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Mercury Phosphates with the Triangular Hg_3^{4+} Cluster: $(Hg_3)_3(PO_4)_4$ and $(Hg_3)_2(HgO_2)(PO_4)_2$[1]

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Hydrothermal treatment of microcrystalline $(Hg_2)_2P_2O_7$ in diluted phosphoric acid or demineralized water at 400°C yields colorless crystals of $(Hg_3)_3(PO_4)_4$ and yellow crystals of $(Hg_3)_2(HgO_2)(PO_4)_2$, respectively. The crystal structures have been solved and refined from single crystal diffractometer data to residuals $R[F^2 > 2\sigma(F^2)] = 0.021$ and $wR2[F^2] = 0.047$ for $(Hg_3)_3(PO_4)_4$ and $R[F^2 > 2\sigma(F^2)] = 0.028$ and $wR2[F^2] = 0.072$ for $(Hg_3)_2(HgO_2)(PO_4)_2$. The crystal structure of $(Hg_3)_3(PO_4)_4$ ($R3c$ (No. 161), $Z = 6$, $a = 16.3957(10)$ Å, $c = 10.6606(9)$ Å, $V = 2481.9(3)$ Å^3) is isotypic with the corresponding arsenate $(Hg_3)_3(AsO_4)_4$. $(Hg_3)_2(HgO_2)(PO_4)_2$ crystallizes with two formula units in the monoclinic space group $P2_1/c$ (No. 14), with lattice parameters $a = 6.2506(7)$ Å, $b = 9.9366(10)$ Å, $c = 9.6663(12)$ Å, $\beta = 95.783(10)°$, and $V = 597.3(1)$ Å^3, and shows a topological relationship to the mineral *terlinguaite* ($Hg_4O_2Cl_2$). Both phosphates contain tetrahedral PO_4^{3-} groups and the triangular mercury cluster Hg_3^{4+} with $\bar{d}$(Hg–Hg) = 2.666 Å for $(Hg_3)_3(PO_4)_4$ and 2.682 Å for $(Hg_3)_2(HgO_2)(PO_4)_2$, respectively. In the latter compound a linear mercurate group, HgO_2^{2-} with $\bar{d}$(Hg–O) = 2.031(7) Å, is also present. For both structures the three-dimensional connection between the building units is achieved *via* common oxygen atoms. Both compounds disproportionate upon heating ($T > 300$°C) to $Hg_3(PO_4)_2$ and elemental mercury. © 2001 Academic Press

Key Words: **mercury; phosphate; mercury cluster; crystal structure; thermal behavior.**

INTRODUCTION

The crystal chemistry of mercury with its various oxidation states in inorganic compounds might roughly be classified into five parts: amalgams (for a survey on alkali amalgams, see (1)), compounds with divalent Hg^{2+} cations, compounds with Hg_2^{2+} dumbbells, compounds with distinct Hg^{2+} cations besides Hg_2^{2+} groups inside the crystal structure, and finally compounds with polyatomic Hg_n^{x+} clusters. These cluster compounds could be subdivided into linear arrangements of mercury atoms with $n = 3$ (2–4), $n = 4$ (4, 5), and $n = \infty$ (6), systems with a layer arrangement (7), and systems with a triangular configuration of mercury atoms. For the latter the cluster composition is Hg_3^{4+}. A survey on the crystal chemistry of mercury compounds with different oxidation states <II and a comparative crystal chemical analysis has been published recently by Pervukhina *et al.* (8).

Up to now, for the triangular Hg_3^{4+} cationic group, only three representatives for inorganic compounds have been known: the two minerals *terlinguaite* ($Hg_4O_2Cl_2$) (9) and *kutznetsovite* (Hg_3AsO_4Cl) (10), and the synthetic arsenate $(Hg_3)_3(AsO_4)_4$ (11). In the course of our systematic investigations on phosphates containing mercury in different oxidation states [$Hg_2P_2O_7$ (12), $Hg(PO_3)_2$ (13), α-$(Hg_3)_2(PO_4)_2$, β-$(Hg_3)_2(PO_4)_2$, $(Hg_2)_2P_2O_7$ (14), and $(Hg_2)_2(H_2PO_4)(PO_4)$ (15)] we succeeded in the preparation of two new compounds with the Hg_3^{4+} cluster: $(Hg_3)_3(PO_4)_4$ and $(Hg_3)_2(HgO_2)(PO_4)_2$. In this article syntheses, crystal structures, and thermal behavior of these mercury phosphates are reported.

EXPERIMENTAL

Preparation

Single crystals of $(Hg_3)_3(PO_4)_4$ and $(Hg_3)_2(HgO_2)(PO_4)_2$ were obtained as by-products next to the main product α-$(Hg_2)_3(PO_4)_2$ (14) during hydrolysis of microcrystalline $(Hg_2)_2P_2O_7$ (14). Formation of the title compounds might be formulated by the idealized reaction

[1] Contributions on the Thermal Behaviour and Crystal Chemistry of Anhydrous Phosphates, XXVIII. For Contribution XXVII see (13).

