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The Room-Temperature Structures of Mercury Niobium Fluoride, $Hg_{3-\delta}NbF_6$, and Mercury Tantalum Fluoride, $Hg_{3-\delta}TaF_6$

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Abstract. $Hg_{3-\delta}NbF_6$, $\delta = 0{\cdot}119\,(4)$ at 293 K, $M_r = 784{\cdot}8\,(8)$, tetragonal, $I4_1/amd$, $a = 7{\cdot}692\,(1)$, $c = 12{\cdot}679\,(2)$ Å, $V = 750{\cdot}2\,(2)$ Å^3, $Z = 4$, $D_x = 6{\cdot}95\,(1)$ Mg m^{-3}, graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 61$ mm^{-1}, $F(000) = 1302\,(1)$. $Hg_{3-\delta}TaF_6$, $\delta = 0{\cdot}116\,(4)$ at 293 K, $M_r = 873\,(1)$, $I4_1/amd$, $a = 7{\cdot}711\,(1)$, $c = 12{\cdot}714\,(2)$ Å, $V = 756{\cdot}0\,(2)$ Å^3, $Z = 4$, $D_x = 7{\cdot}68\,(1)$ Mg m^{-3}, $\mu = 75$ mm^{-1}, $F(000) = 1431\,(1)$. The structures were refined from 252 and 254 unique diffractometer-measured reflections to a final R (unweighted) of 0·031 and 0·025, respectively. Both compounds are isostructural with $Hg_{3-\delta}AsF_6$ and consist of chains of metallically bonded Hg atoms in an incommensurate MF_6^- host lattice. Anisotropic refinement was performed for the Hg atoms for both the title compounds and $Hg_{3-\delta}SbF_6$; comparison is made of bond lengths in the compounds involving As, Nb, Sb and Ta.

Introduction. Soon after the discovery of the first infinite linear chain compound $Hg_{3-\delta}AsF_6$ in 1973 (Brown, Cutforth, Davies, Gillespie, Ireland & Vekris, 1974) the isostructural compound $Hg_{3-\delta}SbF_6$ was reported (Koteles, Datars, Cutforth & Gillespie, 1976). Recently, two more members of this series, $Hg_{3-\delta}NbF_6$ and $Hg_{3-\delta}TaF_6$, have been prepared (Brown, Gillespie, Morgan, Tun & Ummat, 1984) and their structures are reported here.

Experimental. Crystals of both compounds give X-ray precession photographs essentially identical to those of $Hg_{3-\delta}SbF_6$ (see Fig. 1 of Tun & Brown, 1982). Details of Bragg intensity measurements and structure refinements are summarized in Table 1. The intrachain Hg–Hg distance was calculated from separation of thin diffuse sheets observed on photographs and found to be 2·670 (3) for $Hg_{3-\delta}NbF_6$ and 2·674 (4) Å for $Hg_{3-\delta}TaF_6$. Values of δ reported in the *Abstract* were deduced from the difference between Hg–Hg distances and the a host-lattice dimensions. As in the case of $Hg_{3-\delta}SbF_6$, no structure is visible in the diffuse sheets and we infer that at room temperature there is no ordering of the chains relative to each other. Because both compounds have large X-ray absorption coefficients a good absorption correction is essential. For each crystal we measured two sets of intensities. The first (data set I) was chosen to include all non-equivalent reflections and consisted of a quarter of all the reflections with $2\theta \leq 55°$, the second (data set II) comprised a small number of strong reflections for which all equivalent reflections were measured. This set was used in developing the absorption correction. The crystal of $Hg_{3-\delta}NbF_6$ had an irregular shape (diameter ~0·1 mm) with poorly defined faces and was approximated by a sphere with $\mu R = 3{\cdot}0$. Data sets I and II were combined and equivalent reflections averaged giving an internal agreement factor between equivalent reflections of 0·056 indicating that the spherical approximation was satisfactory. The absorption effects were much more severe for the $Hg_{3-\delta}TaF_6$ crystal which was a thin square plate (0·19 × 0·19 × 0·01 mm) with large (001) faces. In this case we performed a numerical absorption correction by treating the crystal as a polyhedron (*XRAY76*: *ABSORB* routine; Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). The internal agreement factor of data set II was reduced from 0·189 before the correction to 0·023 after.*

