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Polymorphism in mercury(I) selenite(IV): preparation, crystal structures of α -, β - and γ - Hg_2SeO_3 , and thermal behavior of the α - and β -modification

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Abstract

Mercury(I) selenite(IV) is polymorphic and crystallizes at least in three modifications, named α -, β - and γ - Hg_2SeO_3 . Polycrystalline β - Hg_2SeO_3 was prepared by precipitation of a concentrated mercurous nitrate solution with selenous acid. Hydrothermal treatment of the colorless β - Hg_2SeO_3 powder in demineralized water at 250°C (10 days) yields light-yellow single crystals of α - Hg_2SeO_3 which show the highest density of the three modifications. Colorless needle-shaped single crystals of β - Hg_2SeO_3 and very few single crystals of γ - Hg_2SeO_3 co-crystallize from strongly diluted $\text{Hg}_2(\text{NO}_3)_2$ and H_2SeO_3 solutions and were grown by a diffusion technique. All crystal structures were solved and refined from single crystal diffractometer data sets and are based on Hg_2^{2+} dumbbells and trigonal pyramidal SeO_3^{2-} anions as the main building units. A common structural feature of all modifications is the formation of open channels extending parallel to the shortest crystallographic axis. The non-bonding orbitals of the Se^{IV} atoms are stereochemically active and protrude into the channels. Upon heating in an open system under N_2 atmosphere, both α - and β - Hg_2SeO_3 decompose in a well-separated three-step mechanism. The first step ($T > 250^\circ\text{C}$) involves disproportionation into elementary mercury and α - HgSeO_3 which at ca. 400°C subsequently transforms into β - HgSeO_3 . The second step between $T = 400$ and 500°C is accompanied by a loss of Hg and SeO_2 and the formation of the basic salt Hg_3SeO_6 . In the third step, at temperatures between $T = 500^\circ$ and 600°C, this material decomposes completely. Upon heating in a closed system (sealed silica capillaries), β - Hg_2SeO_3 transforms between 320–340°C into the more dense α - Hg_2SeO_3 which on further heating likewise converts into elementary mercury and β - HgSeO_3 .

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1. Introduction

In spite of the fact that many mercury oxoselenite(IV) and oxoselenate(VI) phases have been reported for a very long time, the knowledge about the crystallographic properties and structures of these compounds is still deficient. For example, in the Gmelin textbook on mercury [1] about 20 mercury salts of selenium oxoacids with different oxidation states for both Hg and Se are listed, but only for a few representatives complete structural analyses have been performed in the past, including the α -modification of mercury(II) selenite(IV), HgSeO_3 [2], the acidic $\text{Hg}_3(\text{HSeO}_3)_2(\text{SeO}_3)_2$ [3], the

hemihydrate $\text{HgSeO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ [4], the mercury(II) selenate(VI) hydrate, $\text{HgSeO}_4 \cdot \text{H}_2\text{O}$ [5], and the mercury(I) selenate(VI), Hg_2SeO_4 [6].

In an attempt to synthesize different phases in the system Hg–Se–O already compiled in Ref [1], single crystals of the following compounds were prepared and their crystal structures analyzed: anhydrous HgSeO_4 , the two basic mercury(II) selenates(VI) $\text{HgSeO}_4 \cdot \text{HgO}$ and $\text{HgSeO}_4 \cdot 2\text{HgO}$ [7], the mercury(II) compounds with mixed-valent selenium ($\text{HgSe}^{\text{IV}}\text{O}_3$)₂ · $\text{HgSe}^{\text{VI}}\text{O}_4$ [8] and ($\text{HgSe}^{\text{IV}}\text{O}_3$)₃ · HgSe^{II} [9], and two additional modifications of mercury(II) selenite(IV), β - and γ - HgSeO_3 [9]. As part of this project the preparation and single-crystal growth of mercury(I) selenite(IV), Hg_2SeO_3 , was investigated. Astonishingly, in the most recent review on metal selenites(IV) [10], neither

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properties nor any other data for this simple salt are reported, although preparation, appearance and solubility have presumably been described for the first time by *Berzelius* nearly 200 years ago [11–13].

In this article, single-crystal growth and structural analyses of three modifications of mercury(I) selenite(IV), α -, β - and γ - Hg_2SeO_3 , are reported, and the relations between the crystal structures are briefly discussed. The modification with the highest density is named α - Hg_2SeO_3 , and, according to the decreasing density, the other polymorphs are denoted as β - and γ - Hg_2SeO_3 . Results of the thermal behavior of the α - and β -modification both in an open and a closed system are described.

