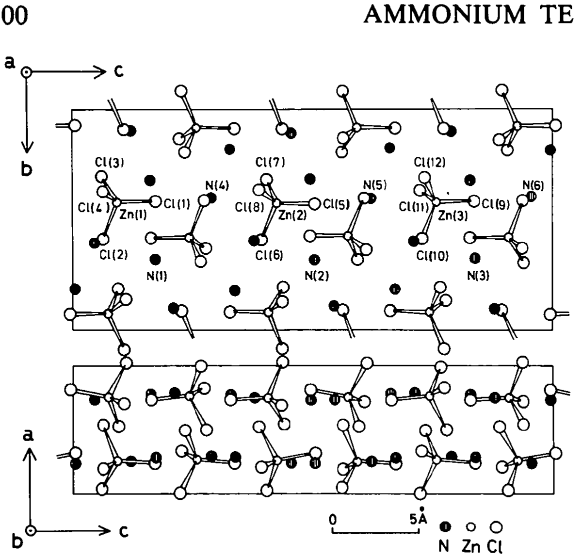

Fig. 1. Arrangement of the atoms viewed along **a** and **b**.

(Mikhail & Peters, 1979), and has a long period of $c = 3c_0$ compared with the structure of the normal phase as in K_2ZnCl_4. It is worth noting, however, that there is a marked difference between $(NH_4)_2[ZnCl_4]$ and K_2ZnCl_4 in the distribution of satellite reflexions based on the structure of the normal phase. In $(NH_4)_2[ZnCl_4]$ many satellite reflexions are observed in the (0*kl*) plane, whereas they are hardly found in the same plane in K_2ZnCl_4 (Itoh, Kataoka, Matsunaga & Nakamura, 1980).

The bond lengths of Zn—Cl, which range from 2·230 to 2·299 Å (mean 2·258 Å), are close to those of $ZnCl_4$ tetrahedra in $Li_2ZnCl_4.2H_2O$ (Jacobi & Brehler, 1969), $ZnCl_2.\frac{4}{3}H_2O$ (Follner & Brehler, 1970), Na_2ZnCl_4 (van Loon & Visser, 1977) and K_2ZnCl_4 (Mikhail & Peters, 1979). The present results show that the maximum differences of Zn—Cl bond lengths in each $ZnCl_4$ tetrahedron are 0·035, 0·038 and 0·055 Å (mean 0·043 Å), while corresponding values in the room-temperature phase (Mikhail, 1980) range from 0·065 to 0·234 Å (mean 0·159 Å). The maximum differences of the Cl—Zn—Cl bond angles in the respective $ZnCl_4$ tetrahedra are 7·6, 8·5 and 8·7° in the present work, whereas they are 13·1, 4·7, 11 and 8·7° in the room-temperature phase (Mikhail, 1980). These facts show that, in the ferroelectric phase, $ZnCl_4$ tetrahedra are less distorted than those in the room-temperature phase. The coordination numbers for the NH_4^+ ions are 8 [N(1), N(2), N(3)] and 5 [N(4), N(5), N(6)], while they are 5, 6, 7 and 8 in the room-temperature phase. These facts suggest that the arrangement of the $ZnCl_4$ tetrahedra and NH_4^+ ions in the ferroelectric phase is more regular than that in the room-temperature phase.

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Structure of Mercury(II) Iodide Nitrate

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Abstract. $HgINO_3$, $M_r = 389 \cdot 53$, orthorhombic, *Pnma*, $a = 7 \cdot 3850\,(26)$, $b = 5 \cdot 2567\,(29)$, $c = 12 \cdot 5277\,(69)$ Å, $Z = 4$, and $D_x = 5 \cdot 32$ Mg m^{-3}. The structure was refined anisotropically from single-crystal diffractometer data to an R value of 0·044 for 610 independent reflexions. An $(HgI^+)_n$ zigzag chain passes through the structure parallel to the a axis. In this chain, Hg is coordinated to two I atoms with an I—Hg—I angle of 158·66°, and the I atoms coordinate two Hg atoms with an Hg—I—Hg angle of 90·25°. The

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NO_3 groups are located with their oxygen planes perpendicular to the plane described by the $(HgI^+)_n$ chain. The O atoms of the NO_3 group are directed towards the Hg atoms. The structure of $HgINO_3$ closely resembles that of Ag_2BrNO_3 if one of the Ag positions of the latter structure is considered as unoccupied.

Introduction. For some years structural investigations of compounds with the general formula $Ag_nX_xA_y$ $(n > x)$, with X = Cl, Br or I and different anions A, have been carried out at this Institute. The investigation aims primarily to clarify the Ag coordination to the halide in solids of this kind, with soft metal ions like Ag^+ in excess over halide.