Experimental structure factors were calculated by taking weighted averages [$\omega = \sigma^{-2}$(counting)] of intensities of equivalent reflections from both data sets after correction for absorption. During refinement (on F) resulting structure factors were weighted with $\omega = [\sigma(\text{total})]^{-2} = [\sigma^2(\text{counting}) + k^2F_o^{\,2}]^{-1}$, k chosen so that σ(total) was equal on average to standard deviation of the independent measurements of structure factors. The initial atomic parameters for both refinements were those of $Hg_{3-\delta}SbF_6$ and, as in the previous case, incommensurate Hg chains were modelled by including partial Hg atoms at close intervals along the chains. After refinement $R_w = 0{\cdot}033$ for $Hg_{3-\delta}NbF_6$ and 0·029 for $Hg_{3-\delta}TaF_6$. The final values of the refined positional parameters are given in Table 2.

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* Details of absorption correction for $Hg_{3-\delta}TaF_6$, lists of positional and thermal parameters of all compounds, observed and calculated structure factors and the results of a similar refinement on $Hg_{3-\delta}SbF_6$ have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39400 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Summary of the structure determination*

When two entries are shown the first corresponds to M = Nb and the second to M = Ta.

Diffractometer: Nicolet $P2_1$
Lattice constants determined from 15 well centred reflections having $10 < 2\theta < 28°$

Data set (I) (includes at least one measurement of every non-equivalent reflection)

Maximum 2θ: 55°
$0 \le h, k \le 10, -16 \le l \le 16$
Standard reflections: 015 and 024, $4\bar{2}0$ and 008
Number of reflections measured: 993, 998
Number of unobserved reflections measured [$I < 3\sigma(I)$]: 357, 221
Number of unique reflections: 252, 254
Number of unique observed reflections: 181, 211

Data set (II) (includes all equivalent reflections for selected large structure factors for testing absorption correction)

$-3 \le h,k,l \le 3$
Standard reflections: 015 and 024, $4\bar{2}0$ and 008
Number of reflections measured: 144 (both compounds)
Number of unique reflections: 14 (both compounds)
Final R_w = 0·033, 0·029 (all reflections)
Weighting scheme: $\omega = [\sigma^2(\text{counting}) + k^2F_o^2]^{-1}$ with k = 0·0109, 0·0180
Standard deviation of an observation of unit weight: 1·83, 1·24
Max. Δ/σ in final cycle: 0·29, 0·13
Av. Δ/σ in final cycle: 0·04, 0·04
Secondary extinction correction (Larson, 1967): $g = 3\ (2) \times 10^{-8}$, $1\ (2) \times 10^{-8}$
Number of variables refined: 25
Scattering factors: neutral atoms from *International Tables for X-ray Crystallography* (1974).
Residual electron density and location:
max: +0·7 e Å^{-3} between Nb—F(2) bonds, 0·8 Å from Nb atom
+2·0 e Å^{-3} mid-point of Ta—F(1) bond
min: −1·1 e Å^{-3} between Nb—F(2) bonds, 2·5 Å from Nb atom
−1·0 e Å^{-3} between Ta—F(2) bonds, 2·3 Å from Ta atom

Table 2. *Atomic positional coordinates and equivalent isotropic thermal parameters* (Å^2 × 10^3)

The positional coordinates are based on the centrosymmetric setting of space group $I4_1/amd$. The upper entry corresponds to $Hg_{3-\delta}NbF_6$ and the lower to $Hg_{3-\delta}TaF_6$.