2. Experimental

2.1. Preparation

Precipitation of a mercurous nitrate solution, slightly acidified with HNO_3 , with a selenous acid solution of 10% mol in excess (e.g. 1.123 g $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Merck, p.A.) and 0.2440 g SeO_2 (Merck, p.A.)), produced colorless, poorly soluble *polycrystalline* β - Hg_2SeO_3 . After washing with mother liquor, ethanol and acetone and drying in an desiccator over CaCl_2 for 2

days, an X-ray powder diffraction (XRPD) pattern of the polycrystalline product was measured on a Philips X'Pert system ($\text{CuK}\alpha_{1,2}$ radiation ($\lambda = 1.54060$, 1.54439 \AA), Bragg–Brentano geometry, silicon single-crystal sample holder, $5\text{--}120^\circ/(2\theta)$, $0.02^\circ/\text{step}$, 10 s/step). Indexation [14] of the so-obtained powder diagram revealed a single-phase product and indicated a C -centred orthorhombic cell. Refinement [15] of the lattice parameters using silicon powder ($a = 5.431021 \text{ \AA}$ [16]) as an internal standard gave $a = 11.1528(3) \text{ \AA}$, $b = 16.2291(4) \text{ \AA}$ and $c = 5.0372(1) \text{ \AA}$. The obtained powder pattern is in good agreement with the simulation calculated on the basis of the subsequently refined single-crystal data (Fig. 1).

Light-yellow *single crystals* of α - Hg_2SeO_3 with an average diameter of ca. 0.05 mm and mostly pinacoidal habit were obtained after hydrothermal treatment of polycrystalline β - Hg_2SeO_3 in demineralized water (steel autoclave equipped with Teflon inlays with 10 cm^3 capacity, filling degree ca. 70%, 10 days, 250°C). No other phase was found by XRPD analysis of these batches. If stoichiometric amounts of $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and SeO_2 were employed as starting materials for syntheses under similar hydrothermal conditions (demineralized water with a few drops of HNO_3 added to increase the solubility and to avoid formation of basic

