Fig. 3. Infrared spectrum of $Pb_4O[Pb_2(BO_3)_3Cl]$ (BO_3 stretching bands indicated by bar).

Table 3. *Infrared spectrum of* $Pb_4O[Pb_2(BO_3)_3Cl]$, *powder in* RbI

Observed IR bands

Wavenumber (cm⁻¹)	Intensity*	Possible assignment
1368	sh	
1355	w	
1297	vs	
1240	vs	v asym–BO_3 stretch
1215	sh	
1185	sh	
1144	s	
1110	vs	
904	m	v sym–BO_3 stretch
752	m	
730	m	γ –BO_3 out of plane
708	vs	
640	m	δ –BO_3 bending
558	vs	'Pb_4O' stretch?
430	m	
390	s	
320	m	external vibrations
295	m	
268	m	

* *sh* shoulder, *w* weak, *m* medium, *s* strong, *vs* very strong.

The B—O distances in the BO_3 groups are spread over a relatively wide range from 1·29 (4) to 1·40 (4) Å and the O—B—O angles are from 115 (2) to 126 (4)°. The planarity of these groups is well preserved and the mean B—O distance of 1·365 (4) Å is comparable with values found in other orthoborates reported by Tennyson (1963), Coulson & Dingle (1968) and Donnay & Donnay (1973). The temperature factors of the BO_3 groups show strong anisotropy which may partly be due to the uncertainties in the absorption correction. In accordance with the calculated distortions of the BO_3 groups the infrared spectrum displays a large splitting of the asymmetric stretching bands of the BO_3 groups in the range from 1368—1110 cm⁻¹, as shown in Fig. 3 and Table 3. The occurrence of the band at 904 cm⁻¹ (associated with the symmetric BO_3 stretching vibration and inactive for a free BO_3 group) also confirms the large distortions of these groups. The Cl atoms occupy a strongly elongated octahedral gap between the Pb atoms. Four Pb—Cl distances are short at 3·01 (2) to 3·13 (2) Å, two more are much longer at 4·02 (2) and 4·41 (2) Å. The mean temperature factor $\bar{U}$ of Cl is very high, due to high anisotropy. The large axis of the thermal ellipsoid is directed parallel to the long Pb—Cl—Pb direction. The positional parameter in this direction shows a large uncertainty, possibly caused by thermal vibrations of large amplitudes or by statistical disordering.

The Pb_4O tetrahedra and the Pb—Pb dumbbells are held together by bonds which are largely covalent. This results in a large distortion of the BO_3 groups which share their O atoms with the aforementioned structure units.

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Trimercury Dinitrate Dioxide, $Hg_3O_2(NO_3)_2$

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Abstract. $M_r = 757\cdot8$, $F(000) = 2542\cdot8$, orthorhombic, *Pbca*, $a = 6\cdot988$ (2), $b = 13\cdot569$ (4), $c = 15\cdot431$ (4) Å, $V = 1463\cdot2$ (5) Å³, $Z = 8$, $D_x = 6\cdot88$ Mg m⁻³, $\lambda(Mo\ K\alpha) = 0\cdot71069$ Å, $\mu(Mo\ K\alpha) = 62\cdot83$ mm⁻¹.

Final $R = 0.058$ for 677 symmetrically independent observed reflections. The structure of $Hg_3O_2(NO_3)_2$ consists of corrugated honeycomb nets of Hg_3O_2, between which NO_3 groups are embedded.

Introduction. In the system $HgO-N_2O_5-H_2O$ Cox (1904) found an anhydrous basic salt with formula $3HgO.N_2O_5$, but of unknown structure. X-ray and infrared powder data of this compound have been reported by Bernstein, Pars & Blumenthal (1957). Experiments intended to produce mercury borates from $Hg(NO_3)_2$ hydrate and boric acid after Ecker (1966) yielded crystals of $Hg_3O_2(NO_3)_2$. The crystal structure has been determined.

Experimental. Single crystals of $Hg_3O_2(NO_3)_2$ were prepared together with $HgO.2B_2O_3$ and $Hg(NO_3)_2$ by slowly heating a mixture of $Hg(NO_3)_2.2H_2O$ and H_3BO_3 (molar ratio: 3·5:1) under O_2 atmosphere up to 773 K for one week in a platinum crucible. The crystals of $Hg_3O_2(NO_3)_2$ could be recognized by their lanceolated shape; the other compounds were characterized by X-ray powder photographs and infrared spectra.

