ELSEVIER

Thermochimica Acta 390 (2002) 113–121

thermochimica
acta

www.elsevier.com/locate/tca

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

M.A.K. Ahmed, H. Fjellvåg, A. Kjekshus*

Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway

Received 20 December 2001; accepted 18 February 2002

Abstract

Reactions between HgO, PbO, or PbO_2 and 2.5–95 wt.% H_2SO_4 are studied at temperatures up to the boiling point of the acid. Depending on the oxide reactant, the H_2SO_4 concentration, and synthesis temperature, $HgSO_4$, $Hg_3O_2(SO_4)$, $PbSO_4$ and $Pb_2O(SO_4)$ are obtained as identified reaction products. The thermal stability of $HgSO_4$, $Hg_3O_2(SO_4)$, $PbSO_4$, $Pb_2O(SO_4)$, and PbO_2 is examined and the results supplement and modify earlier findings. The redetermined crystal structure of $Hg_3O_2(SO_4)$ on the basis of powder neutron diffraction data shows that its space group ($P3_1$) is of lower symmetry than earlier reported ($P3_12_1$).

Keywords: $HgSO_4$; $Hg_3O_2(SO_4)$; $PbSO_4$; $Pb_2O(SO_4)$; PbO_2; Thermal stability

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 PbO_2 toward H_2SO_4 in different concentrations is considered in this paper.

The reaction between HgO and H_2SO_4 has been the subject of many studies [11–14]. Hoitsema [11] reported four solid compounds in the HgO–SO_3–H_2O system: $HgSO_4$, $HgSO_4{\cdot}H_2O$, $3HgO{\cdot}2SO_3{\cdot}2H_2O$ [$Hg_3O(SO_4)_2{\cdot}2H_2O$], and $3HgO{\cdot}SO_3$ [$Hg_3O_2(SO_4)$]. Paić [12,13] confirmed these compounds in reactions between $HgNO_3$, HNO_3 and Na_2SO_4 in sealed tubes at 250 °C. Grinding of $HgSO_4$ or $Hg_3O(SO_4)_2{\cdot}2H_2O$ with HgO is reported to give $Hg_3O_2(SO_4)$ [14], and the same product is obtained [15] by treating $HgSO_4$ with H_2O.

Hoschek [16] reported that $HgSO_4$ is thermally stable up to 400 °C, but decomposes at 500 °C to $Hg_2O(SO_4)$ and subsequently to $Hg_3O_2(SO_4)$ at 650–750 °C. However, the thermal decomposition of $HgSO_4$ 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 $Hg_2O(SO_4)$ [17]. Powder X-ray diffraction (PXD) of the residue after heating $HgSO_4$ at 620 °C confirmed [17] that the product was $Hg_3O_2(SO_4)$.

Structurally well characterised sulfates and oxide sulfates of mercury are $HgSO_4$ [18–22], $HgSO_4{\cdot}H_2O$ [22–25], $Hg_3O_2(SO_4)$ [21,26], $Hg_3O(SO_4)_2{\cdot}2H_2O$ [21], and $Hg_3(OH)_2(SO_4)_2{\cdot}H_2O$ [27,28].

The outcome of the direct reaction between PbO and concentrated H_2SO_4 has been reported to depend on the acid-to-oxide molar ratio. When the ratio exceeds 1 $PbSO_4$ [29] is the only product, whereas when the ratio becomes less than 1 oxide sulfates are

---

* Corresponding author. Tel.: +47-22855560; fax: +47-22855441.
E-mail address: arne.kjekshus@kjemi.uio.no (A. Kjekshus).

