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Single Crystal Growth, Crystal Structure and Thermal Behaviour of Mercury(II) Pyrophosphate Dihydrate

Matthias Weil*

Institute of Chemical Technologies and Analytics – Division of Structural Chemistry,
Vienna University of Technology, A-1060 Vienna, Austria

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Summary. Colourless single crystals of $Hg_2P_2O_7(H_2O)_2$ up to 0.4 mm in length were grown by a diffusion technique starting from aqueous solutions of $Na_4P_2O_7$ and $Hg(NO_3)_2$. The crystal structure is isotypic with that of $Ca_2P_2O_7(H_2O)_2$ and was determined from a four-circle diffractometer data set (space group $P\bar{1}$, $Z=2$, $a=6.9374(7)$, $b=7.4396(8)$, $c=7.9863(7)$ Å, $\alpha=84.685(8)$, $\beta=75.158(8)$, $\gamma=72.818(8)°$, 2413 structure factors, 132 parameters, $R[F^2 > 2\sigma(F^2)]=0.0181$, $wR(F^2 \text{ all})=0.0384$). $Hg_2P_2O_7(H_2O)_2$ is composed of approximately eclipsed $P_2O_7{}^{4-}$ anions and distorted $[HgO_6]$ octahedra and $[HgO_7]$ pentagonal bipyramids as the main building units. The structure is stabilized by inter-water hydrogen bonding and by hydrogen bonding between terminal pyrophosphate oxygen atoms and the water molecules. The P–O distances to the terminal oxygen atoms range from 1.501(4) to 1.536(3) Å, with an average of 1.522 Å; the mean distance of 1.615 Å to the bridging O atom is considerably longer with an (O–P–O) bridging angle of 123.44(19)°. Both Hg atoms have two short Hg–O bonds around 2.17 Å and additional bonds ranging from 2.381(3) to 2.708(4) Å. Upon heating above 160°C, both crystal water molecules are released simultaneously and anhydrous $Hg_2P_2O_7$ is formed which is stable up to ca. 660°C. Above this temperature the material decomposes completely.

Keywords. Mercury I; pyrophosphates; Crystal structure; Thermal behaviour.

Introduction

The toxicity of mercury and its compounds has been known since ancient times. The contamination of soils and water with this heavy metal is a serious environmental problem and the removal/decontamination is often a challenging process. Recently, phosphate-induced mercury stabilization/solidification has been investigated [1] in the face of the very low solubility of mercury phosphates and the well-priced availability of phosphoric acids or soluble phosphates. To optimize

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* Corresponding author. E-mail: mweil@mail.zserv.tuwien.ac.at

formation conditions of the corresponding compounds, a more detailed knowledge of the properties and especially of the structural data of mercury phosphates is necessary. Within the system Hg–P^V–O–(H) numerous phases have been known for a long time [2], and the large structural diversity of the corresponding compounds is caused by the different stable oxidation states of Hg (+1, +4/3, +2) and the feasibility to form condensed and hydrous phosphates. In the meantime, most of these compounds were crystallographically well-characterized, including the anhydrous orthophosphates $Hg^{II}_3(PO_4)_2$ [3], α- and β-$(Hg^I_2)_3(PO_4)_2$ [4], the phosphates with the triangular mercury Hg_3^{4+} cluster, $(Hg_3)_3(PO_4)_4$ and $(Hg_3)_2(HgO_2)(PO_4)_2$ [5], the pyrophosphates $Hg^{II}_2P_2O_7$ [6] and $(Hg^I_2)_2(P_2O_7)$ [4], the polyphosphate $Hg^{II}(PO_3)_2$ [7], as well as the hydrous phases Hg^{II}-HPO_4 [8], $(Hg^I_2)(H_2PO_4)_2$ [9], and $(Hg^I_2)_2(H_2PO_4)(PO_4)$ [10].

In a previous investigation on hydrous and anhydrous mercuric pyrophosphates, preparation and X-ray data of polycrystalline $Hg_2P_2O_7(H_2O)_2$ were reported [11]. However, up to now no structural details for this compound are known. Therefore it seemed appropriate to grow single crystals, to analyze the crystal structure, and to investigate the thermal behaviour of this phase.