X-ray investigations: a small fragment of a crystal was enclosed in a capillary tube to protect it from hydrolysis. Its shape was approximated by the faces $(0\bar{1}0)$ 10 μm, $(0\bar{1}0)$ 10 μm, (001) 20 μm, $(00\bar{1})$ 20 μm, $(\bar{1}0\bar{2})$ 29 μm, $(10\bar{4})$ 29 μm, where the given distances are from the centre of the crystal. Crystal data and X-ray extinctions taken from precession photographs. Lattice constants refined from 16 Bragg reflections measured on a Picker diffractometer.

Data collection: 3350 reflections $(\bar{h}kl-hkl)$ measured in the range $3·5 \leq 2\theta \leq 50°$ on a Picker four-circle diffractometer, graphite monochromator, Mo $K\alpha$ radiation, $\theta/2\theta$ scan technique, scan speed 0·5° min^{-1}, scan range 1·0° below $K\alpha_1$ and 1·0° above $K\alpha_2$, background 2 × 20 s, three standard reflections every 50 reflections (intensity variation less than ± 5%).

Data reduction: Lorentz and polarization corrections in the usual way with a transfer and data-reduction program written by Holub (1982). All further calculations with the program system *SHELXTL* (Sheldrick, 1981) on a NOVA-3 computer. Absorption correction carried out using the Gaussian quadrature method of *SHELXTL* with 376 sampling points and optically measured crystal dimensions as listed above. Averaging gave 1289 symmetrically independent reflections, 699 with $|F| > 4\sigma_F$, σ_F from counting statistics. Merge $R = 0.052$. Atomic scattering factors and anomalous-dispersion coefficients for Hg, N and O from *International Tables for X-ray Crystallography* (1974).

Calculations: structure solved by usual Patterson methods. Starting with the three independent Hg atoms all other atoms were successively found by Fourier maps and refinements. The three Hg atoms alone yielded

$R = 0.099$. Refinements of anisotropic thermal parameters for all atoms yielded values for the light atoms which were not meaningful. The reason seemed to be insufficient absorption correction for this crystal fragment and additionally some disorder for the nitrate groups. The former was noticed for some low-intensity reflections which were given disproportionately high values by the absorption correction. Experiments to describe the crystal shape by other faces gave no better results. Despite the calculated anisotropy of the thermal parameters for the light atoms their positional parameters did not vary significantly in the different absorption-correction models. Therefore only the diagonal elements of the thermal parameters of the light atoms were refined together with all parameters of the ·heavy atoms. Neglecting the 22 reflections mentioned above in the last refinements the results are: $R = 0.058$, $R_w = 0.045$ with $w = 1/\sigma_F^2$, $S = 1·161$, normal probability slope 1·082; final $(\Delta/\sigma)_{mean}$ less than 0·05; final $\Delta\rho$ map showed maxima and minima of about ± 3 e $Å^{-3}$ in the neighbourhood of the Hg atoms.*

Discussion. The crystal structure of $Hg_3O_2(NO_3)_2$ can be regarded as being built up of two corrugated Hg_3O_2 honeycomb nets and of isolated NO_3 groups, one half of them being located between the nets, the other half almost in the interstices of the nets. Atomic coordinates are given in Table 1, interatomic distances and angles in Table 2. Fig. 1 shows the unfolded Hg_3O_2 nets. Each Hg atom forms two nearly collinear bonds to O atoms in the nets with short Hg–O distances ranging from 1·99 (3) to 2·11 (2) Å [mean Hg–O = 2·04 (3) Å, being similar to the value of 2·03 (2) Å found by Aurivillius & Carlson (1958) for hexagonal HgO]. The O–Hg–O angles in the nets range from 167 (2) to 177·6 (2)°. All O atoms in the nets are coordinated to the Hg atoms in a trigonal-pyramidal arrangement so that the Hg_3O_2 nets are folded as shown in Fig. 2. These nets are similar to the Hg_3O_2 nets found in synthetic $HgSO_4.2HgO$ by Nagorsen, Lyng, Weiss & Weiss (1962).

The interstices of the honeycomb nets are occupied on one side by half of the NO_3 groups, the other NO_3 groups connecting two adjacent nets. The corresponding Hg–O distances to the nitrate groups are much longer than those in the nets and range from 2·61 (2) to 2·89 (3) Å. These bonds are formed almost in the equatorial plane perpendicular to the short O–Hg–O bonds. The coordination spheres of the Hg atoms can be considered as shortened and distorted pentagonal or trigonal bipyramids respectively. Therefore the total

coordination number of the Hg atoms can be written as (2 + 5) for Hg(1) and Hg(2) and (2 + 3) for Hg(3) in Wells's (1975) notation.