0040-6031/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0040-6031(02)00084-9

reported to be the products: $PbO{\cdot}PbSO_4$ [$Pb_2O(SO_4)$], $3PbO{\cdot}PbSO_4{\cdot}H_2O$ [$Pb_4O_3(SO_4){\cdot}H_2O$], $4PbO{\cdot}PbSO_4$ [$Pb_5O_4(SO_4)$] [30], and even $5PbO{\cdot}2H_2O$ [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: $PbSO_4 \rightarrow Pb_2O(SO_4) \rightarrow 2PbO \cdot PbSO_4$ [$Pb_3O_2(SO_4)$] $\rightarrow 3PbO \cdot PbSO_4$ [$Pb_4O_3(SO_4)$; or alternatively $Pb_5O_4(SO_4)$] $\rightarrow$ 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: $Pb_2O(SO_4)$, $Pb_3O_2(SO_4)$, and $Pb_4O_3(SO_4)$ [or $Pb_5O_4(SO_4)$]. A wet procedure gave $Pb_2O(SO_4)$, $Pb_5O_4(SO_4)$, and $Pb_4O_3(SO_4){\cdot}H_2O$ [49]. The system $PbO–PbSO_4–H_2O$ has been studied by hydrothermal methods giving $Pb_2O(SO_4)$, $Pb_5O_4(SO_4)$, and $Pb_4O_3(SO_4){\cdot}H_2O$ 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. $Pb_2O(SO_4)$, $Pb_3O_2(SO_4)$, and $Pb_5O_4(SO_4)$ 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], $Pb_2O(SO_4)$ [59–62], α-$Pb_3O_2(SO_4)$ [63–66], β-$Pb_3O_2(SO_4)$ [52,64,67] (high-temperature phase), γ-$Pb_3O_2(SO_4)$ [65,66] (low-temperature phase), $Pb_5O_4(SO_4)$ [52,68,69], and $Pb_4O_3(SO_4){\cdot}H_2O$ [53,70, 71]. The $\alpha \rightarrow \beta$ transformation of $Pb_3O_2(SO_4)$ is reported [72,73] at 450 °C and on further heating $Pb_3O_2(SO_4)$ decomposes to $Pb_2O(SO_4)$ and $Pb_5O_4(SO_4)$.

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 (β-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 (β-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 $Hg_3O_2(SO_4)$ 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 °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 $Hg_3O_2(SO_4)$ (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	$Hg_3O_2(SO_4)$ 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	$Pb_2O(SO_4)$[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 $Hg_3O_2(SO_4)$ 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	*a* (pm)	*b* (pm)	*c* (pm)	β (°)	V ($\times 10^6$ pm^3)	M(20)[a]
$HgSO_4$ [18]	Orthorhombic	478.05 (4)	481.58 (4)	657.60 (5)		151.40 (2)	105.5
$HgSO_4 \cdot H_2O$ [22]	Orthorhombic[b]	788.23 (7)	542.26 (4)	897.25 (7)		383.51 (5)	144.9
$Hg_3O_2(SO_4)$ [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
$Pb_2O(SO_4)$ [62]	Monoclinic	1376.1 (3)	566.0 (2)	704.1 (2)	115.86 (2)	493.55	
α-$Pb_3O_2(SO_4)$ [65]	Monoclinic[d]	718.6 (1)	578.9 (1)	805.8 (1)	102.40 (1)	327.334	
$Pb_5O_4(SO_4)$ [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 $HgSO_4$ solution in 10 wt.% H_2SO_4 at RT.

[c] Sample obtained by hydrolysis of $HgSO_4$.

[d] Residue after heating $PbSO_4$ to ca. 1095 °C.

[e] Residue after heating $PbSO_4$ to ca. 1150 °C.