Results and Discussion

Fournier & Capestan have proposed an orthorhombic cell for $Hg_2P_2O_7(H_2O)_2$ with lattice parameters: $a = 7.755$, $b = 9.90$, $c = 7.18$ Å, $Z = 4$ [11]. Based on these values, the calculated X-ray density of 7.36 g·cm^{-1} is much too high for such a compound and therefore the given cell is doubtful. In fact, $Hg_2P_2O_7(H_2O)_2$ crystallizes in the triclinic crystal system and shows a considerably lower density of 5.3 g·cm^{-1}. Nevertheless, the reported unindexed X-ray powder pattern (PDF-entry #30–0839) is in agreement with the present single crystal data.

The thermal decomposition of $Hg_2P_2O_7(H_2O)_2$ takes place in two steps (Fig. 1, Eqs. 1, 2). Above ca. 160°C, the two crystal water molecules are removed

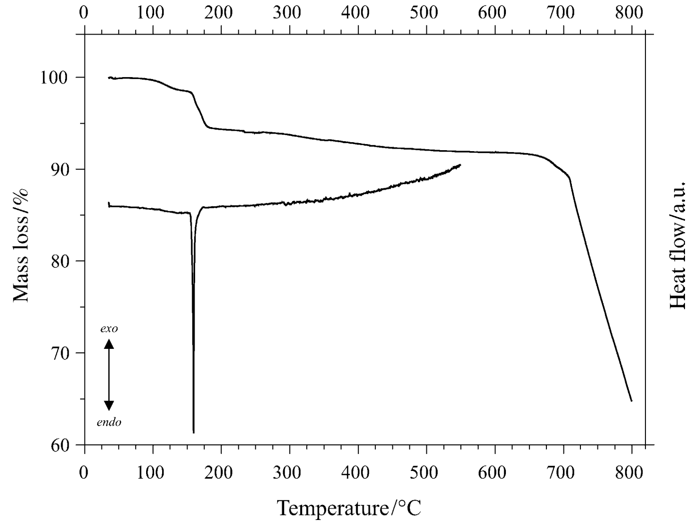

Fig. 1. TG and DSC curves of the thermal decomposition of $Hg_2P_2O_7(H_2O)_2$

simultaneously and anhydrous $Hg_2P_2O_7$ is formed (Eq. 1) which was proved by subsequent XRPD of the heated material. This phase is stable up to 660°C, in very good agreement with literature data [2] and the value determined from temperature-dependent *Guinier* photographs [6].

$$\mathrm{Hg_2P_2O_7(H_2O)_{2,s}} \rightarrow \mathrm{Hg_2P_2O_{7,s}} + 2\mathrm{H_2O,_{g}}\,(\uparrow)$$

$$\text{(obs. mass loss: 5.7\%; th.: 5.9\%)} \qquad \text{(Eq. 1)}$$

$$\mathrm{Hg_2P_2O_{7,\,s}} \rightarrow 2\mathrm{Hg,_{g}}(\uparrow) + \mathrm{O_{2,\,g}}(\uparrow) + \tfrac{1}{2}\mathrm{P_4O_{10},_{g}}(\uparrow) \qquad \text{(Eq. 2)}$$

Di- or pyroanions of the type $X_2O_7{}^{n-}$ (X = Si, Ge: $n = 6$; P, As, V: $n = 4$; S, Cr: $n = 2$) with four-coordinated X atoms adopt various types of conformation (eclipsed, staggered, and corresponding intermediates), and their bridging angles (X–O–X) show a high flexibility and range from 118° up to 180°. Peculiarities of these anions have been reviewed in detail in the past [17, 18]. For hydrous phases with the general formula $M^{II}{}_2X_2O_7(H_2O)_2$ (X = P, As, V) only three structure families are known up to now: A monoclinic structure (space group $P2_1/n$, $Z = 4$) is realized for the isotypic compounds with X = P: M = Mg [19], Mn [20], Co [21], Fe [22], and X = As: M = Mg [23], Mn [24], Co [25], Ni [25], and Zn [23], whereas both $Ca_2V_2O_7(H_2O)_2$ [26] and $Ca_2P_2O_7(H_2O)_2$ [27] crystallize with two formula units in space group $P\bar{1}$, but in two different structure types. In the majority of cases, mercury(II) compounds show a unique crystal chemistry [28] and close structural relations to corresponding compounds of other divalent metals with comparable ionic radii are rarely observed. Thus $Hg_2P_2O_7(H_2O)_2$ is an exception, because it is isotypic with the above-mentioned calcium compound, $Ca_2P_2O_7(H_2O)_2$[a]. The latter is of considerable biological interest since it plays an important role in biological mineralization procedures and is involved in crystal deposition diseases, in particular in chondrocalcinosis (pseudogout) [29].

