

On synthesis, structure, and thermal stability of mercury and lead sulfates and oxide sulfates

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Abstract

Reactions between HgO, PbO, or PbO₂ and 2.5–95 wt.% H₂SO₄ are studied at temperatures up to the boiling point of the acid. Depending on the oxide reactant, the H₂SO₄ concentration, and synthesis temperature, HgSO₄, Hg₃O₂(SO₄), PbSO₄ and Pb₂O(SO₄) are obtained as identified reaction products. The thermal stability of HgSO₄, Hg₃O₂(SO₄), PbSO₄, Pb₂O(SO₄), and PbO₂ is examined and the results supplement and modify earlier findings. The redetermined crystal structure of Hg₃O₂(SO₄) on the basis of powder neutron diffraction data shows that its space group (P3₁) is of lower symmetry than earlier reported (P3₁2₁).

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1. Introduction

As a continuation of earlier investigations of reactions between binary oxides (of iodine [1–5], titanium [6], tin [7], zirconium [8], hafnium [8], tellurium [9], and molybdenum [10]) and concentrated sulfuric acid, the behaviour of HgO, PbO, and PbO₂ toward H₂SO₄ in different concentrations is considered in this paper.

The reaction between HgO and H₂SO₄ has been the subject of many studies [11–14]. Hoitsema [11] reported four solid compounds in the HgO–SO₃–H₂O system: HgSO₄, HgSO₄·H₂O, 3HgO·2SO₃·2H₂O [Hg₃O(SO₄)₂·2H₂O], and 3HgO·SO₃ [Hg₃O₂(SO₄)]. Paic [12,13] confirmed these compounds in reactions between HgNO₃, HNO₃ and Na₂SO₄ in sealed tubes at 250 °C. Grinding of HgSO₄ or Hg₃O(SO₄)₂·2H₂O with

HgO is reported to give Hg₃O₂(SO₄) [14], and the same product is obtained [15] by treating HgSO₄ with H₂O.

Hoschek [16] reported that HgSO₄ is thermally stable up to 400 °C, but decomposes at 500 °C to Hg₂O(SO₄) and subsequently to Hg₃O₂(SO₄) at 650–750 °C. However, the thermal decomposition of HgSO₄ as seen by TG and DTA indicates that the degradation occurs in one step at 550–750 °C, and without the formation of the intermediate Hg₂O(SO₄) [17]. Powder X-ray diffraction (PXD) of the residue after heating HgSO₄ at 620 °C confirmed [17] that the product was Hg₃O₂(SO₄).

Structurally well characterised sulfates and oxide sulfates of mercury are HgSO₄ [18–22], HgSO₄·H₂O [22–25], Hg₃O₂(SO₄) [21,26], Hg₃O(SO₄)₂·2H₂O [21], and Hg₃(OH)₂(SO₄)₂·H₂O [27,28].

The outcome of the direct reaction between PbO and concentrated H₂SO₄ has been reported to depend on the acid-to-oxide molar ratio. When the ratio exceeds 1 PbSO₄ [29] is the only product, whereas when the ratio becomes less than 1 oxide sulfates are

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reported to be the products: $\text{PbO} \cdot \text{PbSO}_4$ [$\text{Pb}_2\text{O}(\text{SO}_4)$], $3\text{PbO} \cdot \text{PbSO}_4 \cdot \text{H}_2\text{O}$ [$\text{Pb}_4\text{O}_3(\text{SO}_4) \cdot \text{H}_2\text{O}$], $4\text{PbO} \cdot \text{PbSO}_4$ [$\text{Pb}_5\text{O}_4(\text{SO}_4)$] [30], and even $5\text{PbO} \cdot 2\text{H}_2\text{O}$ [31] at a suitable concentration of H_2SO_4 .

Numerous procedures are reported for the preparation of PbSO_4 , e.g., from Pb [32–36], PbO [37], PbO_2 [38], or Pb^{2+} -containing [39,40] solutions.

Thermal decomposition of PbSO_4 has been reported to occur between 800–860 [41–45] and 1200 °C with gradual [46] rather than distinct features on thermal analysis profiles. Nevertheless, the thermal decomposition of PbSO_4 is suggested [16,43] to take place in several steps: $\text{PbSO}_4 \rightarrow \text{Pb}_2\text{O}(\text{SO}_4) \rightarrow 2\text{PbO} \cdot \text{PbSO}_4$ [$\text{Pb}_3\text{O}_2(\text{SO}_4)$] $\rightarrow 3\text{PbO} \cdot \text{PbSO}_4$ [$\text{Pb}_4\text{O}_3(\text{SO}_4)$]; or alternatively $\text{Pb}_5\text{O}_4(\text{SO}_4) \rightarrow \text{PbO}$. (High-temperature PXD maintains [47] that there occurs a transformation from the room temperature (RT) form of PbSO_4 to a cubic, high-temperature form at 900 °C.)