30 wt.% H_2SO_4. In line with this, $HgSO_4$(s) (or $HgSO_4$(s) and $Hg_3O_2(SO_4)$(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) $HgSO_4$-(solv), from which $HgSO_4$(s) is deposited when the solutions become saturated in the concentration range 30–95 wt.% H_2SO_4. Simple mechanistic steps like these appear to comply with the clear degree of covalent character of both HgO [79,80] (reactant) and $HgSO_4$ [18] (product). Similarly, it is conceivable that $Hg_3O_2(SO_4)$(s) is formed from $HgSO_4$(solv) and H_2O(solv) (or derivatives thereof in H_2SO_4) in the concentration range 2.5–25 wt.% H_2SO_4, the relative yields of $HgSO_4$(s) and $Hg_3O_2(SO_4)$(s) being here determined (see Table 1) by the accessible amount of H_2O(solv). The latter findings comply with the fact that $Hg_3O_2(SO_4)$(s) is the hydrolysis product of $HgSO_4$(s) (see below). The observation of trace deposits of $Hg_3O_2(SO_4)$(s) on the wall of the reaction vessel above the solution in many experiments (in particular for 30–45 wt.% H_2SO_4) is a consequence of splashes from the boiling solution and drops of condensed water from the reflux cooler.

3.2. Hydrolysis of $HgSO_4$(s) and its reverse reaction

Treatment of $HgSO_4$(s) by distilled H_2O gives $Hg_3O_2(SO_4)$(s) (confirmed by PXD) and H_2SO_4 (confirmed by chemical analysis) in quantitative correct amounts. The reverse reaction from $Hg_3O_2(SO_4)$(s) to $HgSO_4$(s) can also be performed by means of 40–95 wt.% H_2SO_4. However, in this case $HgSO_4$(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 $HgSO_4$ from solutions of 10–20 wt.% H_2SO_4

$HgSO_4$ was subjected to recrystallisation from nearly saturated solutions with 10–20 wt.% H_2SO_4. After slow evaporation of the solvent at RT (in a desiccator with concentrated H_2SO_4 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 $HgSO_4 \cdot H_2O$ whereas both $HgSO_4$ and $HgSO_4 \cdot H_2O$ were found among the smaller crystals.

3.4. Lead(II) oxide as reactant

$PbSO_4$, $Pb_2O(SO_4)$, and an unidentified component (probably oxide sulfate) were obtained as solid products from reaction between PbO and H_2SO_4 in different concentrations. The yields of $PbSO_4$ and $Pb_2O(SO_4)$ 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.% H_2SO_4 and ca. 5 h with 2.5 wt.% H_2SO_4. Phase-pure $PbSO_4$ was obtained as the only solid product in the concentration range 10–95 wt.% H_2SO_4 and for an acid-to-oxide molar ratio exceeding 1.0 (confirmed here for 1.1–17.7). However, $Pb_2O(SO_4)$ and traces of $PbSO_4$ made up the solid product for acid-to-oxide ratios less than 1.0 (at least down to 0.53) and near 5 wt.% H_2SO_4. With 2.5 wt.% H_2SO_4 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 PbO_2 and H_2SO_4 in different concentrations was $PbSO_4$, either phase-pure or in admixture with unreacted PbO_2. The progressing reaction is evidenced by the evolution of O_2(g) (most clearly seen for 70–95 wt.% H_2SO_4) resulting from thermal decomposition of PbO_2 and/or its reaction with H_2SO_4. To what extent there occurs a pure thermal decomposition of PbO_2, and, if so, how far down in the decomposition sequence $\beta\text{-}PbO_2 \rightarrow \alpha\text{-}PbO_x \rightarrow \beta\text{-}PbO_x \rightarrow Pb_3O_4 \rightarrow PbO$ (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 PbO_2 as reactant. It was also noted that the yield of $PbSO_4$ decreases with decreasing H_2SO_4 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 $HgSO_4$ and $Hg_3O_2(SO_4)$ 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, SO_3 (and/or SO_2), and O_2, are subjected to evaporation over the temperature ranges concerned. However, $Hg_3O_2(SO_4)$ was detected in the residue after heating $HgSO_4$ 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 $Hg_3O_2(SO_4)$ complies with the findings in Ref. [17] and confirms the instability of $Hg_3O_2(SO_4)$ in the temperature range 550–750 °C.