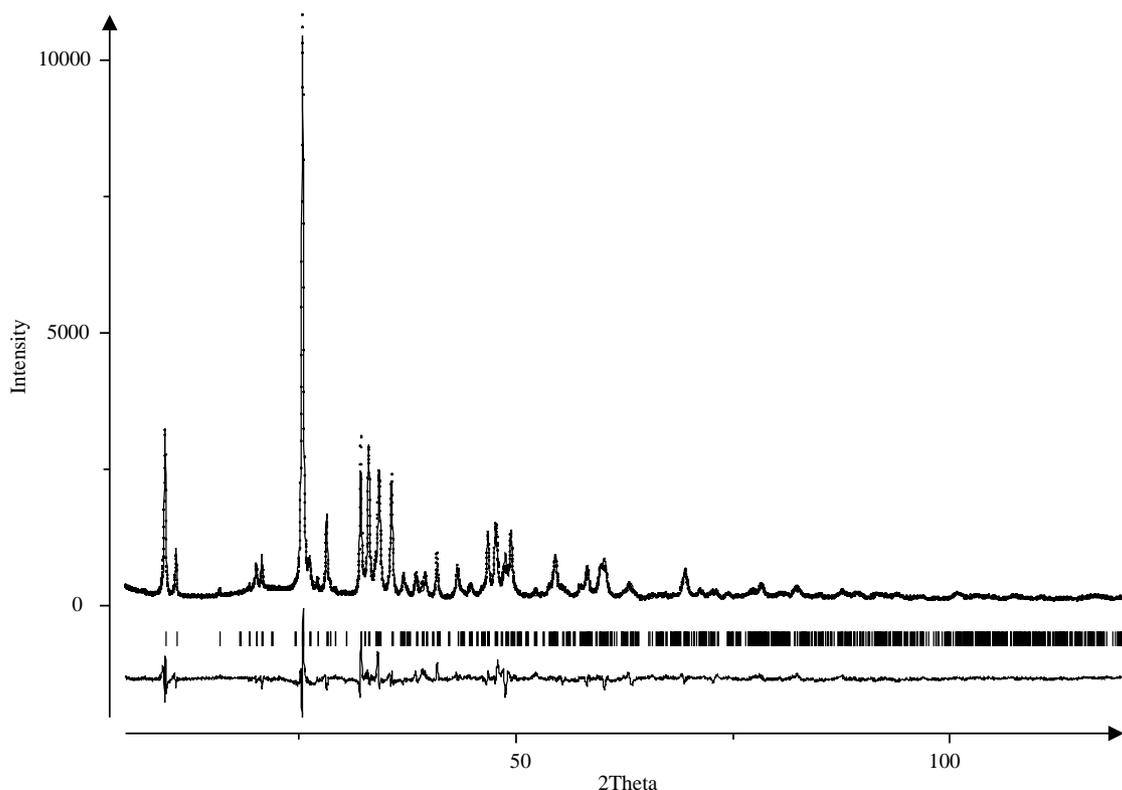


Fig. 1. β - Hg_2SeO_3 . The Rietveld plot [15] with comparison of observed (points) and calculated profiles (solid line) and the corresponding difference pattern.

salts), only few α - Hg_2SeO_3 was obtained and α - HgSeO_3 [2] was the main phase for these batches. Dissolution of polycrystalline β - Hg_2SeO_3 in a boiling diluted nitric acid solution and subsequent recrystallization during controlled cooling (10°C h^{-1}) yielded also single crystals of α - Hg_2SeO_3 , but the crystals prepared by this method were considerably poorer in quality than the hydrothermally synthesized material.

Single crystals of β - Hg_2SeO_3 and γ - Hg_2SeO_3 were grown by a diffusion technique. Two 100 ml beakers containing diluted solutions of $\text{Hg}_2(\text{NO}_3)_2$ and H_2SeO_3 , respectively, were placed in a larger beaker. The small beakers were filled up to the maximum level to avoid bubbles remaining in the solution. Then a paper filter was placed on top of the fringes and 5 l demineralized water were carefully charged into the larger beaker without removing the paper filters. A few drops of concentrated nitric acid were added to the demineralized water to increase the solubility of the mercurous nitrate and to prevent formation of basic salts. This device was then placed in a dark room and set aside for 3 weeks. At the bottom of the large beaker and on top of the paper filter placed on the small beaker with the mercurous nitrate solution, single crystals different in habit and color (light-yellow prisms and very thin and fragile colorless needles up to several mm in length) had formed. Although it was not possible to separate larger amounts of the so-obtained crystal mixtures for single-phase measurements, XRPD analyses revealed α - Hg_2SeO_3 (light-yellow prisms) and β - Hg_2SeO_3 (needles) as the two phases in the bulk material. The presence of the γ -phase could only be detected by single-crystal analyses of some of the colorless needles as described in the following section.

2.2. Structure determination

In case of α - Hg_2SeO_3 , hydrothermally grown crystals were chosen for the data collection. Only very few needle-shaped single crystals grown during the diffusion experiment were suitable for subsequent structure determinations. Their quality was checked by preliminary optical investigations under a polarizing microscope. Intensity data for all crystals examined were measured on a Siemens SMART system equipped with a CCD camera and monochromatized $\text{MoK}\alpha$ radiation. Surprisingly, for some of the needle shaped crystals, the cell determination resulted in a completely different cell than expected for β - Hg_2SeO_3 , but for some crystals the C -centered cell as determined by indexation of the powder pattern was confirmed and in agreement with the powder data. This was evidence that during the diffusion experiment a third modification of Hg_2SeO_3 (or a completely different compound in the system Hg-Se-O(-H)) had formed which had not been detected by the previous XRPD analysis of the bulk material. The

two kinds of needle-shaped crystals could not be distinguished by optical methods, but the quality of the measured intensity data was considerably better for crystals with the unexpected cell than for those of the β -modification.