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equations:

$$3\,(Hg_2)_2P_2O_{7,s} + 6\,HgO_s + 2\,H_3PO_4 \xrightarrow[H_2O]{\Delta} 2\,(Hg_3)_3(PO_4)_{4,s} + 3\,H_2O \quad [1]$$

$$(Hg_2)_2P_2O_{7,s} + 3\,HgO_s \xrightarrow[H_2O]{\Delta} (Hg_3)_2(HgO_2)(PO_4)_{2,s}. \quad [2]$$

In experiments using stoichiometric mixtures of $(Hg_2)_2P_2O_7$ and HgO (e.g., 150 mg $(Hg_2)_2P_2O_7$, 66 mg HgO, and 1 ml 1 wt% H_3PO_4 for $(Hg_3)_3(PO_4)_4$; 150 mg $(Hg_2)_2P_2O_7$, 100 mg HgO, and 1 ml demineralized water for $(Hg_3)_2(HgO_2)(PO_4)_2$), high amounts of α-$(Hg_2)_3(PO_4)_2$ were present, but the content of $(Hg_3)_3(PO_4)_4$ and $(Hg_3)_2(HgO_2)(PO_4)_2$ was much higher compared to experiments without the addition of HgO.

The experiments were carried out under hydrothermal conditions in H_3PO_4 (ca. 1% by weight) for preparation of $(Hg_3)_3(PO_4)_4$ or demineralized water for preparation of $(Hg_3)_2(HgO_2)(PO_4)_2$. Approximately 150 mg $(Hg_2)_2P_2O_7$ was charged in thick-walled Duran glass ampoules, which were filled with 1 ml liquid. The ampoules were then cooled in liquid nitrogen and sealed under dynamic vacuum, so that the filling capacity was ca. 60%. Several of the ampoules prepared in this way were placed in a steel autoclave, which was filled with *n*-pentane as an agent for counterpressure. The autoclave was heated with 50°C h^{-1} to 400°C, kept at this temperature for 12 h, and cooled down to room temperature with a cooling rate of 4°C h^{-1}. After filtration and washing with ethanol and acetone, a crystal mixture of α-$(Hg_2)_3(PO_4)_2$ and $(Hg_3)_3(PO_4)_4$ (in 1% H_3PO_4) or α-$(Hg_2)_3(PO_4)_2$ and $(Hg_3)_2(HgO_2)(PO_4)_2$ (in demineralized water) resulted. For the latter in some experiments very few dark brown opaque crystals of yet unknown composition were also obtained. These crystals were often intergrown with α-$(Hg_2)_3(PO_4)_2$ or showed clearly visible multiple twinning. Therefore a structure or chemical analysis was not yet possible. In some experiments small amounts of elemental mercury occurred for both experimental procedures. Owing to different colors and shapes, single crystals could be separated mechanically under a microscope (α-$(Hg_2)_3(PO_4)_2$: orange, cuboid; $(Hg_3)_3(PO_4)_4$: colourless, spheroidal; $(Hg_3)_2(HgO_2)(PO_4)_2$: yellow, monoclinic prismatic).

Microcrystalline $(Hg_3)_3(PO_4)_4$ was also prepared by coprecipitation of a stoichiometric solution of mercurous and mercuric nitrate with a solution of sodium dihydrogenorthophosphate(V) in excess. For this purpose 1 mmol $(Hg_2)(NO_3)_2 \cdot 2\,H_2O$ (561 mg, Fluka, p.A.) and 1 mmol $Hg(NO_3)_2 \cdot H_2O$ (342 mg, Merck, p.A.) were dissolved in 40 ml H_2O that was acidified with 1 ml concentrated HNO_3. This solution was added dropwise to a solution of 2 mmol $Na_2HPO_4 \cdot 2\,H_2O$ (356 mg, Merck, p.A.) in 20 ml H_2O. During precipitation the phosphate solution was stirred and kept warm at ca. 70°C. A colorless solid precipitated that turned to a light yellow after a few minutes. After addition of the mercury solution the reaction mixture was stirred and kept at that temperature for 30 min. Then the solid was filtered from the warm solution; subsequently washed with mother liquor, water, ethanol, and acetone; and dried in a desiccator over $CaCl_2$ for 3 days. The XRD pattern showed no impurities.

Structure Determinations

Crystals suitable for structure determination were selected under a polarizing microscope and mounted on thin glass filaments. Their quality was checked by preliminary Weissenberg and precession photographs. Intensity data were selected on a SMART system (Siemens) equipped with a CCD camera using monochromatized Mo$K\bar{\alpha}$ radiation with $\lambda = 0.71073$ Å. All intensity data were corrected for Lorenz and polarization effects. Further details of the data collection are listed in Table 1.

Due to systematic errors caused by absorption effects on single crystals, lattice parameters for both phosphates were refined from Guinier powder diagrams (Cu$K\alpha_1$ radiation, $\lambda = 1.54051$ Å, α-quartz as internal standard) with the program SOS (16). The obtained lattice parameters and the Guinier powder pattern of microcrystalline $(Hg_3)_3(PO_4)_4$ revealed isotypism with the corresponding arsenate $(Hg_3)_3(AsO_4)_4$ (11), whose atomic coordinates were used as starting parameters for structure refinement with the SHELX97 program package (17). The crystal structure of $(Hg_3)_2(HgO_2)(PO_4)_2$ was solved by determination of mercury atoms with the help of a Patterson synthesis using the same program. The positions of phosphorus and oxygen were obtained from subsequent difference-Fourier maps. In the final refinement cycles for both data sets, corrections of extinction effects were applied (SHELX97) and anisotropic displacement parameters for all atoms were allowed. Due to high absorption coefficients of $\mu = 83.64\ mm^{-1}$ for $(Hg_3)_3(PO_4)_4$ and $\mu = 89.92\ mm^{-1}$ for $(Hg_3)_2(HgO_2)(PO_4)_2$, an absorption correction was applied to both data sets with the program HABITUS (18). The crystal shape was optimized by minimizing R_i. The so derived habitus was the basis of the numerical absorption correction. Final atomic coordinates and selected distances and angles for both compounds are listed in Tables 2 and 3, respectively. Anisotropic displacement parameters are given in Table 4. The structure representations were produced with the program ATOMS (19). Further details on crystal structure analyses for $(Hg_3)_3(PO_4)_4$ and $(Hg_3)_2(HgO_2)(PO_4)_2$ are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the literature citation, the names of the authors, and the depository number CSD-411299 for $(Hg_3)_3(PO_4)_4$ and CSD-411300 for $(Hg_3)_2(HgO_2)(PO_4)_2$.