The TG curves of $PbSO_4$ and $Pb_2O(SO_4)$ were also relatively featureless with indications of a two-step decomposition for $PbSO_4$ (ca. 895–1010 and 1010–1130 °C) and a single step for $Pb_2O(SO_4)$ (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 $PbSO_4$ with different maximum TG instrument temperatures. With 980 °C as the maximum temperature the residue proved to be a mixture of $PbSO_4$ (major phase) and $Pb_2O(SO_4)$. On stepwise increasing the maximum temperature to 1050 °C the amount of $PbSO_4$ decreased and at 1075 °C the residue was almost pure $Pb_2O(SO_4)$. Further increase of the maximum temperature to 1090 °C gave a mixture of $Pb_2O(SO_4)$ and $Pb_3O_2(SO_4)$ (white) and at 1100 °C the residue of $Pb_3O_2(SO_4)$ had become almost phase-pure. With 1125 °C as the maximum temperature a mixture of $Pb_3O_2(SO_4)$ and $Pb_5O_4(SO_4)$ (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 $PbSO_4$ and $Pb_2O(SO_4)$ is at ca. 895 and 845 °C, respectively. Hence, $Pb_2O(SO_4)$ is thermally unstable in the temperature range where $PbSO_4$ 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 β-PbO_2*

The thermal behaviour of β-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. $Pb_{12}O_{19}$ and β-PbO_x, $x \approx 1.44$ vs. $Pb_{12}O_{17}$).

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 $Hg_3O_2(SO_4)$

The crystal structure of $Hg_3O_2(SO_4)$ has earlier been refined in space group $P3_12_1$ on the basis of single-crystal Weissenberg X-ray diffraction data [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 $P3_12_1$ converged well. However, a satisfactory fit could only be obtained when allowing large displacement

Table 3
Atomic coordinates (with calculated standard deviations in parentheses) for $Hg_3O_2(SO_4)$ as derived from Rietveld analysis of PND data at 298 K. Space group $P3_1$; $a = 704.80(5)$ 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)

Table 4
Selected interatomic distances (pm) and bond angles (°) (with calculated standard deviations in parentheses) for $Hg_3O_2(SO_4)$

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 exited 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 $z[\mathrm{Hg}(3)] = 0$. 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 nonphysical displacement factors. The obtained reliability factors are $\chi^2 = 1.95$, $R_{\mathrm{wp}} = 0.062$ and $R_{\mathrm{p}} = 0.05$. 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 $\cdots$O–Hg–O–Hg–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 $Pb_2O(SO_4)$ [59–62] suggest that