The crystal structure of $Hg_2P_2O_7(H_2O)_2$ exhibits $[HgO_6]$ and $[HgO_7]$ polyhedra and a pyrophosphate anion as the main building units. The three-dimensional network is achieved by sharing common oxygen atoms between both $[HgO_x]$ polyhedra and the P_2O_7 group which also serves as a monodentate ligand to both Hg atoms. Additional stabilization of the structure is achieved by two types of hydrogen bonding: (1) by inter-water hydrogen bonding, and (2) by hydrogen bonding between terminal pyrophosphate oxygen atoms and the water molecules (Fig. 2).

Like in the mercury(II) phosphates $Hg_3(PO_4)_2$ [3], $Hg_2P_2O_7$ [6], and $Hg(PO_3)_2$ [7] as well as in other mercury(II) oxocompounds, both Hg atoms show a pronounced $[2 + x]$ coordination which is caused by the *sp*-hybridization of the metal centre. For the title compound, short Hg–O distances around 2.17 Å and a nearly linear (O–Hg–O) angle of ca. 167° are observed. The remaining O atoms show

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[a] The reported cell of $Ca_2P_2O_7(H_2O)_2$ [27] can be transformed into the chosen setting of $Hg_2P_2O_7(H_2O)_2$ by the matrix $\boldsymbol{P} = \begin{pmatrix} 0 & 0 & -1 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix}$

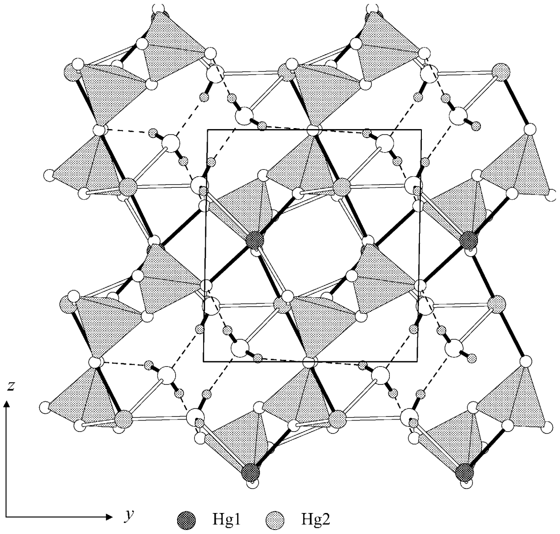

Fig. 2. Projection of the crystal structure along [100]; the unit cell is outlined and the pyrophosphate anion is plotted in the polyhedral representation; short Hg–O bonds are given as solid lines, longer Hg–O bonds as open lines; hydrogen bonding is indicated by dotted lines

considerably longer Hg–O distances, ranging from 2.381(3) to 2.510(4) Å for the six-coordinated Hg1 and from 2.510(3) to 2.708(4) Å for the seven-coordinated Hg2 atom. The corresponding coordination figures might be described as a distorted octahedron around Hg1 and a distorted pentagonal bipyramid around Hg2 (Fig. 3). For both Hg atoms, the nearest "non-bonding" O atoms are located at a distance of ca. 3.25 Å. In the isotypic Ca compound both metal atoms are seven-coordinated with Ca–O distances ranging from ca. 2.3 to 2.7 Å.