TABLE 1
$(Hg_3)_3(PO_4)_4$ and $(Hg_3)_2(HgO_2)(PO_4)_2$: Crystallographic Data and Specifications of Data Collection, Structure Solution, and Refinement

	$(Hg_3)_3(PO_4)_4$	$(Hg_3)_2(HgO_2)(PO_4)_2$
Diffractometer	SMART CCD system (Siemens)	
Radiation; wavelength (Å)	Mo$K\bar{\alpha}$ 0.71073	
Temperature	22(2)	
Crystal dimensions (mm^3)	$0.04 \cdot 0.04 \cdot 0.06$	$0.26 \cdot 0.22 \cdot 0.10$
Crystal description	Colorless spheroid	Yellow monoclinic prism
Absorptrion correction	Numerical using HABITUS (18)	
Space group	$R3c$ (No. 161)	$P2_1/c$ (No. 14)
Formula units	6	2
Lattice parameters, powder/single crystal		
a (Å)	16.3957(10)/16.3708(13)	6.2506(7)/6.2461(2)
b (Å)		9.9366(10)/9.9243(4)
c (Å)	10.6606(9)/10.6491(9)	9.6663(12)/9.6635(4)
β (°)		95.783(10)/95.784(10)
V ($Å^3$)	2481.9(3)/2471.6(7)	597.3(1)/595.94(7)
Formula weight ($g\,mol^{-1}$)	2185.19	1626.07
μ (mm^{-1})	83.64	89.92
X-ray density ($g\,cm^{-3}$)	8.722	9.041
Range $\theta_{min} - \theta_{max}$ (°)	2.48–28.28	2.95–29.95
Range h; k; l	$-21 \rightarrow 21$; $-21 \rightarrow 21$; $-14 \rightarrow 14$	$-8 \rightarrow 8$; $-13 \rightarrow 13$; $-13 \rightarrow 13$
Structure solution and refinement	$(Hg_3)_3(AsO_4)_4$ (11)	SHELXL97 (17)
Measured reflections	10,668	8665
Independent reflections	1372	1732
Observed reflections [$I > 2\sigma(I)$]	1339	1634
R_i	0.053	0.076
Coefficients of transmission T_{min}; T_{max}	0.0599; 0.1371	0.0019; 0.0351
Number of parameters	89	89
Extinction coefficient (SHELXL97)	0.000138(8)	0.0060(2)
Difference electron density ($e^-\,Å^{-3}$) Δ_{max}; Δ_{min}	1.75; -1.46	2.85; -2.32
$R[F^2 > 2\sigma(F^2)]$; w$R2$(F^2 all)[a]	0.0209; 0.047	0.028; 0.072
Flack parameter	$-0.002(17)$	
Goof	1.064	1.23

[a] $w = 1/(\sigma^2(F_o^2) + (aP)^2 + bP)$ with $P = (F_o^2 + 2F_c^2)/3$.

Thermal Behavior

For experiments on the thermal behavior of the title compounds temperature-dependent Guinier diagrams were recorded. For this purpose crystals were ground and placed in small silica capillaries (∅, 0.3 mm) that were sealed after being filled. The capillaries were placed in a sample holder and heated with an air stream with $6°C\,h^{-1}$ in the range 25–700°C. Due to high mercury vapor pressure, the capillaries burst at ca. 680°C for $(Hg_3)_3(PO_4)_4$ and ca. 530°C for $(Hg_3)_2(HgO_2)(PO_4)_2$.

RESULTS AND DISCUSSION

Preparation

The present results and those that have already been discussed for the formation of α-$(Hg_2)_3(PO_4)_2$ (14) show that the hydrothermal formation of mercury phosphates starting from $(Hg_2)_2P_2O_7$ follows a complicated interplay of different redox, protolysis, and precipitation equilibria. In a first step the pyrophosphate anion hydrolyses at higher temperatures (Eq. [3]). The formed dihydrogenorthophosphate(V) anion is in equilibrium with HPO_4^{2-} and PO_4^{3-} (Eq. [4]), like the different mercury cations among each other (Eq. [5]). Exceeding of the solubility product during decrease of temperature leads to the crystallization of the complex salts α-$(Hg_2)_3(PO_4)_2$, $(Hg_3)_3(PO_4)_4$, and $(Hg_3)_2(HgO_2)(PO_4)_2$ (Eq. [7]). The existence of elemental mercury obtained in small amounts during some experiments could also be explained (Eq. [5a]). Solid phases containing discrete Hg^{2+} cations were not observed. The pH of the solutions plays an important role on product formation. While crystals of $(Hg_3)_3(PO_4)_4$ were only obtained by working in diluted phosphoric acid (pH ≈ 1), crystals of $(Hg_3)_2(HgO_2)(PO_4)_2$ were found only by working in demineralized water. In the latter the concentration of $[H^+]$ is much lower compared to diluted phosphoric acid, so that the equilibrium (Eq. [6]) is shifted to the right side and the basic mercurate phosphate is