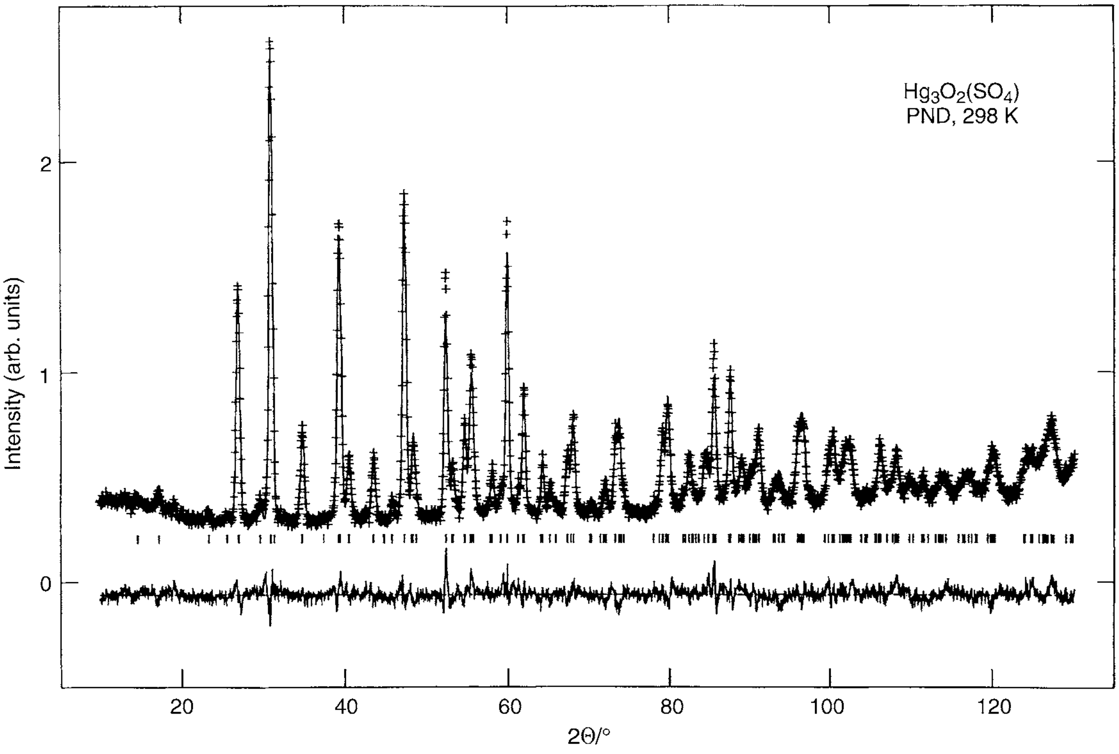

Fig. 1. Rietveld refinements (upper line) of PND data (crosses; $\lambda = 155.5$ pm; 2400 data points; 488 Bragg reflections) for $Hg_3O_2(SO_4)$. Positions of Bragg reflections are marked with bars. The difference between observed and calculated intensities is shown by the bottom line.

