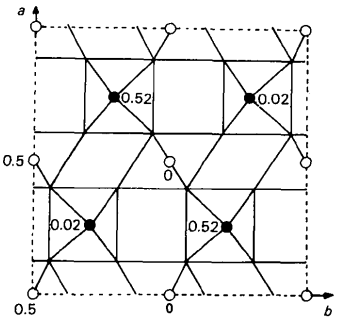

Fig. 3. Projection of the $MnAlF_5$ structure on (001). Full circles: Al atoms, open circles: Mn atoms.

distances O—F(1) [2·560 (8) Å] lying in the range 2·56–2·86 Å, characteristic of O—H···F hydrogen bonds in crystalline hydrates of metal fluorides (Simonov & Bukvetsky, 1978).

The organization of these layers may be compared to that of the octahedra in $MnAlF_5$ (Rimsky, Thoret & Freundlich, 1970); considering the layers shown in Fig. 1, if we remove all the water molecules, apply a **c**/2 translation and connect adjacent layers by means of the F(1) atoms, we obtain the $MnAlF_5$ three-dimensional network (Hg^{2+} for Mn^{2+} and Fe^{3+} for Al^{3+}) shown in Fig. 3.

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Structure of Mercury(I,II) Iodide Oxide, Hg_2OI

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Abstract. $M_r = 544·08$, monoclinic, $C2/c$, $a = 17·603$ (8), $b = 6·981$ (5), $c = 6·701$ (5) Å, $\beta = 101·61$ (2)°, $V = 807$ (1) Å^3, $Z = 8$, $D_x = 8·96$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 853$ cm^{-1}, $F(000) = 1768$, $T = 295$ K. Single crystals obtained by hydrothermal synthesis at 470 K. Final $R = 0·036$ for 979 unique reflections. The structure is built up of layers with bond distances Hg^I—Hg^I 2·534, Hg—O 2·13–2·16 and Hg—I 3·05–3·14 Å. The layers are connected by Hg—O bonds (2·47 Å) to form a three-dimensional structure.

Introduction. Mercury(I,II) compounds are rare and only $Hg_4O_2Cl_2$, the mineral terlinguaite, has been structurally investigated (Ščavničar, 1956; Aurivillius & Folkmarsson, 1968). In this structure there are linearly coordinated Hg^{II} atoms and Hg_3 groups, forming equilateral Hg triangles, with a formal oxidation number of $\frac{4}{3}$ for each Hg. The Hg—Hg distance within the triangle is 2·708 Å, much longer than the Hg—Hg bonds of 2·48–2·54 Å found in Hg^I compounds, but considerably shorter than $Hg^{II}\cdots Hg^{II}$ contacts (> 3·4 Å) and even shorter than the closest Hg—Hg distance of 2·99 Å found in α-Hg (Barrett, 1957).

In order to investigate further mercury(I,II) compounds two new oxide halides have been synthesized, Hg_2OI and $Hg_8O_4Br_3$ (Stålhandske, 1983). It has so far not been possible to prepare a bromide oxide with the same stoichiometry as terlinguaite.

Experimental. Crystals grown by hydrothermal synthesis at 450 K from a stoichiometric mixture of yellow HgO and HgI_2. Plate-shaped dark-red crystal 0·22 × 0·11 × 0·04 mm. CAD-4 diffractometer, graphite-monochromatized Mo K radiation, ω–2θ scan, width (0·60 + 0·50 tanθ)°, max. recording time 180 s. Three standard reflections, no significant variations. Lattice

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parameters based on 20 diffractometer θ values. 5069 symmetry-dependent reflections, $\theta \le 30°$, $-24 \le h \le 24$, $0 \le k \le 9$, $-9 \le l \le 9$, averaged to 988 symmetry-independent reflections with $I > 3\sigma(I)$, 9 with $h + k \neq 2n$. Lp and absorption corrections, transmission factors 0·008–0·07. Atomic positions by Patterson and Fourier techniques. Full-matrix least-squares refinements, anisotropic temperature factors for non-O atoms, $\sum w(|F_o| - |F_c|)^2$ minimized, $w^{-1} = [\sigma^2|F_o| + (0{\cdot}015|F_o|)^2 + 2{\cdot}0]$. Refinements in $P2/c$ and $C2/c$. $P2/c$ gave larger standard deviations and positional parameters not significantly different from those in $C2/c$. Final refinement in $C2/c$ with 979 reflections, $R = 0{\cdot}036$, $wR = 0{\cdot}044$, $S = 1{\cdot}8$. Correction for secondary extinction (Zachariasen, 1967), $g = 0{\cdot}43\ (3) \times 10^{-4}$. $(\Delta/\sigma)_{max} = 0{\cdot}02$, final $\Delta\rho$ excursions $\le 2{\cdot}5$ e Å^{-3}. Scattering factors and anomalous-dispersion factors from *International Tables for X-ray Crystallography* (1974). Programs used: see Lundgren (1982).