TABLE 2
$(Hg_3)_3(PO_4)_4$ and $(Hg_3)_2(HgO_2)(PO_4)_2$: Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å²)

Atom	Wyckoff position	x	y	z	U_{eq}[a]
$(Hg_3)_3(PO_4)_4$					
Hg1	18*b*	0.05799(3)	0.16780(4)	1.34678(5)	0.02206(13)
Hg2	18*b*	0.14759(4)	0.38785(3)	0.03765(4)	0.01841(13)
Hg3	18*b*	0.20662(3)	0.04335(4)	0.14356(4)	0.02104(13)
P1	18*b*	0.2357(2)	0.2626(2)	0.1443(3)	0.0092(5)
P2	6*a*	0	0	0.0554(4)	0.0095(9)
O1	18*b*	0.0920(5)	0.0096(6)	− 0.0012(8)	0.0122(16)
O2	18*b*	0.1584(6)	0.2607(7)	0.0558(8)	0.0153(17)
O3	18*b*	0.1911(6)	0.2064(7)	0.2651(8)	0.021(2)
O4	18*b*	0.2840(6)	0.2138(6)	0.0807(8)	0.0149(17)
O5	18*b*	0.3001(6)	0.0244(6)	0.0061(8)	0.0157(17)
O6	6*a*	0	0	0.1962(13)	0.014(3)
$(Hg_3)_2(HgO_2)(PO_4)_2$					
Hg1	4*e*	0.23678(5)	0.14050(4)	0.34801(4)	0.01492(12)
Hg2	4*e*	− 0.01493(6)	0.34789(4)	0.41321(4)	0.01649(13)
Hg3	4*e*	− 0.18775(6)	0.11624(4)	0.31134(5)	0.02105(14)
Hg4	2*b*	− 0.5	0.5	0.5	0.01376(14)
P	4*e*	− 0.4988(4)	0.3495(2)	0.1470(3)	0.0100(4)
O1	4*e*	− 0.4967(11)	0.2047(7)	0.2073(7)	0.0118(12)
O2	4*e*	0.1851(11)	0.5337(7)	0.4357(7)	0.0127(13)
O3	4*e*	0.5404(11)	0.1580(8)	0.4924(8)	0.0165(14)
O4	4*e*	0.2754(12)	0.4068(8)	0.1611(9)	0.0180(14)
O5	4*e*	0.3184(12)	− 0.0682(7)	0.2703(8)	0.0166(14)

[a] $U_{eq} = (\frac{1}{3})\sum_i \sum_j U_{ij} a_i a_j \mathbf{a}_i \, \mathbf{a}_j$.

crystallized (Eq. [7c]). The liberation of protons in Eq. [6] also has an influence on hydrolysis of the pyrophosphate anion (Eq. [3]) and the equilibria between different orthophosphate anions (Eq. [4]). These considerations are in agreement with experimental results. The used demineralized water had a pH of ca. 6 (caused by solution of CO_2), while the solution at the end of the experiments had a pH of ca. 4.

(1) Hydrolysis

$$(Hg_2)_2P_2O_{7,s} + H_2O + 2\ H^+ \xrightarrow{\Delta} 2\ Hg_2^{2+} + 2\ H_2PO_4^- \quad [3]$$

(2) Protolysis of the orthophosphate(V) ion

$$H_2PO_4^- = HPO_4^{2-} + H^+ \quad [4a]$$

$$HPO_4^{2-} = PO_4^{3-} + H^+ \quad [4b]$$

(3) Redox equilibria of different mercury species

$$Hg_2^{2+} = Hg^{2+} + Hg \quad [5a]$$

$$Hg_2^{2+} + Hg^{2+} = Hg_3^{4+} \quad [5b]$$

$$Hg + 2\ Hg^{2+} = Hg_3^{4+} \quad [5c]$$

(4) Formation of mercurate

$$Hg^{2+} + 2\ H_2O = HgO_2^{2-} + 4\ H^+ \quad [6]$$

(5) Crystallization

$$3\ Hg_2^{2+} + 2\ PO_4^{3-} \rightarrow (Hg_2)_3(PO_4)_{2,s} \quad [7a]$$

$$3\ Hg_3^{4+} + 4\ PO_4^{3-} \rightarrow (Hg_3)_3(PO_4)_{4,s} \quad [7b]$$

$$2\ Hg_3^{4+} + HgO_2^{2-} + 2\ PO_4^{3-} \rightarrow (Hg_3)_2(HgO_2)(PO_4)_{2,s} \quad [7c]$$

TABLE 3
$(Hg_3)_3(PO_4)_4$ and $(Hg_3)_2(HgO_2)(PO_4)_4$: Selected Interatomic Distances (Å) and Angles (°) as Obtained from Lattice Constants (Guinier Data) and Positional Parameters