	x	y	z	U_{eq}*
Hg(1)†	0	$\frac{1}{32}$	−0·0011 (6)	61
	0	$\frac{1}{32}$	−0·0007 (5)	
Hg(2)†	0	$\frac{3}{32}$	−0·0008 (5)	59
	0	$\frac{3}{32}$	−0·0009 (4)	55
Hg(3)†	0	$\frac{5}{32}$	0·0009 (4)	57
	0	$\frac{5}{32}$	0·0014 (4)	53
Hg(4)†	0	$\frac{7}{32}$	0·0020 (2)	56
	0	$\frac{7}{32}$	0·0023 (2)	52
Nb	0	$\frac{1}{4}$	$\frac{3}{8}$	40
Ta	0	$\frac{1}{4}$	$\frac{3}{8}$	31
F(1)	0	$\frac{1}{4}$	0·2272 (6)	89
	0	$\frac{1}{4}$	0·2268 (9)	79
F(2)	0·673 (1)	$x+\frac{1}{4}$	$\frac{7}{8}$	68
	0·673 (1)	$x+\frac{1}{4}$	$\frac{7}{8}$	63

* $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

† The incommensurate chains are represented by four closely spaced Hg atoms with a partial occupancy corresponding to the expected stoichiometry.

Table 3. *Bond lengths and other important distances* (Å) *in* $Hg_{3-\delta}NbF_6$ *and* $Hg_{3-\delta}TaF_6$ *and comparison with* $Hg_{3-\delta}AsF_6$ *and* $Hg_{3-\delta}SbF_6$

	$Hg_{3-\delta}AsF_6$¶	$Hg_{3-\delta}SbF_6$**	$Hg_{3-\delta}NbF_6$	$Hg_{3-\delta}TaF_6$
M—F(1) (×4)	1·702 (2)	1·84 (1)	1·874 (8)	1·884 (12)
M—F(2) (×2)	1·720 (2)	1·88 (1)	1·885 (6)	1·884 (6)
Hg–Hg* (intrachain)	2·670 (5)	2·66 (2)	2·670 (3)	2·674 (4)
u_0†	0·07 (1)	0·037 (4)	0·026 (3)	0·030 (3)
Chain–chain‡	3·24 (2)	3·23 (1)	3·222 (7)	3·239 (6)
F(1)–chain§	2·87 (1)	2·86 (1)	2·86 (1)	2·86 (1)
F(2)–chain§	2·981 (5)	2·98 (1)	2·971 (4)	2·983 (2)

* Measured from the spacing between the diffuse sheets on the precession photographs.

† The maximum displacement (Å) of the chain from the straight configuration.

‡ The closest contact distance between the two neighbouring perpendicular chains which is greater than $c/4$ by $2u_o$.

§ Shortest distance to the neighbouring chain.

¶ From Brown, Datars & Gillespie (1982).

** From Tun & Brown (1982).

Discussion. The new compounds are almost identical in structure and dimension to $Hg_{3-\delta}SbF_6$ (Tun & Brown, 1982) except that the octahedral MF_6 ions do not show the tetragonal distortion found in the other two members of the series. The undulation of the chains with the periodicity of the host lattice originally observed in $Hg_{3-\delta}AsF_6$ by Schultz, Williams, Miro, MacDiarmid & Heeger (1978) is identical to that found in $Hg_{3-\delta}SbF_6$ (see Table 3).

In the present refinements, unlike the earlier ones, anisotropic temperature factors were refined for the partial Hg atoms. Each refinement was initially started with isotropic temperature factors for Hg atoms. At the end of the refinement the value of U_{22} (along the chain) was held fixed but U_{11} and U_{33} were allowed to vary separately. For the purpose of comparison a similar refinement was also carried out for $Hg_{3-\delta}SbF_6$ using the structure factors previously reported (Tun & Brown, 1982). The results of this new refinement have been deposited.* In all structures U_{11} does not vary significantly along the chain but U_{33}, which measures the thermal motion parallel to the undulations, is significantly smaller at those points where the chain is clamped in the z direction by a neighbouring chain and an F(1) atom, *i.e.* the points where the chain displacement is a maximum. The unexpectedly large value of U_{11} for all atoms in $Hg_{3-\delta}NbF_6$ is probably an artifact of the very simple absorption correction used. In other respects the temperature factors are essentially the same as those in $Hg_{3-\delta}SbF_6$, in particular the exceptionally large value of U_{22} for F(1) which we previously attributed to disorder arising from bonding with the incommensurate Hg chain.