Lead oxide sulfates have also been reported [48–52] prepared by melting together PbO and PbSO_4 in different ratios: $\text{Pb}_2\text{O}(\text{SO}_4)$, $\text{Pb}_3\text{O}_2(\text{SO}_4)$, and $\text{Pb}_4\text{O}_3(\text{SO}_4)$ [or $\text{Pb}_5\text{O}_4(\text{SO}_4)$]. A wet procedure gave $\text{Pb}_2\text{O}(\text{SO}_4)$, $\text{Pb}_5\text{O}_4(\text{SO}_4)$, and $\text{Pb}_4\text{O}_3(\text{SO}_4) \cdot \text{H}_2\text{O}$ [49]. The system $\text{PbO} \text{--} \text{PbSO}_4 \text{--} \text{H}_2\text{O}$ has been studied by hydrothermal methods giving $\text{Pb}_2\text{O}(\text{SO}_4)$, $\text{Pb}_5\text{O}_4(\text{SO}_4)$, and $\text{Pb}_4\text{O}_3(\text{SO}_4) \cdot \text{H}_2\text{O}$ as reaction products [53]. The latter compound has also been obtained [54] by refluxing a 3:1 molar mixture of PbO and PbSO_4 in H_2O . $\text{Pb}_2\text{O}(\text{SO}_4)$, $\text{Pb}_3\text{O}_2(\text{SO}_4)$, and $\text{Pb}_5\text{O}_4(\text{SO}_4)$ are moreover obtained by oxidation of PbS in air [16,55].

Despite the existence of a large number of publications concerning lead sulfate and oxide sulfates, the only structurally well characterised compounds are: PbSO_4 [56–58], $\text{Pb}_2\text{O}(\text{SO}_4)$ [59–62], $\alpha\text{-Pb}_3\text{O}_2(\text{SO}_4)$ [63–66], $\beta\text{-Pb}_3\text{O}_2(\text{SO}_4)$ [52,64,67] (high-temperature phase), $\gamma\text{-Pb}_3\text{O}_2(\text{SO}_4)$ [65,66] (low-temperature phase), $\text{Pb}_5\text{O}_4(\text{SO}_4)$ [52,68,69], and $\text{Pb}_4\text{O}_3(\text{SO}_4) \cdot \text{H}_2\text{O}$ [53,70,71]. The $\alpha \rightarrow \beta$ transformation of $\text{Pb}_3\text{O}_2(\text{SO}_4)$ is reported [72,73] at 450 °C and on further heating $\text{Pb}_3\text{O}_2(\text{SO}_4)$ decomposes to $\text{Pb}_2\text{O}(\text{SO}_4)$ and $\text{Pb}_5\text{O}_4(\text{SO}_4)$.

2. Experimental

2.1. Starting materials

Mercury(II) oxide (HgO (red), Fluka; 98%, p.a., orthorhombic, $a = 551.82(5)$ pm, $b = 660.97(7)$ pm,

$c = 352.00(3)$ pm), lead(II) oxide ($\beta\text{-PbO}$ (yellow), Riedel-deHaen; purum; >99%, orthorhombic, $a = 549.16(6)$ pm, $b = 475.34(8)$ pm, $c = 589.24(6)$ pm), lead(IV) oxide ($\beta\text{-PbO}_2$, Riedel-deHaen; purum; >99.5%, tetragonal, $a = 495.65(3)$ pm, $c = 338.65(4)$ pm), and concentrated H_2SO_4 (Merck; p.a.; 95–97 wt.%, the former value being used throughout this paper), were applied as starting chemicals for the syntheses. Concentrated H_2SO_4 in the range 2.5–95 wt.% H_2SO_4 was made by diluting the as-purchased acid with distilled H_2O .

2.2. Preparations

With HgO as starting chemical, 0.015 mol HgO was added to 15 ml 30–95 wt.% H_2SO_4 or 10 ml 2.5–30 wt.% H_2SO_4 in a round-bottomed flask equipped with a reflux cooler. The mixtures were stirred with a magnet stirrer, and heated at the boiling point (BP) for 1 day (d). Then the stirring and heating were turned off. After cooling to RT a white precipitate was obtained for 50–95 wt.% H_2SO_4 . For 30–45 wt.% H_2SO_4 a white precipitate was obtained in a colourless solution with some yellow precipitate on the wall of the reaction vessel (above the solution). For 30 wt.% H_2SO_4 a 10 ml acid volume had to be used to obtain precipitate. White precipitates could also be recovered from (decanted) mother liquors on stirred mixing with (ca. 100 ml) glacial acetic acid (BDH). A yellow precipitate in a colourless solution was obtained for H_2SO_4 concentrations in the range 2.5–25 wt.%.