$(Hg_3)_3(PO_4)_4$

Hg1–O3	2.131(9)	Hg2–O2	2.187(8)	Hg3–O5	2.252(8)
O1	2.382(8)	O4	2.275(8)	O1	2.275(8)
O2	2.590(8)	O5	2.502(8)	O4	2.515(8)
Hg2	2.6489(7)	Hg3	2.6418(6)	Hg2	2.6418(6)
Hg3	2.7086(7)	Hg1	2.6489(7)	Hg1	2.7086(7)
O6	2.904(8)	O3	3.078(9)	O2	3.015(9)
O1	2.947(8)	O5	3.182(9)	O3	3.094(10)
				O6	3.145(3)
P1–O4	1.536(9)	P2–O6	1.502(15)		
O3	1.539(9)	O1 (3*x*)	1.559(8)		
O5	1.547(8)				
O2	1.567(8)				

∠(Hg2, Hg1, Hg3) 59.077(17)
∠(Hg3, Hg2, Hg1) 61.591(18)
∠(Hg2, Hg3, Hg1) 59.333(18)

$(Hg_3)_2(HgO_2)(PO_4)_2$

Hg1–O3	2.246(7)	Hg2–O2	2.228(7)	Hg3–O4	2.175(8)
O5	2.281(7)	O2	2.228(7)	O1	2.264(7)
O1	2.343(7)	O5	2.600(7)	O2	2.526(7)
Hg3	2.6524(6)	Hg3	2.6871(6)	O3	2.593(7)
Hg2	2.7054(6)	Hg1	2.7054(6)	Hg1	2.6524(6)
O4	3.048(8)			Hg2	2.6871(6)
P	3.183(2)				
Hg4–O2 (2*x*)	2.031(7)	P–O3	1.541(8)		
O1 (2*x*)	2.854(7)	O4	1.541(7)		
O5 (2*x*)	3.029(8)	O5	1.548(7)		
		O1	1.552(7)		

∠(Hg3, Hg1, Hg2) 60.192(15)
∠(Hg3, Hg2, Hg1) 58.927(15)
∠(Hg1, Hg3, Hg2) 60.880(15)
∠(O2, Hg4, O2) 180

Note. All distances shorter than 3.20 Å are listed.

Structure

Both mercury phosphates $(Hg_3)_3(PO_4)_4$ and $(Hg_3)_2(HgO_2)(PO_4)_2$ contain as structural features the triangular Hg_3^{4+} cluster and tetrahedral PO_4^{3-} groups. Additionally, in $(Hg_3)_2(HgO_2)(PO_4)_2$ a linear HgO_2^{2-} group is present, which counts for the anionic part of the crystal structure and is typical for oxomercurates (20). Hence $(Hg_3)_2(HgO_2)(PO_4)_2$ is formulated as basic mercury($\frac{4}{3}$) mercurate(II) phosphate. In both crystal structures the linkage between the building units is achieved *via* common oxygen atoms (Figs. 1 and 3).

In comparison to monovalent mercury oxo compounds with Hg_2^{2+} dumbbells and a mean $\bar{d}$(Hg–Hg) = 2.514 Å (21) the distances d(Hg–Hg) within the Hg_3^{4+} triangles are elongated. This is caused by space required for the additional molecular orbitals needed for two-electron, three-center bonding. Assuming D_{3h} symmetry for the Hg_3^{4+} triangle the overlap of the 6s orbitals of each mercury atom generates a bonding MO a_1' and two degenerate antibonding orbitals e', which are perpendicular to the Hg_3 plane (22). For both compounds the mean distances, $\bar{d}$(Hg–Hg) = 2.666 Å for $(Hg_3)_3(PO_4)_4$ and 2.682 Å for $(Hg_3)_2(HgO_2)(PO_4)_2$, inside a triangle are in the same range and are similar to those found in *terlinguaite* with $\bar{d}$(Hg–Hg) = 2.666 Å and *kutznetsovite* with $\bar{d}$(Hg–Hg) = 2.675 Å. These Hg–Hg bonds are ≈0.12 Å shorter compared to the mean $\bar{d}$(Hg–Hg) = 2.795 Å within compounds with organic chelate ligands (23–27).[2] The intra-annular angles ∠(Hg, Hg, Hg) of 59.08(2)°, 61.59(2)°, and 59.33(2)° for $(Hg_3)_3(PO_4)_4$ and 58.87(3)°, 60.26(3)°, and 60.87(3)° for $(Hg_3)_2(HgO_2)(PO_4)_2$ deviate only slightly from an ideal equilateral triangle.

In addition to the two mercury neighbors within the triangle each mercury atom of $(Hg_3)_3(PO_4)_4$ is surrounded by three oxygen atoms at distances 2.131(9) Å ≤ $\bar{d}$(Hg–O) ≤ 2.590(8) Å (Fig. 2). The more distant oxygen atoms in the second coordination sphere have distances >2.9 Å and interact less with the mercury atoms. A comparable situation is found for $(Hg_3)_2(HgO_2)(PO_4)_2$ with 2.175(8) Å ≤ (Hg–O) ≤ 2.600(7) Å. Hg1 and Hg2 show CN = 5 (3x O, 2x Hg). Hg3 is bonded to an additional oxygen atom thus having CN = 6. In the second coordination sphere more distant oxygen atoms show distances >3 Å.