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* See deposition footnote.

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$Na_7Nb_{15}W_{13}O_{80}$ – A New Type of Tunnel Structure Studied by X-ray Diffraction and HREM Techniques

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Abstract. $M_r = 5224{\cdot}5$, orthorhombic, *Pmab*, $a = 21{\cdot}962\ (2)$, $b = 17{\cdot}763\ (2)$, $c = 3{\cdot}9165\ (3)$ Å, $V = 1527{\cdot}9\ (3)$ Å^3, $Z = 1$, $D_m = 5{\cdot}61\ (1)$, $D_x = 5{\cdot}664\ (1)$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu(\text{Mo } K\alpha) = 241$ cm^{-1}, $F(000) = 2292{\cdot}7$, $T = 293$ K, $R = 0{\cdot}058$ for 936 independent reflexions. The structure is built up of pentagonal columns connected to each other directly and *via* a string of MO_6 octahedra, running parallel to the *c* axis. Large tunnels with an S-shaped cross section are formed, in which the Na atoms are statistically distributed. Four of the five heavy-atom sites are randomly occupied by Nb and W; the fifth entirely by Nb. X-ray and electron diffraction experiments indicate that the K and Ag analogues are isostructural. HREM images of the K compound confirm the structure.

Introduction. In the course of our studies of compounds with solid-electrolyte properties we have investigated among others the system $NaNbO_3$–Nb_2O_5–WO_3 in some detail (Hörlin, Marinder & Nygren, 1982). Besides an extended region where a phase of tetragonal tungsten-bronze type (or tripled TTB) is stable we found a new phase with the approximate composition $Na_{0.27}Nb_{0.53}W_{0.47}O_{2.87}$.

Experimental. Samples of the title compound were prepared by heating finely ground mixtures of $NaNbO_3$, Nb_2O_5 and WO_3 (all of high purity) in proportions close to 4:2:7. The reactions were carried out in sealed platinum tubes, at 970 K for 1 d and 1170 K for 3 or 4 d. A small amount of the microcrystalline product was mixed with a large excess of sodium chloride, sealed in an evacuated silica tube and heated to 1170 K. Slow cooling of the melt (~ 1 K h^{-1}) for 4 d, quenching and dissolving the sodium chloride in water produced a residue containing several crystalline phases, *inter alia* a single crystal of the title compound.

D_m determined from the apparent loss of weight in *n*-hexane. X-ray powder pattern registered in a Guinier–Hägg focusing camera with monochromatized Cu $K\alpha_1$ radiation, and evaluated as described elsewhere (Hörlin, Marinder & Nygren, 1982) to give the lattice parameters.* Electron optical investigations on the microcrystalline sample made with a Siemens ELMISKOP 102 and, later, with a JEOL JEM 200 CX, in a way described recently (Marinder & Sundberg, 1984). Dimensions of the single crystal ($0{\cdot}004 \times 0{\cdot}031 \times 0{\cdot}237$ mm) determined in a device constructed from a single-crystal orienter with a quarter χ-circle and a Nikon measuring microscope equipped with an Epi-Illuminator (Marinder, 1984).

Weissenberg photographs taken to check the quality of the crystal and to verify its symmetry. Diffraction intensities measured on a PW 1100 four-circle diffractometer (Mo $K\alpha$, graphite monochromator), 4° <

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* JCPDS Diffraction File No. 34-1486. See also deposition footnote.

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