When the reactions were considered completed the reaction vessel was left untouched until the products were well separated from the mother liquors. The liquid phase, mainly acid, was removed by decantation and the precipitate thus obtained was transferred to a beaker containing ca. 100 ml glacial acetic acid, stirred for 15 min, filtered and washed with glacial acetic acid and acetone (Prolabo). The entire washing procedure was repeated twice. The product was then transferred to a desiccator, dried and kept under ambient conditions.

The 0.015 mol PbO was added to 15 ml H_2SO_4 (2.5–95 wt.%) in a round-bottomed flask. The mixtures were heated at BP for 1 day under stirring. The stirring and heating were then stopped. After cooling to RT a white precipitate had formed. The precipitate was treated as above.

The 0.015 mol PbO_2 was added to 15 ml H_2SO_4 (2.5–95 wt.%) in a round-bottomed flask. The mixtures were heated at BP for 1 day under stirring. For 70–95 wt.% H_2SO_4 a gas started to evolve after ca. 10 min heating and this reaction stage continued for about 1.5 h. After the gas evolution had stopped the temperature settled at the BP of the solution. A distinct reaction stage pattern was not observed for 2.5–65 wt.% H_2SO_4 . After cooling the reaction mixture to RT a grey (for 70–95 wt.% H_2SO_4) or black (for 2.5–65 wt.% H_2SO_4) precipitate was obtained. The precipitate was treated as above.

2.3. Powder X-ray and neutron diffraction and refinements

All samples were characterised by PXD using Guinier–Hägg cameras (Cu $K\alpha_1$ radiation, Si as internal standard). The position of the Bragg reflections was obtained from the films by means of a Nicolet L18 scanner using the SCANPI program system [74]. The diffraction patterns of structurally unknown phases were attempted indexed with the help of the TREOR program [75]. Unit cell parameters were obtained by least-squares refinements using the CELLKANT program [76].

High resolution powder neutron diffraction (PND) data for $\text{Hg}_3\text{O}_2(\text{SO}_4)$ were collected at 10 and 298 K with the PUS two-axis diffractometer ($\lambda = 155.5$ pm, focussing Ge(511) monochromator) at the JEEP II reactor, Kjeller, Norway. The sample was contained in a cylindrical vanadium holder with 3 mm inner diameter. A Displex cooler was used at 10 K. The diffraction pattern was recorded using two detector banks, each covering 20° in 2θ and each containing a stack of seven position sensitive detectors [77].

The GSAS (general structure analysis system) software [78] was used for Rietveld refinements of the PND data. Nuclear scattering lengths were taken from the GSAS library. The background was modelled as a cosine Fourier series polynomial (12 terms). The peak shape was modelled by a pseudo-Voigt function. The PND data used for the least-square refinements included 2400 data points (2θ range 10 – 130° , step size 0.05°).

2.4. Thermoanalyses

Thermogravimetric (TG) analysis was generally performed between 20 and 800°C with a Perkin Elmer

TGA 7 system. Samples of 15–40 mg were placed in Al_2O_3 crucibles and the heating rate was $10^\circ\text{C min}^{-1}$, with nitrogen atmosphere.

3. Results and discussion

3.1. Mercury(II) oxide as reactant

Phase-pure HgSO_4 (white) and HgSO_4 in admixture with $\text{Hg}_3\text{O}_2(\text{SO}_4)$ (yellow) are the only solid products obtained from reaction between HgO (red) and 30–95 and 2.5–25 wt.% H_2SO_4 , respectively (Table 1). The yields of HgSO_4 were generally very good but decreased significantly toward the lower limit (~ 30 wt.% H_2SO_4) of the HgSO_4 domain. The progressing reaction is evidenced by the dissolution of HgO and a sudden subsequent appearance of white or yellow precipitates in clear colourless solutions. In the parallels with 15 ml (common to the rest of the series) 30 wt.% H_2SO_4 only clear colourless solution was obtained. However, on reduction of the volume of the acid to 10 ml, precipitates were also obtained with

Table 1
Solid products obtained from reaction (for 1 day at BP) between HgO (red), PbO (yellow) or PbO_2 , and H_2SO_4 in different concentrations

Reactant	H_2SO_4 (wt.%)	Product	Yield (%)
HgO	2.5–25	$\text{Hg}_3\text{O}_2(\text{SO}_4)$ and HgSO_4^a	
	30	HgSO_4^b	30
	40–45	HgSO_4^b	82
	50–95	HgSO_4	88–95
PbO	2.5	Unidentified	
	5	$\text{Pb}_2\text{O}(\text{SO}_4)^c$	92
	10–95	PbSO_4	98
PbO_2	5	PbO_2	
	10–40	PbO_2 (major) and PbSO_4^a	
	45–60	PbO_2 and PbSO_4^a	
	65	PbSO_4^d	
	70–95	PbSO_4	98

^a Relative amounts depend on H_2SO_4 concentration and acid-to-oxide ratio.

