	6645 (75)	−2034 (29)	4863 (55)	37 (7)

* Anisotropic temperature factor, $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^*)]$, with parameters:

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg	38 (1)	34 (1)	22 (1)	9 (1)	5 (1)	10 (1)

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‡ The list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42111 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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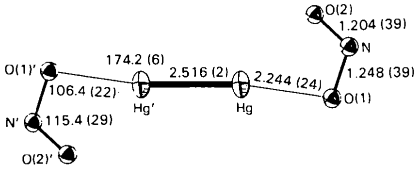

Fig. 1. The centrosymmetric $Hg_2(NO_2)_2$ complex with atom numbering, bond lengths (Å) and angles (°).

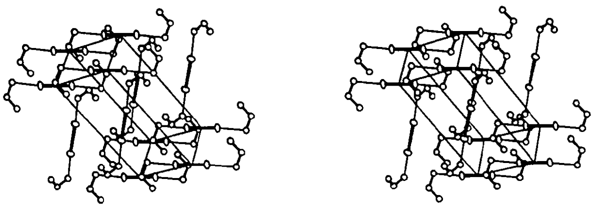

Fig. 2. A stereoscopic view of the structure.

Discussion. The structure of the $Hg_2(NO_2)_2$ molecular unit is shown in Fig. 1, which also gives the bond lengths and bond angles. The non-bonded Hg—O distances, $Hg\cdots O(2)$ $(x-1,\ y,\ z) = 2{\cdot}93\,(2)$ and $Hg\cdots O(1)$ $(x,\ -\frac{1}{2}-y,\ -\frac{1}{2}+z) = 2{\cdot}84\,(2)$ Å, suggest some interaction, since the van der Waals radius of oxygen is 1·4 Å and the closest Hg—Hg distance in solid mercury is estimated to be ~3·0 Å (Evans, 1978). Similar weak interactions have been noted in $Hg_2(BrO_3)_2$ (Dorm, 1967) and in Hg_2SO_4 and Hg_2SeO_4 (Dorm, 1969). The bonded —O—Hg—Hg—O system is approximately linear and the molecular unit is planar (deviations from the best plane are all $<0{\cdot}01$ Å) and centrosymmetric. The N—O bond lengths correspond with that observed, for instance, in sodium nitrite, 1·240 (3) Å (Kay, Frazer & Ueda, 1962).

The crystal packing, illustrated in Fig. 2, shows no special features. The average volume occupied per atom is 17·0 Å^3; the $Hg_2(NO_2)_2$ molecules pack together in quite a compact way. The Hg atoms are four-coordinated, involving the bonding and non-bonding interactions discussed above.

We thank the University of South Africa and the University Grants Division of the Council for Scientific and Industrial Research for financial support and Dr P. van Rooyen of the National Chemical Research Laboratory for data collection.

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Acta Cryst. (1985). C**41**, 998–1003

Structure of $Pb_3O_2(OH)_2$ by Rietveld Analysis of Neutron Powder Diffraction Data

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(*Received* 3 *December* 1984; *accepted* 6 *February* 1985)

Abstract. $M_r = 687{\cdot}58$, tetragonal, $P\bar{4}2_1c$, $a = 8{\cdot}0226\,(3)$, $c = 9{\cdot}3183\,(4)$ Å, $V = 599{\cdot}69\,(7)$ Å^3, $Z = 4$, $D_x = 7{\cdot}619$ g cm^{-3}, $\lambda = 1{\cdot}893$ Å, $\mu = 0{\cdot}433$ cm^{-1}, $F(000) = 1757$ fm^2, $T = 295$ K, $R_{wp} = 0{\cdot}0356$ for 2900 step intensities, $R_B = 0{\cdot}0116$ for 221 reflections. The structure consists of discrete dodecahedral clusters with composition $Pb_6O_4(OH)_4$ and $\bar{4}$ symmetry, fixed in position at the corners and centre of the unit cell by eight hydrogen bonds of length 1·87 (2) Å and by van der Waals interactions between Pb lone-pair orbitals. The two distinct Pb atoms are square-pyramidally coordinated by two O atoms and two OH groups. Both O atoms are trigonally coordinated by Pb, but are significantly displaced from the plane of these atoms as a result of their bonds to H. Thermal decomposition (essentially complete in the temperature range 410–460 K) and infrared absorption (no structural water) properties are also described.

0108-2701/85/070998-06$01.50