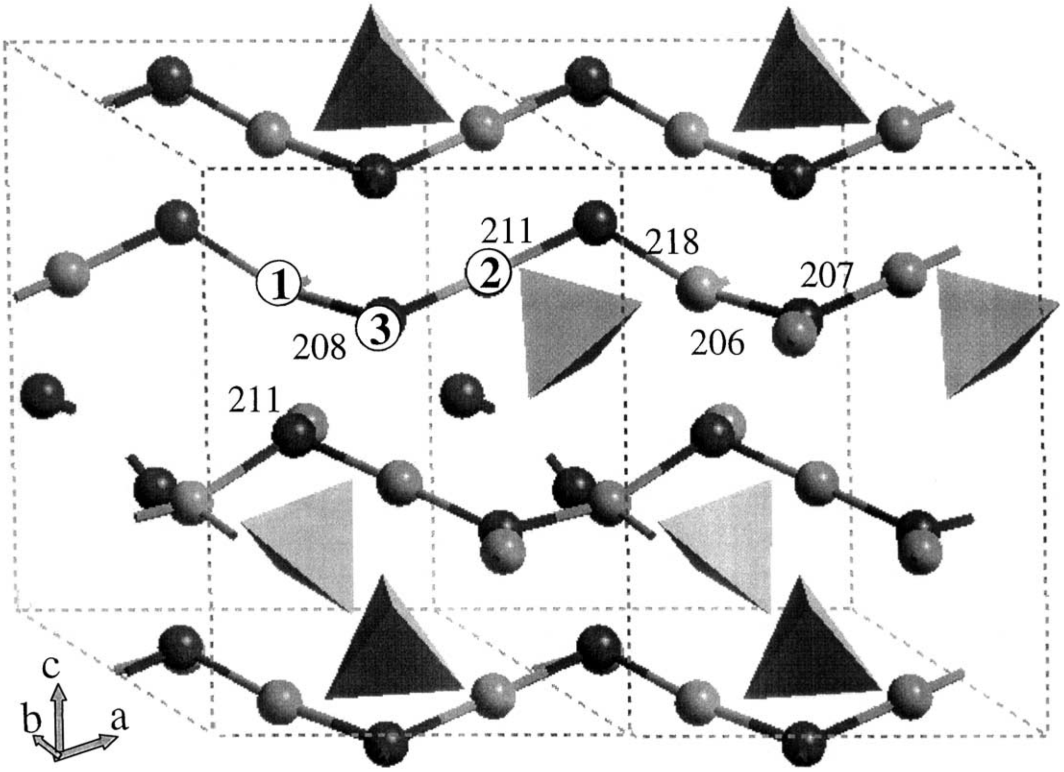

Fig. 2. The crystal structure of $Hg_3O_2(SO_4)$. Sulfate groups are shown as tetrahedra, black spheres represent O and grey spheres Hg. The numbering of Hg atoms and the length of Hg–O distances are marked.

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

Acknowledgement

This project has received financial support from the Research Council of Norway.

References

[1] K. Selte, A. Kjekshus, Acta Chem. Scand. 24 (1970) 1912.
[2] S. Furuseth, K. Selte, H. Hope, A. Kjekshus, B. Klewe, Acta Chem. Scand. Ser. A 28 (1974) 7.
[3] M.A.K. Ahmed, H. Fjellvåg, A. Kjekshus, Acta Chem. Scand. 48 (1994) 537.
[4] H. Fjellvåg, A. Kjekshus, Acta Chem. Scand. 48 (1994) 815.
[5] M.A.K. Ahmed, H. Fjellvåg, A. Kjekshus, Acta Chem. Scand. 49 (1995) 457.
[6] M.A.K. Ahmed, H. Fjellvåg, A. Kjekshus, Acta Chem. Scand. 50 (1995) 275.
[7] M.A.K. Ahmed, H. Fjellvåg, A. Kjekshus, Acta Chem. Scand. 52 (1998) 305.
[8] M.A.K. Ahmed, H. Fjellvåg, A. Kjekshus, Acta Chem. Scand. 53 (1999) 24.
[9] M.A.K. Ahmed, H. Fjellvåg, A. Kjekshus, J. Chem. Soc., Dalton Trans. (2000) 4542.
[10] A.F. Christiansen, H. Fjellvåg, A. Kjekshus, B. Klewe, J. Chem. Soc., Dalton Trans. (2001) 806.
[11] C. Hoitsema, Z. Phys. Chem. 17 (1895) 651.
[12] M. Paić, Bull. Soc. Chim. Fr. 47 (1930) 1254.
[13] M. Paić, Ann. Chim. 19 (1933) 427.
[14] M. Paić, C.R. Hebd. Seances Acad. Sci. 190 (1930) 1014.
[15] E.V. Margulis, Yu.S. Remizov, Zh. Neorg. Khim. 8 (1963) 2290.
[16] G. Hoschek, Monatsh. Chem. 93 (1962) 826.
[17] S.A. Tariq, J.O. Hill, J. Therm. Anal. 21 (1981) 277.
[18] K. Aurivillius, C. Stålhandske, Z. Kristallogr. 153 (1980) 121.
[19] A. Bonefačić, Croat. Chem. Acta 35 (1963) 195.
[20] P.A. Kokkoros, P.J. Rentzeperis, Z. Kristallogr. 119 (1963) 234.
[21] A. Bonefačić, Croat. Chem. Acta 34 (1962) 119.
[22] K. Aurivillius, Ark. Kemi 23 (1965) 205.