Subsequent structure analyses were performed with the SHELX97 program package [17] and the expected formula Hg_2SeO_3 was confirmed for all measured crystals. All structures were solved by determination of the mercury atoms using direct methods and by location of the selenium and oxygen atoms from subsequent Fourier syntheses. Owing to the high absorption ($\mu \approx 75 \text{ mm}^{-1}$) and the anisotropic crystal habit, an absorption correction was applied for all data sets. In case of α - Hg_2SeO_3 , the crystal shape was optimized by minimizing the internal R_i value for symmetry-related reflections using the program HABITUS [18]. The so-derived habit was the basis for the numerical absorption correction. In the case of the needle-shaped crystals of β - and γ - Hg_2SeO_3 , distances of indexed faces were measured¹ and used for the analytical absorption correction as implemented in the SHELXTL program [19]. In the final refinement cycles for all data sets, corrections of extinction effects were applied (SHELX97) and anisotropic displacement parameters allowed for all atoms in α - and γ - Hg_2SeO_3 . All investigated β - Hg_2SeO_3 crystals were racemically twinned. For the finally chosen crystal a twin ratio of approximately 1:1 was determined (Flack parameter [20] = 0.54(15)). No additional symmetry for this structure was suggested by the PLATON program [21]. Owing to the poor quality of the β - Hg_2SeO_3 crystals, Se and O atoms were refined isotropically with the U_{eq} parameters restrained for all oxygen atoms. Further details of single-crystal measurement and refinement for all modifications are summarized in Table 1, and final atomic coordinates and anisotropic displacement parameters are listed in Tables 2 and 3, respectively. Selected interatomic distances and angles, as well as the bond-valence sums (BVS), are given in Table 4. The structure representations were produced with the program ATOMS [22]. Additional crystallographic information on each compound 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 numbers listed at the end of Table 1.

2.3. Thermal analyses

The thermal behavior of single-phase material of α - Hg_2SeO_3 and β - Hg_2SeO_3 was examined both in a closed system using temperature-dependent Guinier photographs (sealed silica capillaries with 0.3 mm diameter, heating rate of 8°C h^{-1} in the range 50–650°C) and in an

¹For both polymorphs, the short c -axis is the needle axis.

Table 1
Details of data collection and structure refinement

Compound	α -Hg ₂ SeO ₃	β -Hg ₂ SeO ₃	γ -Hg ₂ SeO ₃
Diffractionmeter	Siemens SMART CCD detector	Siemens SMART CCD detector	Siemens SMART CCD detector
Radiation; λ (Å)	MoK α ; 0.71073	MoK α ; 0.71073	MoK α ; 0.71073
Temperature (°C)	22(2)	22(2)	22(2)
Crystal dimensions (mm ³)	0.06 × 0.04 × 0.02	0.22 × 0.007 × 0.005	0.22 × 0.010 × 0.009
Crystal color; shape	Light-yellow; pinacoid	Colorless; needle	Colorless; needle
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group, no.	<i>P</i> 2 ₁ / <i>n</i> , 14	<i>C</i> mc2 ₁ , 36	<i>rb</i> am, 72
Formula units <i>Z</i>	4	8	8
<i>a</i> (Å)	8.6177(8)	11.1528(3) / (11.142(3)) ^a	10.4293(16)
<i>b</i> (Å)	5.0224(4)	16.2291(4) / (16.265(4)) ^a	11.8522(19)
<i>c</i> (Å)	10.3958(9)	5.0372(1) / (5.029(2)) ^a	7.8324(12)
β (deg)	104.109(2)		
<i>V</i> (Å ³)	436.37(7)	911.73(4) / 911.4(5) ^a	968.2(3)
<i>V</i> / <i>Z</i> (Å ³)	109.09	113.97	121.03
Formula weight (g · mol ⁻¹)	528.14	528.14	528.14
μ (mm ⁻¹)	78.472	75.116	70.738
X-ray density (g · cm ⁻³)	8.039	7.695	7.247
Range θ_{\min} – θ_{\max}	2.76 – 30.23	2.22 – 24.99	2.60 – 30.25
Range <i>h</i>	–11 → 12	–13 → 13	–14 → 13
<i>k</i>	–6 → 7	–19 → 19	–16 → 14
<i>l</i>	–14 → 14	–5 → 5	–10 → 11
Absorption correction	HABITUS [18]	SHELXTL [19]	SHELXTL [19]
Structure refinement	SHELX97 [17]	SHELX97 [17]	SHELX97 [17]
Measured reflections	4555	5780	3484
Independent reflections	1279	832	760
Obs. reflections [<i>I</i> > 2 σ (<i>I</i>)]	1054	672	574
<i>R</i> _{<i>i</i>}	0.0464	0.1021	0.0484
Trans. coef. <i>T</i> _{min} ; <i>T</i> _{max}	0.0821; 0.2464	0.1834; 0.6896	0.2282; 0.5799
Number of parameters	56	35	32
Ext. coef. (SHELXL97)	0.00466(16)	0.00020(6)	0.00027(2)
Diff. elec. dens. max; min	1.37 (0.79, Hg2);	6.75 (0.73, Se);	1.39 (0.84, Hg);
(<i>e</i> ⁻ Å ⁻³) (dist. (Å), atom)	–1.14 (1.31, Hg1)	–5.64 (0.78, O1)	–1.34 (0.69, Hg)
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0230	0.0879	0.0215
w <i>R</i> ₂ (<i>F</i> ² all)	0.0468	0.2058	0.0489
Goodness-of-fit	1.046	1.187	0.970
CSD number	412302	412303	412304