Like in $Ca_2P_2O_7(H_2O)_2$, the pyrophosphate anion displays an approximately eclipsed conformation (Fig. 3) with a bridging angle (P2–O5–P1) = 123.44(19)° and a dihedral angle along (O4, P1, O5, P2 and O6) = 33.14(20)°. The average torsion angle between the terminal pyrophosphate backbone atoms O4 and O6 and the (P–O–P) bridge is −161.2° [(O4–P1–O5–P2) = −157.2(2)°; (O6–P2–O5–P1) = −165.2(2)°]. In agreement with other pyrophosphates, the P–O distances to the bridging O_b atom are considerably longer ($\bar{d}(P–O_b) = 1.615$ Å) than the distances to the terminal O_t atoms ($\bar{d}(P–O_t) = 1.522$ Å).

The coordination numbers of the O atoms range from 2 to 3. The two-coordinated atoms O4 and O6 have one Hg atom and one P atom as coordination partners and, additionally, are involved in hydrogen bonding, whereas the pyrophosphate bridging atom O5 is exclusively bonded to both P atoms; all three-coordinated O atoms are bonded to two Hg atoms and one P atom. The two water molecules form one inter-water hydrogen bond and three hydrogen bonds to the terminal backbone oxygen atoms O4 and O6 (see Table 1).

For all atoms in the structure, results of the bond-valence analysis, using the parameters provided by *Brese* and *O'Keeffe* [30], are within the scope of the expected values. The presence of crystal water and of a pyrophosphate group is clearly reflected in the corresponding vibrational spectrum (Fig. 4, Table 2). The

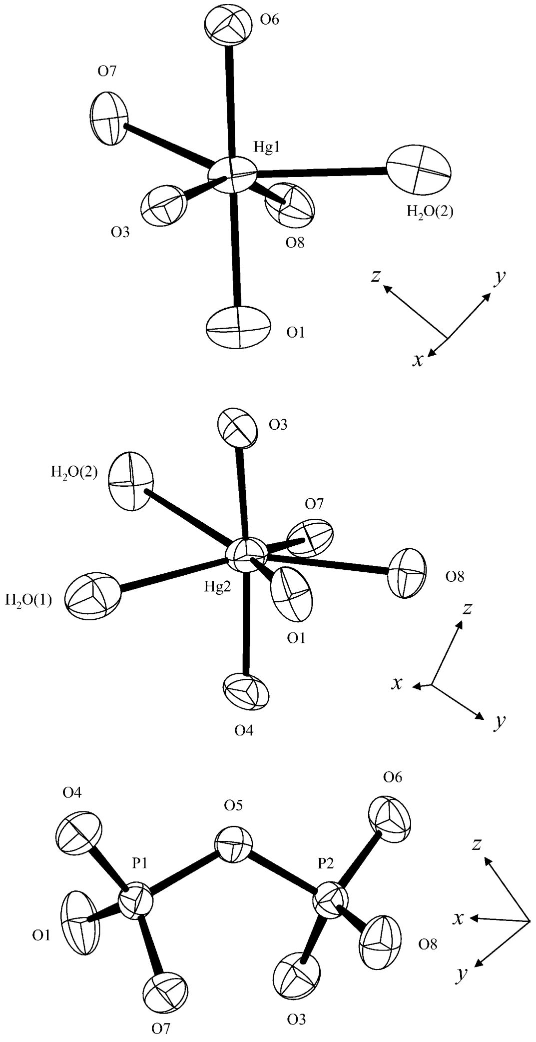

Fig. 3. Plot of the $[Hg1O_6]$ and $[Hg2O_7]$ polyhedra and the pyrophosphate anion with displacement ellipsoids drawn at the 90% probability level

Table 1. Details of hydrogen bonding [Å, °]

D–H	*d*(D–H)	*d*(H..A)	<DHA	*d*(D..A)	A
H_2O_1-H1	0.806	2.093	158.58	2.858	O4
H_2O_1-H2	0.822	2.008	169.63	2.821	O6
H_2O_2-H3	0.817	2.036	171.30	2.847	O6
H_2O_2-H4	0.866	1.895	165.60	2.743	H_2O_1
∠(H1-H_2O_1-H2)	115(6)				
∠(H3-H_2O_2-H4)	107(6)				

obtained values for the terminal (PO_3) stretching modes and for the symmetric and antisymmetric (P–O–P) bridge stretching vibrations are in the same range as for other pyrophosphates with a bent (P–O–P) bridge [31–33].