Cationic complexes of Hg_2I^{3+} [analogous to $Ag_nI^{(n-1)+}$] have been detected in aqueous solutions of $Hg(NO_3)_2$ and KI by Raman spectroscopy (Clark & Woodward, 1965) and current investigations at this Institute by Raman spectroscopy and liquid X-ray diffraction give evidence for similar species in dimethyl sulphoxide solutions. Hence, it was considered to be of great interest to extend the structural studies of Ag^I compounds to analogous compounds with metal ions of soft character, like binary compounds formed in the system HgI_2–$Hg(NO_3)_2$. The title compound has already been described as $HgI_2.Hg(NO_3)_2$ in the early literature (Kraut, 1885). A preliminary structure report has been given (Persson, 1980).

Single crystals of $HgINO_3$ were prepared by the following procedure. KI was added to an aqueous solution of 4 M $Hg(NO_3)_2$ and ~3 M HNO_3 at about 330 K until no more of the initially formed red HgI_2 was dissolved ($c_{KI} \simeq 0{\cdot}9$ M). After filtration at this temperature thin, colourless needle-shaped single crystals were obtained on cooling.

$HgINO_3$ is stable for at least a few days in dry air at room temperature. The surface of the crystals becomes light yellow after about one week in air, probably due to the formation of yellow HgI_2. This surface reaction had no serious effect on the X-ray intensities collected (see below). Table 1 gives information concerning the collection of intensities, and the refinement. The method employed for data collection has been described (Elding, 1976). Weissenberg photographs revealed the Laue class mmm and the systematic absences $0kl$: $k + l = 2n + 1$, and $hk0$: $h = 2n + 1$.

By comparison with the Ag_2BrNO_3 structure (Persson & Holmberg, 1977) we observed a conformity of both space group ($Pnma$) and cell dimensions (an elongation of a of about 0·5 Å for $HgINO_3$ only) for the two compounds. This observation suggested a similarity of the structures in spite of the different metal-to-halide ratios. The Weissenberg photographs of the two compounds also showed intensity patterns which had some features in common.

Table 1. *Crystal data, and details of the collection and reduction of the intensity data, and of the least-squares refinement*

Crystal size (mm)	0·081 × 0·469 × 0·056
Radiation (Nb filter)	Mo $K\alpha$ (λ = 0·71073 Å)
Take-off angle (°)	3
$\Delta\omega$ (°) (ω–2θ scan)	$0{\cdot}90 + 0{\cdot}50 \tan\theta$
$\Delta\theta$ (°)	3–30
Minimum number of counts in a scan	3000
Maximum recording time (s)	180
μ(Mo $K\alpha$) (mm^{-1})	37·81
Range of transmission factor	0·113–0·227
Number of measured reflexions	2395
Number of measured independent reflexions	635
Number of reflexions given zero weight	25
Number of independent reflexions used in the final refinement, m	610
Number of parameters refined, n	34
$R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0·044
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}$	0·041
$S = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(m-n)]^{1/2}$	1·28
a (weighting function)	0·022

The intensity data were collected on a single-crystal diffractometer (CAD-4). Dependent reflexions were recorded ($\frac{3}{8}$ of the sphere of reflexion) and after absorption correction the data were reduced to an independent data set by using the program *SORTA*, which sorts and averages equivalent reflexions. The cell dimensions were improved by least-squares refinement of 46 reflexions (Danielsson, Grenthe & Oskarsson, 1976). The wavelength used for the determination of the cell dimensions was 0·70930 Å (Mo $K\alpha_1$).

Three standard reflexions ($\bar{2}12$, 214, and 411), checked every second hour, showed a small decrease in intensity in the middle of the collection period, probably caused by a small continuous change of the centring of the crystal. After recentring they showed random fluctuations. The middle part of the intensity data were thus scaled with the expression $Y = 1{\cdot}0 - (0{\cdot}72 \times 10^{-3})X$, where X is the total time in hours that the crystal had been exposed to X radiation. The absorption correction was performed according to Busing & Levy (1957, 1967) using the numerical-integration method of Gauss. The morphology of the crystal was described by eight planes.

The positions of the Hg and I atoms were found using the *MULTAN* 78 system of computer programs (Germain, Main & Woolfson, 1971). The O and N atoms were revealed in a subsequent difference synthesis. Full-matrix least-squares refinement, minimizing $\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$, was performed with weights $w = 1/[\sigma_c^2/(4F_o^2) + (aF_o)^2]$. The value of a was chosen to make the average values $\langle w(\lvert F_o\rvert - \lvert F_c\rvert)^2\rangle$ almost equal in different $\lvert F_o\rvert$ and $\sin\theta$ intervals. Three scale factors, and positional and anisotropic thermal parameters were refined (Table 1).