The mean $\bar{d}$(P–O) of the two crystallographically independent PO_4 tetrahedra in $(Hg_3)_3(PO_4)_4$ is 1.548 Å for P1 and 1.545 Å for P2. In relation to the other distances d(P–O) the distance d(P2–O6) = 1.502(12) Å is very short. This is caused by the exclusive coordination of this oxygen atom to phosphorus without an additional coordination partner, whereas all other oxygen atoms show further coordination to two Hg (O1, O2, O4, and O5) or one Hg (O3). The intratetrahedral angles ∠(O, P, O) with 105.8(5)° ≤ 109.5° ≤ 111.7(5)° for P1 and 106.0(4)° ≤ 109.5° ≤ 112.8(5)° for P2 are close to the geometry of an ideal tetrahedron. In $(Hg_3)_2(HgO_2)(PO_4)_2$ the geometrical situation with $\bar{d}$(P–O) = 1.548 Å and ∠(O, P, O) = 106.4(4)° ≤ 109.5° ≤ 112.7(4)° is similar. The coordination numbers of the oxygen atoms of that compound range from 2 to 4 (O4: 1x Hg + 1x P; O1, O3, O5: 2x Hg + 1x P; O2: 4x Hg).

[2] The value of 2.795 Å was calculated as the arithmetic mean $\bar{d}$(Hg–Hg) of nine crystallographically determined structures containing the Hg_3^{4+} cluster. The distances d(Hg–Hg) within these structures range from 2.717(2) to 2.9553(14) Å.

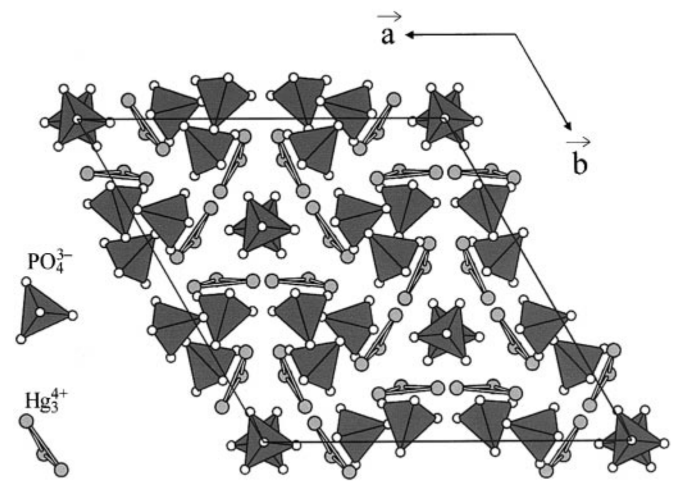

FIG. 1. $(Hg_3)_3(PO_4)_4$. Projection of the structure along the c axis. For a better clarity Hg–O bonds are omitted.

Typical for the oxomercurate group HgO_2^{2-} found in $(Hg_3)_2(HgO_2)(PO_4)_2$ is the linear oxygen coordination of mercury and a very short Hg–O bond of 2.031(7) Å. This value is in accordance with the mean distance $\bar{d}$(Hg–O) = 2.001 Å, which was calculated as the arithmetic mean of 13 Hg–O bonds of mercurate groups described in the literature (20). The more distant oxygen atoms show bond length >2.8 Å, which makes the crystal chemical situation of mercurates comparable to both modifications of HgO (orthorhombic form (28): $d(Hg–O)_{short}$ = 2.039 Å, 2.067 Å, $d(Hg–O)_{long}$ > 2.807 Å, ∠(O, Hg, O) = 178.34°; trigonal form (29): $d(Hg–O)_{short}$ = 2.0339 Å, $d(Hg–O)_{long}$ > 2.78 Å, ∠(O, Hg, O) = 174.96°).

The structure of $(Hg_3)_2(HgO_2)(PO_4)_2$ shows a topological relationship to the mineral *terlinguaite* with its empirical formula $Hg_4O_2Cl_2$. The crystal structure of this mineral comprises the Hg_3^{4+} cluster and the linear HgO_2^{2-} groups as well, and therefore *terlinguaite* might alternatively be specified as a mercury($\frac{4}{3}$) mercurate(II) chloride $(Hg_3)(HgO_2)Cl_2$. In comparison to $(Hg_3)_2(HgO_2)(PO_4)_2$ the phosphate groups are substituted by chlorine and due to neutrality of charge one Hg_3^{4+} cluster is missing per formula unit. The structural frameworks for both compounds are comparable, which is symbolized in Fig. 3. For *terlinguaite* the triangular plane of Hg_3^{4+} is parallel to the crystallographic b axis,