^b Trace amounts of $\text{Hg}_3\text{O}_2(\text{SO}_4)$ deposited on the wall of the reaction vessel above the solution.

^c Contaminated with trace amounts of PbSO_4 .

^d Contaminated with trace amounts of PbO_2 .

Table 2
Unit cell dimensions (e.s.d. in parentheses) at RT for sulfates and oxide sulfates of mercury and lead

Compound	Symmetry	<i>a</i> (pm)	<i>b</i> (pm)	<i>c</i> (pm)	β (°)	<i>V</i> ($\times 10^6$ pm ³)	<i>M</i> (20) ^a
HgSO ₄ [18]	Orthorhombic	478.05 (4)	481.58 (4)	657.60 (5)		151.40 (2)	105.5
HgSO ₄ ·H ₂ O [22]	Orthorhombic ^b	788.23 (7)	542.26 (4)	897.25 (7)		383.51 (5)	144.9
Hg ₃ O ₂ (SO ₄) [21,26]	Trigonal ^c	704.69 (4)	704.69 (4)	1001.9 (1)		430.90 (7)	114.7
PbSO ₄ [56]	Orthorhombic	695.78 (4)	847.85 (4)	539.88 (3)		318.48 (3)	152.7
Pb ₂ O(SO ₄) [62]	Monoclinic	1376.1 (3)	566.0 (2)	704.1 (2)	115.86 (2)	493.55	
α -Pb ₃ O ₂ (SO ₄) [65]	Monoclinic ^d	718.6 (1)	578.9 (1)	805.8 (1)	102.40 (1)	327.334	
Pb ₅ O ₄ (SO ₄) [68,69]	Monoclinic ^e	729.2 (3)	1164.4 (5)	1149.3 (5)	90.92 (3)	975.63	

^a Figure of merit.

^b Sample obtained by slow evaporation of HgSO₄ solution in 10 wt.% H₂SO₄ at RT.

^c Sample obtained by hydrolysis of HgSO₄.

^d Residue after heating PbSO₄ to ca. 1095 °C.

^e Residue after heating PbSO₄ to ca. 1150 °C.

30 wt.% H₂SO₄. In line with this, HgSO₄(s) (or HgSO₄(s) and Hg₃O₂(SO₄)(s) in the appropriate acid concentration range) could be extracted from mother liquors by treatment with glacial acetic acid. All solid products were characterised by PXD and the unit cell data listed in Table 2 confirm that the formulae assigned to the products in Table 1 match those of earlier studies [18,21,26].

The present observations lead one to suggest that the dissolved mercury-containing species involved in these syntheses is simple (unpolymeric) HgSO₄(solv), from which HgSO₄(s) is deposited when the solutions become saturated in the concentration range 30–95 wt.% H₂SO₄. Simple mechanistic steps like these appear to comply with the clear degree of covalent character of both HgO [79,80] (reactant) and HgSO₄ [18] (product). Similarly, it is conceivable that Hg₃O₂(SO₄)(s) is formed from HgSO₄(solv) and H₂O(solv) (or derivatives thereof in H₂SO₄) in the concentration range 2.5–25 wt.% H₂SO₄, the relative yields of HgSO₄(s) and Hg₃O₂(SO₄)(s) being here determined (see Table 1) by the accessible amount of H₂O(solv). The latter findings comply with the fact that Hg₃O₂(SO₄)(s) is the hydrolysis product of HgSO₄(s) (see below). The observation of trace deposits of Hg₃O₂(SO₄)(s) on the wall of the reaction vessel above the solution in many experiments (in particular for 30–45 wt.% H₂SO₄) is a consequence of splashes from the boiling solution and drops of condensed water from the reflux cooler.

3.2. Hydrolysis of HgSO₄(s) and its reverse reaction

Treatment of HgSO₄(s) by distilled H₂O gives Hg₃O₂(SO₄)(s) (confirmed by PXD) and H₂SO₄ (confirmed by chemical analysis) in quantitative correct amounts. The reverse reaction from Hg₃O₂(SO₄)(s) to HgSO₄(s) can also be performed by means of 40–95 wt.% H₂SO₄. However, in this case HgSO₄(solv) occurs as an intermediate, and extraction of the dissolved amounts from the mother liquors by treatment with glacial acetic acid may be necessary to obtain good yields.