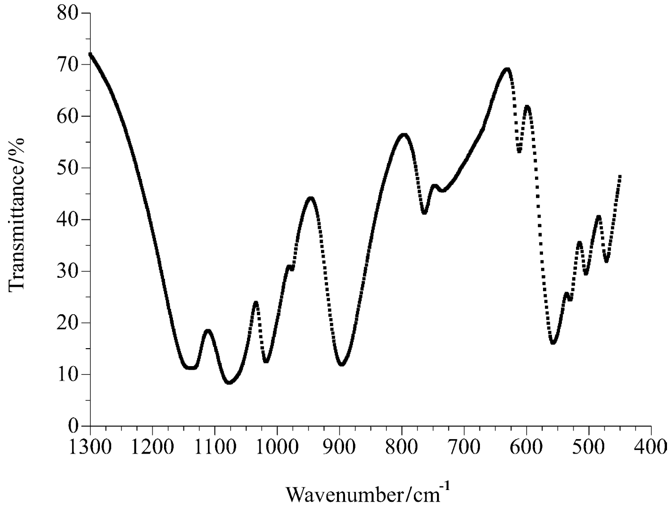

Fig. 4. Infrared spectrum of $Hg_2P_2O_7(H_2O)_2$ in the range $\bar{\nu} = 1300–400\,cm^{-1}$; the corresponding band assignments are given in Table 2

Table 2. IR absorption frequencies [cm^{-1}], estimated intensities, and band assignments[a]

3350	s	$\bar{\nu}(H_2O)$
1654	m	$\delta(H_2O)$
1139	s	
1077	s	$\bar{\nu}_{as}(PO_3)+\bar{\nu}_s(PO_3)$
1017	s	
976	w	
896	s	$\bar{\nu}_{as}(POP)$
763	m	$\bar{\nu}_s(POP)$
738	w	
611	m	$\delta(PO_3) + \rho(PO_3)$
557	s	
530	w	
504	m	
471	m	

[a] $\bar{\nu}_s$ = symmetric stretching, $\bar{\nu}_{as}$ = antisymmetric stretching, δ = bending, ρ = rocking, s = strong, m = medium, w = weak.

Experimental Section

Preparation: Single phase polycrystalline $Hg_2P_2O_7(H_2O)_2$ was prepared by adding a slightly acidified mercury(II) nitrate solution drop by drop to an excess solution of $Na_4P_2O_7$ which was also slightly acidified with a few drops of concentrated nitric acid. Reverse addition ($Na_4P_2O_7$ solution added to the mercury(II) nitrate solution) leads to precipitation of the anhydrous mercury(II) pyrophosphate, $Hg_2P_2O_7$ [6]. All reagents used were of analytical quality and purchased from Merck, Darmstadt.

Single crystals of the title compound were grown by a diffusion technique: A small beaker filled with acidified mercury(II) nitrate solution up to the maximum level was placed into a large beaker; on top of the small beaker's fringe a paper filter was deposited as a diffusion barrier. Additionally, the paper filter was pinned down with a thin glass slide to avoid sinking of the paper filter during filling of the large beaker and to minimize the diffusion pathway from the small into the large beaker. Then diluted $Na_4P_2O_7$ solution was filled carefully into the large beaker so that the small beaker was completely immerged into this solution. This device was then placed in a dark room and set aside for three weeks. After this crystallization period, a few well-shaped colourless and translucent single crystals up to 0.4 mm length of the title compound were grown on top of the glass slide and on top of the paper filter.