[23] C. Stålhandske, Acta Crystallogr., Sect. B 36 (1980) 23.
[24] L.K. Templeton, D.H. Templeton, A. Zalkin, Acta Crystallogr. 17 (1964) 933.
[25] A. Bonefačić, Acta Crystallogr. 14 (1961) 116.
[26] G. Nagorsen, S. Lyng, A. Weiss, A. Weiss, Angew. Chem. Int. Ed. Engl. 1 (1962) 115.
[27] K. Aurivillius, C. Stålhandske, Z. Kristallogr. 144 (1976) 1.
[28] G. Björnlund, Acta Chem. Scand., Ser. A 28 (1974) 169.
[29] V. Khlopin, V. Kuznetsova, Acta Physicochim. URSS 11 (1939) 661.
[30] J. Burbank, J. Electrochem. Soc. 113 (1966) 10.
[31] H. Bode, Angew. Chem. 73 (1961) 553.
[32] G. Archdale, J.A. Harrison, J. Electroanal. Chem. Interf. Electrochem. 43 (1973) 321.
[33] A.N. Fleming, J.A. Harrison, Electrochim. Acta 21 (1976) 905.
[34] P.A. Mackay, British Patent 155,945 (1919).
[35] P.A. Mackay, US Patent 1,485,794 (1924).
[36] A.P. Cassou, French Patent 635,134 (1927).
[37] D.L. Hammick, J. Chem. Soc. 111 (1917) 379.
[38] P. Ruetschi, J. Sklarchuk, R.T. Angstadt, Electrochim. Acta 8 (1963) 333.
[39] Y. Suzuki, Yamagata Daigaku Kiyo Kogaku 16 (1980) 77.
[40] S.C. Smith, British Patent 239,559 (1924).
[41] H.N. Terem, S. Akalan, C.R. Hebd. Seances Acad. Sci. 232 (1951) 973.
[42] V. Mostovich, Zh. Russ. Metall. O-va. 1 (1915) 303.
[43] V.D. Ponomarev, I.R. Polyvyannyi, Izv. Akad. Nauk Kaz. SSR, Ser. Gorn. Dela, Metall. Stroit. Stroimat. (1956) 47.
[44] E.V. Margulis, Y.S. Remizov, Sb. Nauchn. Tr.—Vses. Nauchno-Issled. Gornometall. Inst. Tsvetn. Met. (1960) 171.
[45] G.A. Kolta, M.H. Askar, Thermochim. Acta 11 (1975) 65.
[46] R.M. Gruver, J. Am. Ceram. Soc. 34 (1951) 353.
[47] M. Spiess, R. Gruehn, Z. Naturforsch. B 34 (1979) 431.
[48] R. Schenck, Met. Erz. 23 (1926) 408.
[49] J.J. Lander, J. Electrochem. Soc. 95 (1949) 174.
[50] E.V. Margulis, N.I. Kopylov, Zh. Neorg. Khim. 9 (1964) 763.
[51] G. Tridot, J.C. Boivin, D. Thomas, J. Therm. Anal. 1 (1969) 35.
[52] H.W. Billhardt, J. Electrochem. Soc. 117 (1970) 690.
[53] H.J. Kuzel, Neues Jahrb. Miner. Monatsh. (1973) 110.
[54] E. Schwarzmann, K.H. Ognibeni, J. Haase, Z. Naturforsch. B 26 (1971) 851.
[55] G. Hoschek, Neues Jahrb. Miner. Monatsh. (1962) 68.
[56] M. Miyake, I. Minato, H. Morikawa, S.-I. Iwai, Am. Miner. 63 (1978) 506.
[57] K. Sahl, Beitr. Miner. Petrogr. 9 (1963) 111.
[58] R.J. Hill, J. Appl. Crystallogr. 25 (1992) 589.
[59] W.P. Binnie, Acta Crystallogr. 4 (1951) 471.
[60] K. Sahl, Z. Kristallogr. 132 (1970) 99.
[61] B.F. Mentzen, A. Latrach, J. Appl. Crystallogr. 16 (1983) 430.
[62] B.F. Mentzen, A. Latrach, J. Bouix, A.W. Hewat, Mater. Res. Bull. 19 (1984) 549.
[63] K. Sahl, Z. Kristallogr. 156 (1981) 209.