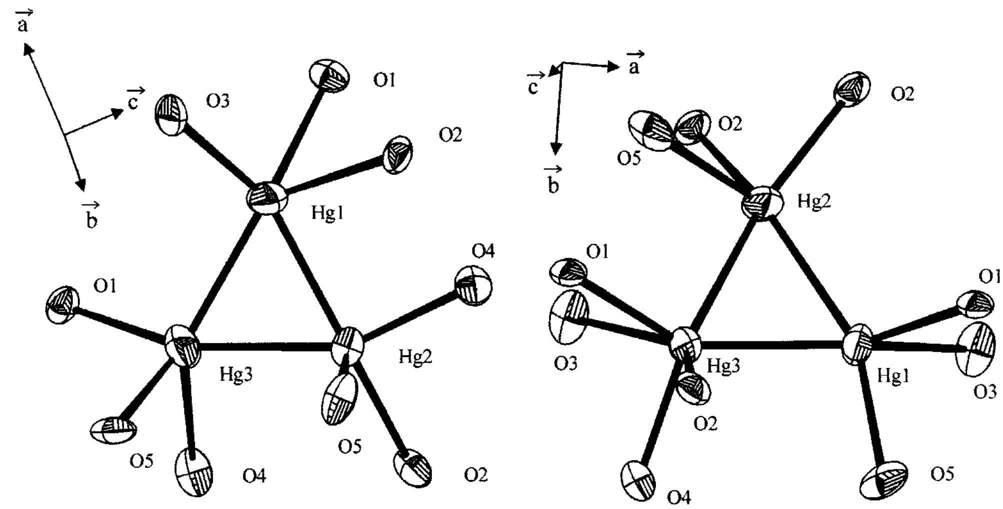

FIG. 2. ORTEP plot (32) of the first oxygen coordination sphere around the Hg_3^{4+} triangles in $(Hg_3)_3(PO_4)_4$ (left) and $(Hg_3)_2(HgO_2)(PO_4)_2$ (right). Displacement ellipsoids are drawn at the 85% probability level.

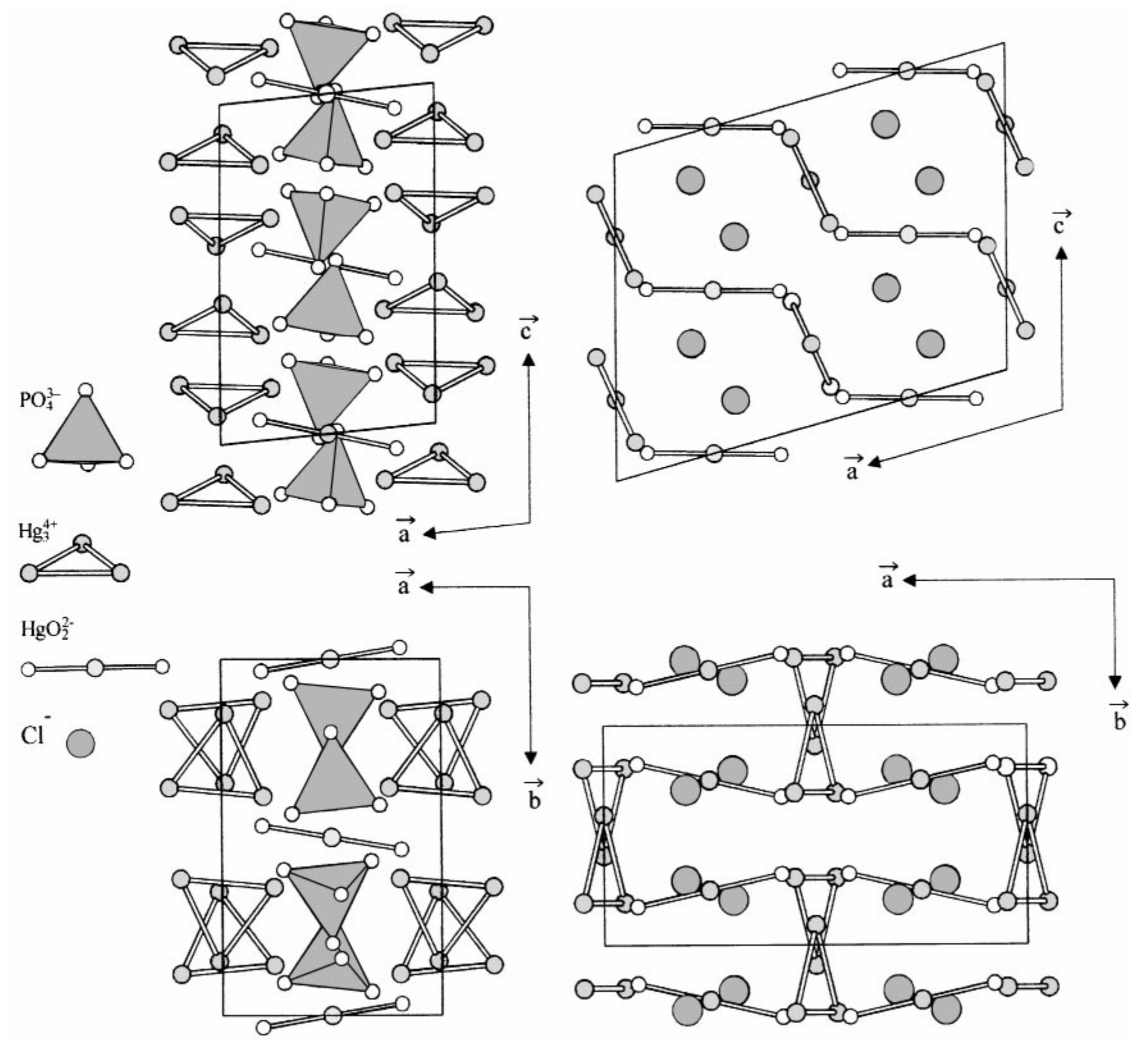

FIG. 3. Comparison between the structures of $(Hg_3)_2(HgO_2)(PO_4)_2$ (left) and *terlinguaite* ($Hg_4O_2Cl_2$; right). Projection of the structures along the *b* axis (top) and the *c* axis (bottom). For a better clarity Hg–O bonds are omitted.