Single crystal diffraction intensities of $Hg_2P_2O_7(H_2O)_2$ were collected in the $\omega/2\theta$-scan technique on a CAD4 (Nonius) four-circle diffractometer. The full reciprocal sphere was measured and three control reflections were recorded every 5 hours; no significant variation of the corresponding intensities was observed during the entire data collection. The measured intensities were corrected for *Lorentz* and

Table 3. Details of data collection and structure refinement

Temperature/°C	22(2)
Formula weight/g·mol^{-1}	611.15
Diffractometer	CAD4 (Nonius)
Radiation; λ/Å	Mo K$\bar{\alpha}$; 0.71073
Space group (no.)	$P\bar{1}$ (# 2)
Formula units Z	2
Crystal dimensions/mm	$0.10 \cdot 0.07 \cdot 0.03$
Crystal description	colourless parallelepiped
a/Å	6.9374(7)
b/Å	7.4396(8)
c/Å	7.9863(7)
α/°	84.685(8)
β/°	75.158(8)
γ/°	72.818(8)
V/Å^3	380.59(7)
μ/mm^{-1}	40.734
X-Ray density/g·cm^{-3}	5.333
Range $\theta_{min} - \theta_{max}$	2.64 – 30.97
Range	
h	$-10 \rightarrow 10$
k	$-10 \rightarrow 10$
l	$-11 \rightarrow 11$
Structure refinement	SHELX97 [13]
Measured reflections	4824
Independent refelections	2413
Obs.reflections [$I > 2\sigma(I)$]	1944
R_i	0.0266
Absorption correction	HABITUS [12]
Transmission coefficients T_{min}; T_{max}	0.0935; 0.2530
Number of parameters	132
Extinction coefficient (SHELXL97)	0.0129(3)
Diff. elec. dens. max; min/	2.07 (0.78, Hg1)
e$^-$·Å^{-3} (dist./Å, atom)	−1.25 (1.03, Hg1)
$R[F^2 > 2\sigma(F^2)]$	0.0181
$wR2(F^2$ all)	0.0384
Goof	1.019
CSD number	413085

polarization effects, and an absorption correction was applied using the program HABITUS [12] by minimizing the R_i value of 14 ψ-scanned reflections and subsequent optimisation of the crystal shape. The so derived habit was the basis of the numerical absorption correction. The crystal structure was solved by direct methods and refined with the SHELX97 program package [13]. In the final least-squares cycles all non H-atoms were refined anisotropically. The positions of the H atoms of the water molecules were taken from the final difference *Fourier* maps and then refined using soft constraints. The highest difference peaks were located close to the mercury positions. Checks by the PLATON program [14] revealed no higher symmetry. Further details of data collection and structure refinement are summarized in Table 3. Final atomic coordinates, equivalent isotropic displacement parameters and selected interatomic distances, as well as angles and bond-valence parameters [15] are given in Tables 4 and 5. Details of hydrogen bonding are listed in Table 1. Additional crystallographic information on $Hg_2P_2O_7(H_2O)_2$ is available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, e-mail: crysdata@fiz-karlsruhe.de, by quoting the literature citation, the name of the author, and the depository number listed at the end of Table 3. Drawing of structural details were produced using the program ATOMS [16].

Table 4. Atomic coordinates and isotropic displacement parameters [Å^2]

Atom	*Wyckoff* Position	*x*	*y*	*z*	U_{eq}
Hg1	2*i*	0.19273(3)	0.23042(2)	0.52302(2)	0.01345(6)
Hg2	2*i*	0.73746(3)	0.36657(3)	0.24734(2)	0.01466(6)
P1	2*i*	0.22329(18)	0.53759(16)	0.18768(14)	0.0093(2)
P2	2*i*	0.32924(18)	0.79656(16)	0.36363(14)	0.0090(2)
O1	2*i*	0.0083(5)	0.4287(5)	0.7254(5)	0.0189(7)
H_2O_1	2*i*	0.1130(6)	0.1705(6)	0.0588(5)	0.0216(8)
O3	2*i*	0.1626(5)	0.7595(5)	0.5202(4)	0.0155(7)
O4	2*i*	0.2678(6)	0.4927(5)	−0.0018(4)	0.0150(7)
O5	2*i*	0.2751(5)	0.7340(4)	0.1969(4)	0.0115(6)
O6	2*i*	0.3067(5)	0.0068(5)	0.3285(4)	0.0137(6)
O7	2*i*	0.3601(5)	0.3886(5)	0.2825(4)	0.0139(6)
O8	2*i*	0.4533(5)	0.3132(5)	0.6294(4)	0.0148(6)
H_2O_2	2*i*	0.7224(6)	0.0322(6)	0.2399(5)	0.0204(7)
H1	2*i*	0.161(10)	0.255(8)	0.015(8)	0.029(9)
H2	2*i*	0.166(10)	0.110(9)	0.135(7)	0.029(9)
H3	2*i*	0.608(7)	0.013(10)	0.265(8)	0.029(9)
H4	2*i*	0.787(10)	−0.019(9)	0.140(6)	0.029(9)