3.3. Recrystallisation of HgSO₄ from solutions of 10–20 wt.% H₂SO₄

HgSO₄ was subjected to recrystallisation from nearly saturated solutions with 10–20 wt.% H₂SO₄. After slow evaporation of the solvent at RT (in a desiccator with concentrated H₂SO₄ as drying agent), mixtures of colourless crystals appeared. Some of the crystals were small and plate-shaped whereas the majority were larger and rectangular. X-ray diffraction (Table 2) showed that the larger crystals were HgSO₄·H₂O whereas both HgSO₄ and HgSO₄·H₂O were found among the smaller crystals.

3.4. Lead(II) oxide as reactant

PbSO₄, Pb₂O(SO₄), and an unidentified component (probably oxide sulfate) were obtained as solid

products from reaction between PbO and H₂SO₄ in different concentrations. The yields of PbSO₄ and Pb₂O(SO₄) were generally very good. As the reaction proceeds the yellow colour of the reactant is rapidly converted to white. The entire conversion from reactant to product took ca. 2 min in the case of 95 wt.% H₂SO₄ and ca. 5 h with 2.5 wt.% H₂SO₄. Phase-pure PbSO₄ was obtained as the only solid product in the concentration range 10–95 wt.% H₂SO₄ and for an acid-to-oxide molar ratio exceeding 1.0 (confirmed here for 1.1–17.7). However, Pb₂O(SO₄) and traces of PbSO₄ made up the solid product for acid-to-oxide ratios less than 1.0 (at least down to 0.53) and near 5 wt.% H₂SO₄. With 2.5 wt.% H₂SO₄ and acid-to-oxide ratio of ca. 0.25 the particle size of the solid product had become so small that it appeared as PXD amorphous (microcrystalline) and identification was accordingly impossible.

3.5. Lead(IV) oxide as reactant

The only solid product obtained from reactions between PbO₂ and H₂SO₄ in different concentrations was PbSO₄, either phase-pure or in admixture with unreacted PbO₂. The progressing reaction is evidenced by the evolution of O₂(g) (most clearly seen for 70–95 wt.% H₂SO₄) resulting from thermal decomposition of PbO₂ and/or its reaction with H₂SO₄. To what extent there occurs a pure thermal decomposition of PbO₂, and, if so, how far down in the decomposition sequence $\beta\text{-PbO}_2 \rightarrow \alpha\text{-PbO}_x \rightarrow \beta\text{-PbO}_x \rightarrow \text{Pb}_3\text{O}_4 \rightarrow \text{PbO}$ (see below) it extends, is unclear. However, the possibility that the pure thermal decomposition goes all the way to PbO seems excluded by the high temperatures involved in the later stages [81] of the sequence (even taking particle size effects [82] into account). In fact, PbO was never seen in any of the products obtained with PbO₂ as reactant. It was also noted that the yield of PbSO₄ decreases with decreasing H₂SO₄ concentration. Whether this is a consequence of the acid concentration alone, the reduced BP alone, or a combination of the two is unknown.

3.6. Effect of heat on the reaction products

The TG curves of HgSO₄ and Hg₃O₂(SO₄) showed thermal decomposition in one step (one sharp peak in

DTG), located in the range 600–755 °C for the former and 545–735 °C for the later. The remarkable feature is that $\Delta m/m_0 = 1$ for these degradation reactions, implying that all decomposition products, viz., HgO or Hg, SO₃ (and/or SO₂), and O₂, are subjected to evaporation over the temperature ranges concerned. However, Hg₃O₂(SO₄) was detected in the residue after heating HgSO₄ to 620 °C in the TG instrument (the sample being subjected to temperatures above 600 °C for, say, 10–20 min). On the other hand, the one step feature of the TG curve for Hg₃O₂(SO₄) complies with the findings in Ref. [17] and confirms the instability of Hg₃O₂(SO₄) in the temperature range 550–750 °C.

The TG curves of PbSO₄ and Pb₂O(SO₄) were also relatively featureless with indications of a two-step decomposition for PbSO₄ (ca. 895–1010 and 1010–1130 °C) and a single step for Pb₂O(SO₄) (ca. 845–1080 °C). The residue obtained with a maximum TG instrument temperature of 1200 °C was a mixture of α - and β -PbO (major phase). The findings prompted tests of PbSO₄ with different maximum TG instrument temperatures. With 980 °C as the maximum temperature the residue proved to be a mixture of PbSO₄ (major phase) and Pb₂O(SO₄). On stepwise increasing the maximum temperature to 1050 °C the amount of PbSO₄ decreased and at 1075 °C the residue was almost pure Pb₂O(SO₄). Further increase of the maximum temperature to 1090 °C gave a mixture of Pb₂O(SO₄) and Pb₃O₂(SO₄) (white) and at 1100 °C the residue of Pb₃O₂(SO₄) had become almost phase-pure. With 1125 °C as the maximum temperature a mixture of Pb₃O₂(SO₄) and Pb₅O₄(SO₄) (orange) was obtained. The amount of the latter phase was found to increase gradually up to about 1170 °C maximum TG instrument temperature, above which PbO starts to appear. In conclusion the onset of the thermal decomposition of PbSO₄ and Pb₂O(SO₄) is at ca. 895 and 845 °C, respectively. Hence, Pb₂O(SO₄) is thermally unstable in the temperature range where PbSO₄ undergoes decomposition. The present findings are in good agreement with the thermal decomposition data found in the literature (see Section 1).