TABLE 4
$(Hg_3)_3(PO_4)_4$ and $(Hg_3)_2(HgO_2)(PO_4)_2$: Anisotropic Displacement Parameters (Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
			$(Hg_3)_3(PO_4)_4$			
Hg1	0.0148(2)	0.0389(3)	0.0169(2)	0.0085(2)	0.00294(18)	0.0167(2)
Hg2	0.0292(3)	0.0167(2)	0.0128(2)	0.00183(18)	−0.00140(19)	0.0141(2)
Hg3	0.0184(2)	0.0293(3)	0.0107(2)	0.00281(19)	−0.00099(17)	0.0084(2)
P1	0.0081(13)	0.0100(13)	0.0094(12)	−0.0019(10)	−0.0018(10)	0.0045(11)
P2	0.0118(14)	0.0118(14)	0.005(2)	0	0	0.0059(7)
O1	0.008(4)	0.015(4)	0.014(4)	−0.004(3)	−0.002(3)	0.006(3)
O2	0.019(4)	0.025(5)	0.011(4)	−0.005(3)	−0.005(3)	0.019(4)
O3	0.017(5)	0.036(6)	0.011(4)	0.007(4)	0.005(3)	0.014(4)
O4	0.022(4)	0.018(4)	0.013(4)	−0.002(3)	0.000(3)	0.016(4)
O5	0.013(4)	0.009(4)	0.020(4)	−0.001(3)	0.008(3)	0.001(3)
O6	0.016(4)	0.016(4)	0.011(7)	0	0	0.008(2)
			$(Hg_3)_2(HgO_2)(PO_4)_2$			
Hg1	0.00877(17)	0.0149(2)	0.0209(2)	−0.00394(13)	0.00075(12)	0.00122(11)
Hg2	0.01571(18)	0.0104(2)	0.0229(2)	−0.00509(13)	−0.00037(13)	0.00109(12)
Hg3	0.00949(18)	0.0114(2)	0.0413(3)	−0.00218(15)	−0.00252(15)	−0.00138(12)
Hg4	0.0099(2)	0.0150(3)	0.0164(3)	−0.00079(18)	0.00115(16)	−0.00088(16)
P	0.0105(9)	0.0083(10)	0.0109(10)	0.0007(8)	0.0002(8)	0.0000(7)
O1	0.013(3)	0.007(3)	0.016(3)	0.004(2)	0.004(2)	0.001(2)
O2	0.011(3)	0.010(3)	0.016(3)	−0.005(2)	0.000(2)	0.003(2)
O3	0.013(3)	0.026(4)	0.009(3)	−0.006(3)	−0.003(2)	0.002(3)
O4	0.011(3)	0.014(3)	0.029(4)	−0.002(3)	0.005(3)	0.003(3)
O5	0.019(3)	0.014(3)	0.015(3)	−0.002(3)	−0.010(3)	0.006(3)

whereas the Hg_3^{4+} cluster of $(Hg_3)_2(HgO_2)(PO_4)_2$ is somewhat twisted out of that plane.

Thermal Behavior

Like the Hg(I) phosphates α-$(Hg_3)_2(PO_4)_2$, β-$(Hg_3)_2(PO_4)_2$, $(Hg_2)_2P_2O_7$ (14), and $(Hg_2)_2(H_2PO_4)(PO_4)$ (15), $(Hg_3)_3(PO_4)_4$ and $(Hg_3)_2(HgO_2)(PO_4)_2$ disproportionate to elemental mercury and the corresponding mercury(II) phosphate. For $(Hg_3)_3(PO_4)_4$ (Eq. [8]) the decomposition range was 340(10)–400(10)°C. Above 400°C, $Hg_3(PO_4)_2$ (30) was the only phase detected by XRPD. The thermal decomposition of $(Hg_3)_2(HgO_2)(PO_4)_2$ is more complicated. Between 310(10)–405(10)°C a yet unknown phase in the system Hg/P/O was detected. At 370(10)°C, $Hg_3(PO_4)_2$ was formed. This was the only phase observed above 405(10)°C. The formulation of the decomposition reaction for this compound remains speculative, but the following mechanism appears to be reasonable. In a first step $(Hg_3)_2(HgO_2)(PO_4)_2$ disproportionates into Hg(0) and a possible basic orthophosphate(V) $Hg_3(PO_4)_2 \cdot 2HgO$[3] (31) (Eq. [9a]). In a second step $Hg_3(PO_4)_2 \cdot 2HgO$ converts to $Hg_3(PO_4)_2$ and HgO (Eq. [9b]), which subsequently decomposes in elemental mercury and oxygen (Eq. [9c]).

$$(Hg_3)_3(PO_4)_{4,s} \xrightarrow{\Delta} 2\ Hg_3(PO_4)_{2,s} + 3\ Hg_g \qquad [8]$$

$$(Hg_3)_2(HgO_2)(PO_4)_{2,s} \xrightarrow{\Delta} Hg_3(PO_4)_2 \cdot 2HgO_s + 2\ Hg_g \qquad [9a]$$

$$Hg_3(PO_4)_2 \cdot 2HgO_{2,s} \xrightarrow{\Delta} Hg_3(PO_4)_{2,s} + 2\ HgO_s \qquad [9b]$$

$$2\ HgO_s \xrightarrow{\Delta} Hg_g + O_{2,g} \qquad [9c]$$

[3] It is possible that the brown crystals described under Preparation are identical with this phase.

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