[64] B.F. Mentzen, A. Latrach, J. Bouix, P. Boher, P. Garnier, Mater. Res. Bull. 19 (1984) 925.
[65] A. Latrach, B.F. Mentzen, J. Bouix, Mater. Res. Bull. 20 (1985) 853.
[66] A. Latrach, B.F. Mentzen, J. Bouix, Mater. Res. Bull. 20 (1985) 1081.
[67] P. Boher, J.F. Berar, B.F. Mentzen, A. Latrach, C.R. Seances Acad. Sci. Ser. II 298 (1984) 635.
[68] B.F. Mentzen, J.-C. Viala, A. Sartre, J. Bouix, C.R. Seances Acad. Sci. Ser. II 293 (1981) 1053.
[69] I.M. Steele, J.J. Pluth, J. Electrochem. Soc. 145 (1998) 528.
[70] I.M. Steele, J.J. Pluth, J.W. Richardson, J. Solid State Chem. 132 (1997) 173.
[71] F. Vallat-Yoliveau, A. Delahaye-Vidal, M. Figlarz, A. de Guibert, J. Power Sources 55 (1995) 97.
[72] J.C. Boivin, D. Thomas, G. Tridot, C.R. Seances Acad. Sci. Ser. C 267 (1968) 532.
[73] P. Boher, P. Gregoire, P. Garnier, B.F. Mentzen, J. Therm. Anal. 32 (1987) 79.
[74] P.-E. Werner, Program SCANPI-6, Institute of Inorganic Chemistry, Stockholm University, Sweden, 1988.
[75] P.-E. Werner, Program TREOR-5, Institute of Inorganic Chemistry, Stockholm University, Sweden (1988) [see also Z. Kristallogr. 120 (1964) 375].
[76] N.O. Ersson, Program CELLKANT, Chemical Institute, Uppsala University, Sweden, 1981.
[77] B.C. Hauback, H. Fjellvåg, O. Steinsvoll, K. Johansson, O.T. Buset, J. Jørgensen, J. Neutron Res. 8 (2000) 215.
[78] A.C. Larson, R.B. Von Dreele, Program GSAS, LANSCE, MS-H 805, Los Alamos National Laboratory, Los Alamos, NM, 1998.
[79] K. Aurivillius, Acta Chem. Scand. 10 (1956) 852;
K. Aurivillius, Acta Crystallogr. 9 (1956) 685;
K. Aurivillius, Acta Chem. Scand. 18 (1964) 1305.
[80] W.L. Roth, Acta Crystallogr. 9 (1956) 277.
[81] D. Fouque, P. Foulloux, P. Bussiere, D. Weigel, M. Prettre, J. Chim. Phys. 62 (1965) 1088.
[82] J. Foucry, D. Fouque, D. Weigel, B. Imelik, M. Prettre, C.R. Hebd. Seances Acad. Sci. 258 (1964) 4249.
[83] G.L. Clark, R. Rowan, J. Am. Chem. Soc. 63 (1941) 1305.
[84] A. Byström, Ark. Kemi, Miner. Geol. A 20 (1945) 1.
[85] A. Byström, Ark. Kemi, Miner. Geol. A 25 (1947) 1.
[86] T. Katz, Ann. Chim. 5 (1950) 5.
[87] G. Butler, J.L. Copp, J. Chem. Soc. (1956) 725.
[88] J.S. Anderson, M. Sterns, J. Inorg. Nucl. Chem. 11 (1959) 272.
[89] R.T. Angstadt, C.J. Venuto, P. Rüetschi, J. Electrochem. Soc. 109 (1962) 177.
[90] W.B. White, R. Roy, J. Am. Ceram. Soc. 47 (1964) 242.
[91] J. Bousquet, J.M. Blanchad, B.F. Mentzen, Bull. Soc. Fr. Miner. Crystallogr. 94 (1971) 332.
[92] C.A. Sorrel, J. Am. Ceram. Soc. 56 (1973) 613.
[93] P. Boher, P. Garnier, J.R. Gavarri, D. Weigel, J. Solid State Chem. 55 (1984) 54.
[94] Structure Report 27 (1962) 610.
[95] N.E. Brese, M. O'Keeffe, Acta Crystallogr., Sect. B 47 (1991) 192.