3.7. Comments on the thermal decomposition of $\beta\text{-PbO}_2$

The thermal behaviour of $\beta\text{-PbO}_2$ is of interest in relation to our syntheses with this compound as

reactant and a literature search showed considerable discrepancies [81–93], especially with regard to the formulae to be assigned to the phases that appear during the decomposition process. Part of the problem is due to lack of proper structural characterisation of decomposition products, which is important because the oxygen vacancies in some of the intermediates are clearly subjected to various degrees of ordering with subsequent superstructure formation (α - PbO_x , $x \approx 1.57$ vs. $\text{Pb}_{12}\text{O}_{19}$ and β - PbO_x , $x \approx 1.44$ vs. $\text{Pb}_{12}\text{O}_{17}$).

With this background, it was decided to perform some additional test experiments at fixed furnace temperatures (370, 385, and 400 °C for 1–320 h) as well as TG treatment to a predetermined maximum temperature (480–700 °C). These experiments gave products which comply with the available structural data for phases with random and/or ordered distribution of the oxygen vacancies. In addition, a serious complication appeared in that many products proved to be phase impure. The fact that the thermal decomposition experiments by the earlier investigators also may have led to mixtures of these structurally closely related phases provides a natural explanation for some of the discrepancies in the literature. So, the thermal decomposition of PbO_2 appears to deserve renewed attention.

3.8. Redetermined crystal structure of $\text{Hg}_3\text{O}_2(\text{SO}_4)$

The crystal structure of $\text{Hg}_3\text{O}_2(\text{SO}_4)$ has earlier been refined in space group $\text{P}3_12_1$ on the basis of single-crystal Weissenberg X-ray diffraction data

Table 3

Atomic coordinates (with calculated standard deviations in parentheses) for $\text{Hg}_3\text{O}_2(\text{SO}_4)$ as derived from Rietveld analysis of PND data at 298 K. Space group $\text{P}3_1$; $a = 704.80(5)$ pm, $c = 1001.94(8)$ pm

Atoms	x	y	z
Hg(1)	0.3089 (13)	0.8131 (7)	0.9667 (8)
Hg(2)	0.7003 (20)	0.0000 (29)	0.3243 (19)
Hg(3)	0.8132 (7)	0.3089 (13)	0.0000
S	0.2276 (23)	0.0153 (30)	0.3259 (16)
O(1)	0.4821 (19)	0.1497 (17)	−0.0483 (8)
O(2)	0.8660 (30)	0.9776 (27)	0.0687 (24)
O(3)	0.7129 (25)	0.5992 (15)	0.0957 (11)
O(4)	0.1497 (17)	0.4821 (19)	0.0483 (8)
O(5)	0.950 (4)	0.7433 (29)	−0.0851 (23)
O(6)	0.5992 (15)	0.7129 (25)	−0.0957 (11)

[21,26]. The aim of the present PND redetermination was to derive improved atomic coordinates for the oxygen atoms.

The refinements of the PND data in space group $\text{P}3_12_1$ converged well. However, a satisfactory fit could only be obtained when allowing large displacement

Table 4

Selected interatomic distances (pm) and bond angles (°) (with calculated standard deviations in parentheses) for $\text{Hg}_3\text{O}_2(\text{SO}_4)$