The large calculated anisotropy in the thermal parameters for the nitrate groups, especially for those located between the nets could point to some disorder or to strong thermal vibrations of these groups which can be explained by the rather weak bonds to the cations in the nets. Within the nitrate groups distances and angles are in the usual range.
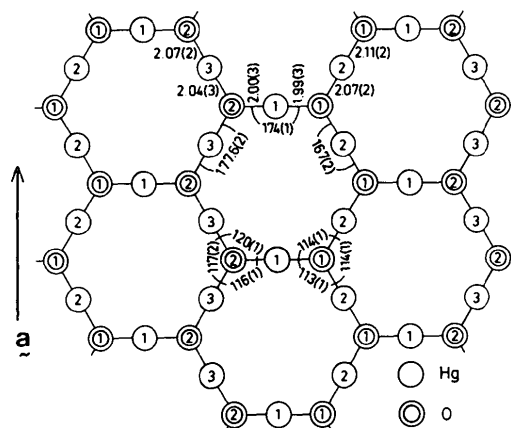

Fig. 1. The unfolded Hg_3O_2 honeycomb net with atomic numbering, bond distances (Å) and angles (°). The translation period in **a** (see arrow) remains unaffected by the unfolding

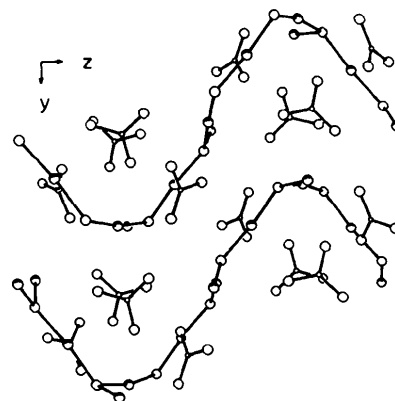### Table 1. Atom coordinates ($\times 10^4$) and temperature factors ($\text{Å}^2 \times 10^3$)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Hg(1)	3936 (2)	630 (2)	8967 (1)	28 (1)
Hg(2)	6317 (2)	9269 (1)	7472 (2)	28 (1)
Hg(3)	6542 (2)	2500 (2)	9972 (2)	30 (1)
O(1)	3896 (27)	9431 (22)	8225 (16)	21 (10)
O(2)	4056 (28)	1734 (24)	9822 (21)	40 (12)
N(1)	2710 (49)	7066 (30)	7294 (22)	28 (13)
N(2)	6053 (48)	5373 (30)	9217 (18)	19 (12)
O(3)	7460 (33)	5633 (26)	9756 (21)	38 (12)
O(4)	6155 (41)	4512 (25)	8941 (22)	49 (12)
O(5)	4719 (33)	6012 (23)	9021 (26)	39 (12)
O(6)	3035 (31)	6213 (24)	7111 (26)	49 (15)
O(7)	2100 (36)	7296 (31)	8059 (21)	57 (16)
O(8)	2817 (49)	7716 (25)	6704 (22)	55 (14)

Fig. 2. Projection of the structure along **a**.

Table 2. Bond lengths (Å) and angles (°) not given in Fig. 1

Hg(1)–O(5^i)	2·61 (2)	Hg(3)–O(8^{ix})	2·64 (3)
–O(7^i)	2·76 (4)	–O(3^{ii})	2·65 (4)
–O(3^{ii})	2·80 (3)	–O(5^x)	2·70 (3)
–O(6^{iii})	2·81 (3)		
–O(3^{iv})	2·81 (3)		
Hg(2)–O(8^v)	2·68 (3)		
–O(6^{vi})	2·75 (3)		
–O(4^{vi})	2·80 (3)		
–O(7^{vii})	2·85 (4)		
–O(4^{viii})	2·89 (3)		
N(1)–O(6)	1·21 (5)	O(6)–N(1)–O(7)	120 (4)
–O(8)	1·27 (5)	O(6) O(8)	119 (4)
–O(7)	1·29 (5)	O(7)– –O(8)	120 (4)
N(2)–O(4)	1·25 (5)	O(3)–N(2)–O(4)	115 (3)
–O(5)	1·31 (5)	O(3)– –O(5)	120 (4)
–O(3)	1·34 (4)	O(4)– –O(5)	126 (3)

Symmetry code
(i) $0·5-x,-0·5 + y, z$
(ii) $1·5-x, -0·5 + y, z$
(iii) $1-x, -0·5 + y, 1·5-z$
(iv) $1-x, 0·5-y, 2-z$
(v) $0·5 + x, y, 1·5-z$
(vi) $1-x, 0·5 + y, 1·5-z$
(vii) $1-x, y, 1·5-z$
(viii) $1·5-x, 0·5 + y, z$
(ix) $1-x, 1-y, 1·5-z$
(x) $1-x, 1-y, 2-z$

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