Table 5. Interatomic distances [Å] and angles [°] for the [HgO_x] polyhedra and the pyrophosphate group; also given are bond-valence-sums (BVS) for all atoms except H_2O molecules

Hg1	O1	O6	O7	O8	O3	H_2O_2
O1	**2.166(3)**	4.339(5)	3.729(5)	2.863(5)	3.146(5)	3.410(6)
O6	165.30(13)	**2.209(3)**	2.950(5)	3.955(5)	3.180(5)	3.391(5)
O7	110.07(13)	79.88(12)	**2.381(3)**	2.971(5)	3.995(5)	4.734(5)
O8	76.80(13)	116.87(12)	76.24(12)	**2.431(3)**	4.907(5)	3.143(5)
O3	83.14(12)	83.44(12)	108.03(11)	159.65(11)	**2.554(3)**	4.178(5)
H_2O_2	89.89(13)	88.36(12)	141.16(12)	76.52(12)	107.17(11)	**2.637(4)**

(*continued*)

Table 5 (*continued*)

Hg2	O4	O3	O8	O7	H_2O_2	O1	H_2O_1
O4	**2.140(3)**	4.268(5)	3.144(5)	3.238(5)	3.866(5)	3.305(5)	3.156(5)
O3	161.98(14)	**2.182(3)**	3.502(5)	3.855(5)	2.962(5)	3.130(5)	3.417(5)
O8	84.70(12)	96.30(12)	**2.510(3)**	3.089(5)	4.804(5)	2.863(5)	4.923(6)
O7	87.71(12)	110.02(12)	75.83(11)	**2.518(3)**	3.043(5)	4.941(5)	4.884(6)
H_2O_2	111.60(13)	77.57(13)	144.97(12)	74.18(12)	**2.528(4)**	4.955(5)	3.140(6)
O1	85.14(13)	78.85(12)	66.46(11)	142.09(11)	142.43(12)	**2.706(4)**	3.361(5)
H_2O_1	80.30(13)	87.96(12)	141.21(12)	138.33(11)	73.61(12)	76.73(11)	**2.708(4)**

P1	O4	O7	O1	O5
O4	**1.513(3)**	2.508(5)	2.509(5)	2.523(5)
O7	111.9(2)	**1.514(3)**	2.529(5)	2.530(4)
O1	110.9(2)	112.2(2)	**1.533(4)**	2.521(5)
O5	107.40(18)	107.79(18)	106.35(19)	**1.616(3)**

∠(P2-O5-P1) 123.44(19)

P2	O8	O6	O3	O5
O8	**1.501(4)**	2.520(5)	2.541(5)	2.541(5)
O6	112.4(2)	**1.532(3)**	2.551(5)	2.459(5)
O3	113.6(2)	112.5(2)	**1.536(3)**	2.507(4)
O5	109.25(19)	102.81(18)	105.41(18)	**1.614(3)**

BVS: Hg1 2.11, Hg2 2.16, P1 4.90, P2 4.88, O1 1.98, O3 2.02, O4 1.96, O5 2.01, O6 1.79, O7 1.89, O8 1.89.

Thermoanalytical measurements were performed in an open system under a flow of N_2 gas on a Mettler-Toledo TG50 (35–800°C, heating rate $5°C\cdot min^{-1}$, corundum crucibles) and a DSC 25 system (35–550°C, heating rate $5°C\cdot min^{-1}$, aluminium capsules).

IR spectra were recorded in N_2 atmosphere on a Perkin-Elmer 16PC FTIR spectrometer in the range $\bar{\nu} = 4400–450\,cm^{-1}$ using a KBr disk as matrix.

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