Hg(1)–O(1)	206.0 (12)
Hg(1)–O(4)	218.0 (12)
Hg(1)–O(5)	237.8 (22)
Hg(1)–O(4)	253.2 (12)
Hg(1)–O(6)	255.4 (17)
Hg(1)–O(6)	278.2 (15)
Hg(1)–Hg(2)	347.1 (17)
Hg(1)–Hg(3)	353.98 (9)
Hg(2)–O(1)	207.0 (22)
Hg(2)–O(4)	211.2 (23)
Hg(2)–O(5)	263.9 (23)
Hg(2)–O(6)	274.6 (17)
Hg(2)–O(3)	280.9 (19)
Hg(2)–O(2)	285.1 (27)
Hg(2)–O(2)	285.7 (22)
Hg(2)–Hg(3)	346.3 (16)
Hg(3)–O(1)	207.9 (12)
Hg(3)–O(4)	211.0 (12)
Hg(3)–O(3)	245.7 (11)
Hg(3)–O(2)	263.3 (18)
Hg(3)–O(3)	265.6 (16)
Hg(3)–O(5)	284.2 (22)
Hg(3)–Hg(1)	353.98 (9)
Hg(3)–Hg(2)	346.3 (16)
S–O(2)	147.7 (23)
S–O(3)	148.1 (17)
S–O(5)	148.2 (32)
S–O(6)	147.1 (14)
O(1)–Hg(1)–O(4)	162.0 (5)
O(1)–Hg(1)–O(5)	100.3 (6)
O(4)–Hg(1)–O(5)	86.3 (6)
O(1)–Hg(2)–O(4)	172.1 (9)
O(1)–Hg(3)–O(3)	87.4 (4)
O(1)–Hg(3)–O(4)	177.8 (6)
O(3)–Hg(3)–O(4)	92.8 (4)
O(2)–S–O(3)	104.5 (9)
O(2)–S–O(5)	118.1 (18)
O(2)–S–O(6)	115.6 (16)
O(3)–S–O(5)	103.5 (16)
O(3)–S–O(6)	106.6 (17)
O(5)–S–O(6)	107.2 (10)

factors for O(2) and O(3) (numbering as in Ref. [26]) with additional improvement when turning to an anisotropic description. Based on the crystal structure, such displacement factors could indicate thermally excited movement of the sulfate tetrahedra. Hence, a new set of experimental data was collected at 10 K. Surprisingly, the large displacement factors were still present.

It was accordingly considered that the large displacement factors were caused by static disorder. Hence, the PXD and PND data were carefully analysed for detecting possible indications of symmetry lowering. No signs of incorrect assignment of the crystal system were found. Hence, the further data analyses were carried out in the lower symmetric space group, $P3_1$. The origin was fixed by setting $z[\text{Hg}(3)] = 0$. Again the refinements converged nicely, however, incorporation of soft distance restraints were required in order to retain acceptable S–O distances for the sulfate tetrahedra (penalty factor $F = 500$ [78]). The refinements gave the same quality of fit

as obtained in $P3_12_1$, however, this time without non-physical displacement factors. The obtained reliability factors are $\chi^2 = 1.95$, $R_{\text{wp}} = 0.062$ and $R_p = 0.05$. Hence, the PND data seem to reveal that the earlier X-ray diffraction study did not give a correct description of the finer structural details. Atomic coordinates are listed in Table 3 and selected bond lengths and bond angles in Table 4. The fit between observed and calculated diffraction profiles is displayed in Fig. 1, and the structural arrangement is illustrated in Fig. 2 (see also Refs. [26,94] for other perspectives of the structure). Fig. 2 and Table 4 indicate that the $\cdots\text{O}-\text{Hg}-\text{O}-\text{Hg}-\text{O}\cdots$ network carries an appreciable degree of covalent character. Bond valence analysis [95] further emphasises this fact in that the short interatomic distances (Table 4) within the network account for 60–70% of the bond valence of Hg (2.00, 1.81, and 1.90 for Hg(1), Hg(2), and Hg(3), respectively). (The bond valence for S is 5.94.) Bond valence considerations on the structural data for HgSO_4 [18–22] and $\text{Pb}_2\text{O}(\text{SO}_4)$ [59–62] suggest that