Table 2. *Positional and equivalent isotropic thermal parameters with estimated standard deviations*

$$B_{eq} = \tfrac{4}{3} \textstyle\sum_i \sum_j \beta_{ij} \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
Hg	0·09719 (7)	$\frac{3}{4}$	0·22176 (5)	4·00 (2)
I	0·39333 (11)	$\frac{3}{4}$	0·10309 (7)	4·22 (2)
N	0·4315 (13)	$\frac{1}{4}$	0·3583 (9)	3·2 (3)
O(1)	0·0691 (14)	$\frac{1}{4}$	0·2022 (10)	4·8 (3)
O(2)	0·3662 (9)	0·4583 (14)	0·3875 (6)	4·5 (2)

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final refinement also included correction for anomalous dispersion by Hg and I. Only two reflexions, 020 and 011, seemed to be affected by extinction and were given zero weight in the final refinement. The dependent data set gave an R value of 0·064 (1434 reflexions) and the independent set a reduction to 0·044 (610 reflexions) which also reduced the standard deviations by a factor of 2.

In the last cycle the shifts in the parameters were less than 0·5% of the estimated standard deviations and the refinement was considered complete. A final difference synthesis showed peaks of height 2·5 e Å^{-3} or less in the vicinity of the heavy atoms, but apart from this it was featureless.

A normal probability plot of $\delta R(i) = [|F_o(i)| - |F_c(i)|]/\sigma|F_o(i)|$ *versus* the values expected for a normal distribution (Abrahams & Keve, 1971) was made. The slope and intercept of the least-squares line, fitted to all data, are 1·28 and 0·12 respectively. The positive intercept may indicate a systematic overestimation of $|F_o| - |F_c|$ (Persson & Holmberg, 1977). If this systematic error in $|F_o|$ is neglected, the value of the slope indicates that $\sigma(|F_o|)$ is underestimated by about 30%. It is still in agreement with the value of the estimated standard deviation of an observation of unit weight (S = 1·28, Table 1). All computations were made on the Univac 1100/80 computer in Lund. Final positional and isotropic thermal parameters are given in Table 2.*

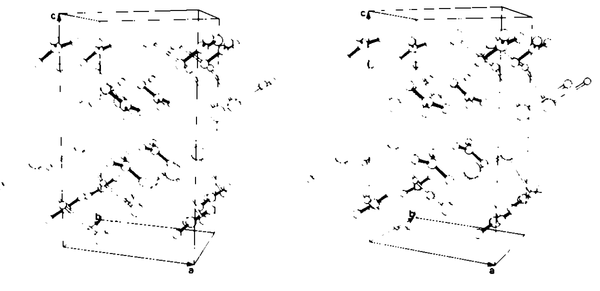

Fig. 1. A stereoscopic pair of drawings showing the contents of the unit cell. Large circles are I and small ones are Hg. Figs. 1 and 2 have been drawn by the program *ORTEP* II (Johnson, 1971).

Table 3. *Selected interatomic distances* (Å) *and angles* (°) *with estimated standard deviations*

Symmetry code

(i)	$\frac{1}{2}+x, \quad y, \frac{1}{2}-z$	(ii)	$x, \frac{1}{2}-y, \quad z$
(iii)	$-\frac{1}{2}+x, \quad y, \frac{1}{2}-z$	(iv)	$1-x, 1-y, \quad -z$
(v)	$x, 1+y, \quad z$	(vi)	$-\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}-z$
(vii)	$x, \frac{3}{2}-y, \quad z$	(viii)	$-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$

Hg–I	2·644 (1)	Hg–I–Hg^{i}	90·25 (4)
Hg–I^{i}	2·661 (1)	I–Hg–I^{iii}	158·66 (4)
Hg–Hg^{i}	3·760 (1)	O(1^{i})–N–O(2)	118·9 (5)
N–O(1^{i})	1·267 (15)	O(1^{i})–N–O(2^{ii})	118·9 (5)
N–O(2)	1·251 (9)	O(2)–N–O(2^{ii})	122·2 (1·0)
N–O(2^{ii})	1·251 (9)		
I–I^{iv}	4·008 (2)		
I–I^{i}	5·214 (2)		
I–I^{v}	5·257 (3)		

Discussion. A stereoview of the unit cell is given in Fig. 1. Selected interatomic distances and angles are listed in Table 3. O(2) is the only atom not located in the mirror planes at $y = \frac{1}{4}$ and $y = \frac{3}{4}$. The structure comprises infinite –I–Hg–I–Hg–I– zigzag chains along **a**. Coplanar pairs of chains are located in the two mirror planes. The NO_3 group is oriented with the O atoms towards the Hg atoms and the oxygen plane is perpendicular to the plane of the zigzag chain and the bond sequence I–Hg–I (Fig. 1). The Hg and I positions are almost identical to the Ag(2) and Br positions in the Ag_2BrNO_3 structure (Persson & Holmberg, 1977). The N and O(2) positions are also almost equal though the NO_3 group as a whole has changed the direction of its oxygen plane. O(1) is directed towards Hg^{i} instead of Hg as would follow from a straightforward comparison with Ag_2BrNO_3.