Discussion. Final atomic coordinates are listed in Table 1* and selected interatomic distances and angles in Table 2. A stereoview of the structure is shown in Fig. 1. The structure of Hg_2OI is quite different from that of terlinguaite, $Hg_4O_2Cl_2$. Hg_2OI may be described as built up of infinite zigzag $-Hg^{II}-O-Hg^{II}-$ chains, running in the y direction, condensed by the Hg^I-Hg^I groups to form folded layers which are further connected to form a three-dimensional structure by weak $Hg^{II}-O$ bonds (Fig. 1). The I atoms, situated in cavities in the layers, are only weakly bonded to Hg^{II}. By substitution of the Hg^I dimers by Hg^{II} atoms in the $(Hg_2O^+)_n$ layers of Hg_2OI, the same types of layers, $(Hg_3O_2^{2+})_n$, are obtained as found in $Hg_3O_2SO_4$ (Nagorsen, Lyng, Weiss & Weiss, 1962) and $Hg_3O_2CrO_4$ (Stålhandske, 1980).

Endless chains with Hg diagonally coordinated by O atoms (Hg–O ~ 2·0–2·1 Å; ∠O–Hg–O ~ 180°) are building elements in many mercury(II) structures. In Hg_2OI the $Hg^{II}-O$ bonds are somewhat longer (Hg–O 2·13, 2·16 Å) and the angle $O-Hg^{II}-O$ smaller (165°) than usually found. This is due to the coordination to a third O atom (Hg–O 2·47 Å) and to two I atoms (Hg–I 3·05, 3·14 Å). If these weak bonds are included in the coordination, the Hg^{II} coordination polyhedron is a distorted square pyramid. The Hg^I-Hg^I bond of 2·53 Å in Hg_2OI is close to the upper limit found in Hg^I compounds (Levason & McAuliffe, 1977). The Hg^I atoms are almost linearly coordinated with an Hg^I-O bond of 2·14 Å. The shortest Hg^I-I distance is 3·47 Å.

* List of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39824 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic coordinates and B or B_{eq} values*

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

	x	y	z	B or B_{eq} (Å^2)
Hg(1)	0·42663 (3)	0·33341 (9)	0·22195 (8)	2·35 (1)
Hg(2)	0·24490 (3)	0·09588 (7)	0·21067 (7)	1·89 (1)
I	0·11394 (5)	0·33246 (13)	0·32323 (14)	2·33 (2)
O	0·3028 (5)	0·3577 (11)	0·1589 (12)	1·47 (11)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

Hg(1)–O	2·141 (8)	Hg(2)–O	2·155 (8)
Hg(1)–Hg(1^i)	2·534 (1)	Hg(2)–O^{iii}	2·471 (8)
		Hg(2)–I	3·051 (1)
Hg(2)–O^{ii}	2·129 (8)	Hg(2)–I^{ii}	3·136 (2)
Hg(1^i)–Hg(1)–O	174·6 (2)	Hg(1)–O–Hg(2)	113·4 (4)
		Hg(1)–O–Hg(2^{iv})	116·8 (4)
O–Hg(2)–O^{ii}	165·3 (1)	Hg(2)–O–Hg(2^{iv})	111·0 (4)
O–Hg(2)–O^{iii}	78·7 (3)	Hg(1)–O–Hg(2^{iii})	109·6 (3)
O^{ii}–Hg(2)–O^{iii}	115·5 (3)	Hg(2)–O–Hg(2^{iii})	101·3 (3)
I–Hg(2)–I^{ii}	169·84 (2)	Hg(2^{iv})–O–Hg(2^{iii})	103·1 (3)
Hg(2)–I–Hg(2^{iv})	69·54 (5)		

Symmetry code: (i) $1-x, y, \frac{1}{2}-z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $\frac{1}{2}-x, \frac{1}{2}-y, -z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

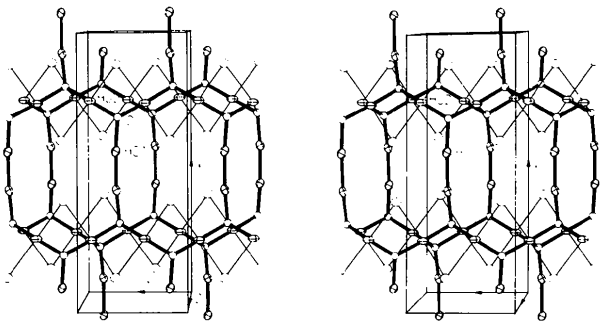

Fig. 1. A stereoview of the structure.

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