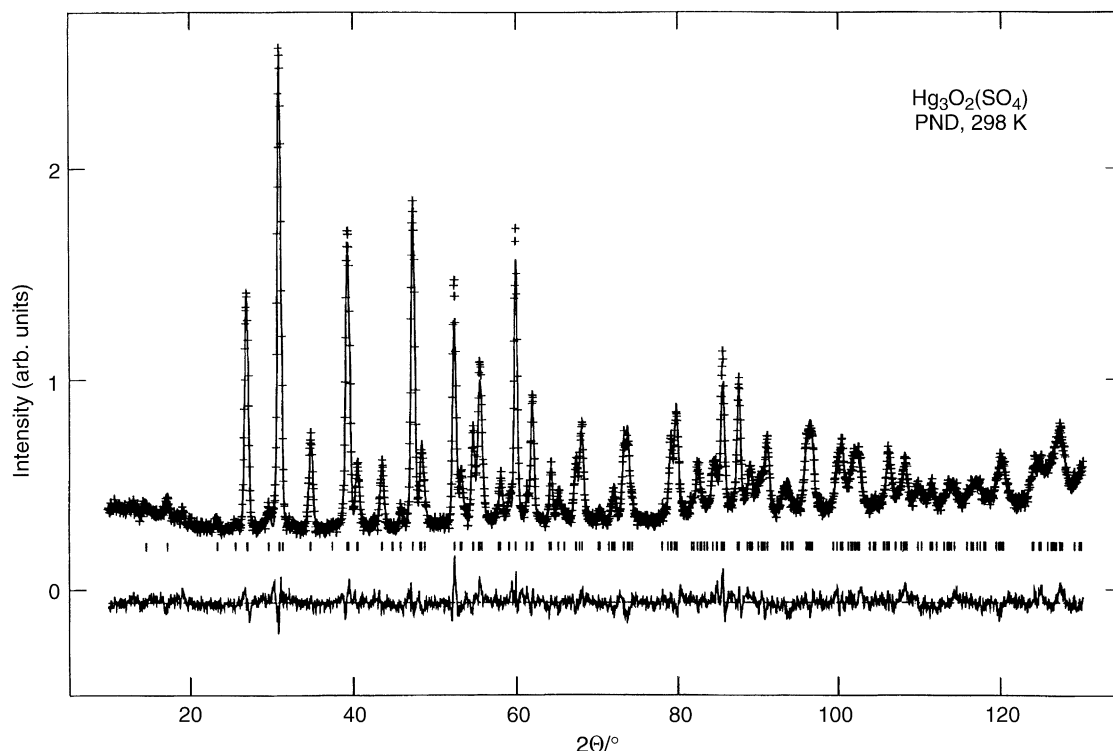


Fig. 1. Rietveld refinements (upper line) of PND data (crosses; $\lambda = 155.5$ pm; 2400 data points; 488 Bragg reflections) for $\text{Hg}_3\text{O}_2(\text{SO}_4)$. Positions of Bragg reflections are marked with bars. The difference between observed and calculated intensities is shown by the bottom line.

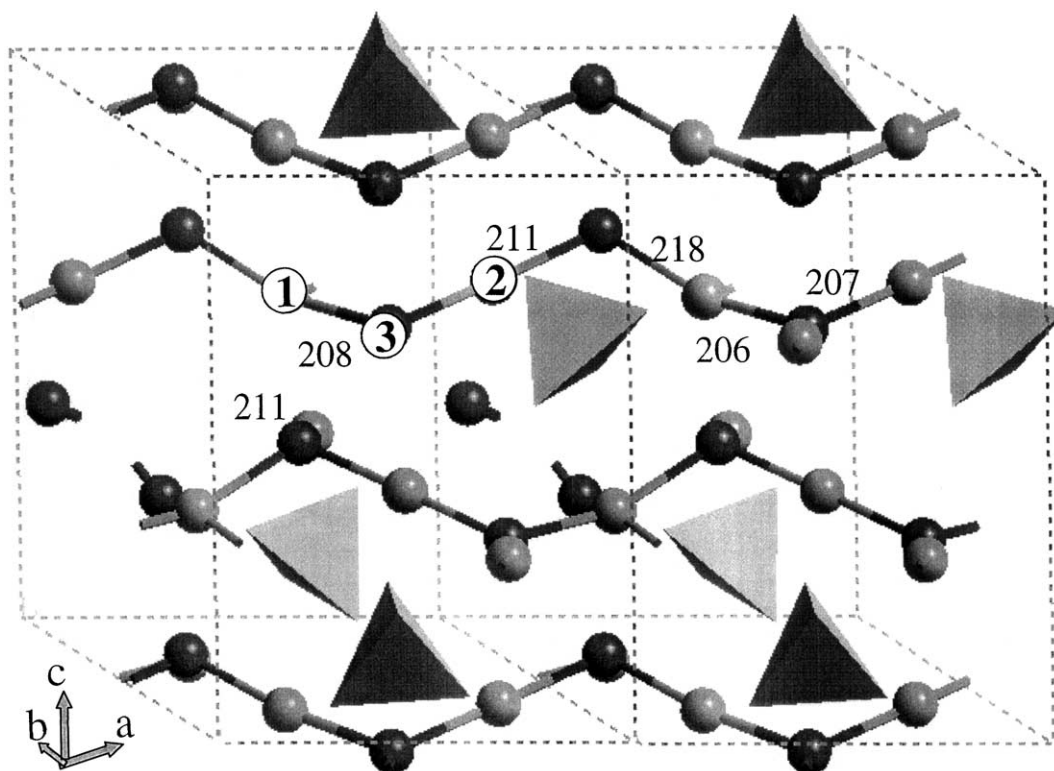


Fig. 2. The crystal structure of $\text{Hg}_3\text{O}_2(\text{SO}_4)$. Sulfate groups are shown as tetrahedra, black spheres represent O and grey spheres Hg. The numbering of Hg atoms and the length of Hg–O distances are marked.

these compounds also carry an appreciable degree of covalence, whereas PbSO_4 [56–58] clearly is of a more ionic nature.

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