The Hg–I distances are 2·64 and 2·66 Å, slightly longer than those previously found for predominantly two-coordinated Hg in yellow HgI_2 (Jeffrey & Vlasse, 1967) and in $Hg_2I_2TiF_6$ (Köhler, Breitinger & Thiele, 1974). The latter compound is built up by $(HgI^+)_n$ chains analogous to those in $HgINO_3$. The bond angle Hg–I–Hg is 90·25° in $HgINO_3$ which compares well with the 89·4 and 97·2° in $Hg_2I_2TiF_6$, whereas the I–Hg–I segment of the $(HgI^+)_n$ chain is considerably less linear in $HgINO_3$. The angle is 158·7°, which is close to the value found for the HgI_2 complex in dimethyl sulphoxide, 159 (2)° (Sandström, 1978*a*). In yellow HgI_2 as well as $Hg_2I_2TiF_6$ the corresponding angle is significantly larger: 178·3 and 175·8°, respectively.

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* Lists of structure factors, anisotropic thermal parameters and root-mean-square components of the thermal displacement along the ellipsoid axes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36426 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

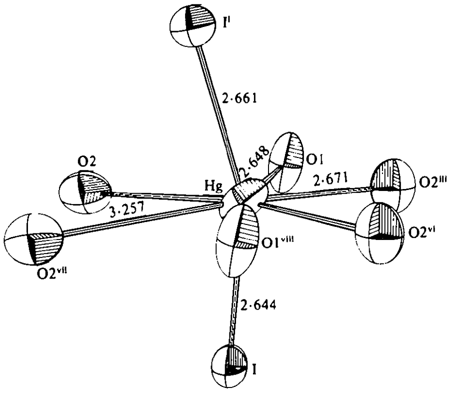

Fig. 2. The environment of the Hg atom. The superscripts are according to Table 3. Distances in Å.

The shortest I–I distance, 4·008 Å, between different layers containing the $(\mathrm{HgI^+})_n$ chain and the $\mathrm{NO_3}$ groups, is in very good agreement with the shortest I—I distance in yellow $\mathrm{HgI_2}$ (4·017 Å; Jeffrey & Vlasse, 1967).

Fig. 2 describes the environment of the Hg atom. Six O atoms form an almost planar ring around Hg, perpendicular to the I—Hg—I plane. There are four O atoms at distances of 2·648 (2) [O(1) and $\mathrm{O(1^{viii})}$] and 2·671 (7) Å [$\mathrm{O(2^{vi})}$ and $\mathrm{O(2^{iii})}$] from Hg, and two O atoms at considerably longer distances of 3·257 (7) Å [O(2) and $\mathrm{O(2^{vii})}$]. The largest deviation of an O atom from the least-squares $\mathrm{O_6}$ plane is 0·152 (9) Å, and Hg is 0·1157 (5) Å outside this plane. The configuration around Hg can thus be described as 2 + 6 [*cf.* the Ag(2) environment in $\mathrm{Ag_2BrNO_3}$]. This assignment is based on purely geometrical considerations, however. The Hg distance to O(2) and $\mathrm{O(2^{vii})}$, 3·26 Å, clearly exceeds the sum of the 12-coordinate Hg metallic radius and the van der Waals radius of O (2·91 Å), which indicates that O(1), $\mathrm{O(1^{viii})}$, $\mathrm{O(2^{vi})}$ and $\mathrm{O(2^{iii})}$ are the only O atoms that may interact more specifically with Hg (*cf.* Fig. 2). Even these four Hg—O distances are comparably long (*cf.* the shortest Hg—O bonds in orthorhombic HgO: 2·04 and 2·07 Å; Aurivillius, 1964). They fall in the range of long distances found in Hg compounds with two short and various longer Hg—O bonds (Sandström, 1978*b*). Even though the interaction between Hg and these O atoms may be weak, it seems reasonable to correlate the large deviation of the I—Hg—I angle from 180° with the difference in influence exerted on Hg by these four O atoms on the one hand, and O(2) and $\mathrm{O(2^{vii})}$ on the other.

$\mathrm{Hg_2I_2TiF_6}$ and $\mathrm{HgINO_3}$ are the only known $\mathrm{Hg^{II}}$ compounds with a bridging single halide and Hg in diagonal coordination, forming endless $(\mathrm{HgI^+})_n$ chains. The structural similarities between $\mathrm{HgINO_3}$ and $\mathrm{Ag_2BrNO_3}$ have been pointed out here, but it should be noted that no such analogy can be found with the chemically closely related compound $\mathrm{Ag_2INO_3}$ (Persson, 1979).

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