^aLattice parameters from the powder refinement with Si powder (*a* = 5.431021 Å [16]), as internal standard, values from the single-crystal measurement are included in parentheses.

open system under flowing N₂ atmosphere using a Mettler-Toledo DSC-25 system for DSC measurements (heating rate 5°C min⁻¹ in the range 35–450°C, Al crucibles) and a TG-50 system (heating rate 5°C min⁻¹ in the range 35–750°C, corundum crucibles) for thermogravimetric measurements. β -Hg₂SeO₃ was employed as polycrystalline material as obtained after the precipitation reaction; coarse-crystalline α -Hg₂SeO₃ as obtained after hydrothermal treatment was used for TG/DSC, whereas the crystals were ground for temperature-dependent Guinier measurements.

3. Results and discussion

Although the refinement of β -Hg₂SeO₃ from the single-crystal data is not very satisfactory (high *R* values

and standard deviations), the structure is considered as essentially correct. Both single-crystal and powder refinements did not reveal any reduction of the symmetry and the results of the Rietveld refinement [15] (Fig. 1) are in good agreement with the given single crystal data. From the crystal chemical point of view, the finally obtained model is plausible with reasonable distances and angles for both SeO₃²⁻ and Hg₂²⁺ groups as discussed below.

All three modifications crystallize in new structure types and are based on Hg₂²⁺ dumbbells and SeO₃²⁻ anions as the main building units. The linkage into the three-dimensional network is achieved via common oxygen atoms. Characteristic features of all structures are open channels extending parallel to the shortest crystallographic axis (Fig. 2). In case of α -Hg₂SeO₃, the channels are running parallel to the *b*-axis and are made

Table 2

Atomic coordinates and equivalent isotropic displacement parameters $U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \cdot a_i^* a_j^* (\text{\AA}^2)$

Atom	Wyckoff position	x	y	z	U_{eq}
<i>α-Hg₂SeO₃</i>					
Hg1	4e	0.83972(4)	0.26278(6)	0.40815(3)	0.02242(10)
Hg2	4e	0.88645(4)	0.20772(6)	0.65734(3)	0.02381(11)
Se	4e	0.03383(9)	0.74486(13)	0.87540(7)	0.01620(16)
O1	4e	0.8683(6)	0.6524(11)	0.7627(6)	0.0269(13)
O2	4e	0.0277(6)	0.0811(10)	0.8555(5)	0.0200(11)
O3	4e	0.1811(6)	0.6555(11)	0.7986(5)	0.0233(12)
<i>β-Hg₂SeO₃</i>					
Hg1	8b	0.1133(2)	0.24272(13)	0.0404(9)	0.0311(9)
Hg2	8b	0.1130(2)	−0.08341(14)	0.0393(13)	0.0331(9)
Se	8b	0.3231(6)	0.1051(4)	0.0798(14)	0.0306(17)
O1	8b	0.190(3)	0.071(2)	0.003(9)	0.018(5) ^a
O2	8b	0.306(3)	0.205(2)	0.007(9)	0.018(5) ^a
O3	8b	0.316(4)	0.101(3)	0.412(8)	0.018(5) ^a
<i>γ-Hg₂SeO₃</i>					
Hg	16k	0.33035(2)	0.10656(2)	0.25385(4)	0.02521(11)
Se	8j	0.03515(8)	0.19879(8)	0	0.0172(2)
O1	8j	0.4600(6)	0.1749(6)	0	0.0248(15)
O2	16k	0.1373(4)	0.2168(4)	0.1678(6)	0.0257(11)

^a Restrained

Table 3

Anisotropic displacement parameters (\AA^2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
<i>α-Hg₂SeO₃</i>						
Hg1	0.02401(17)	0.02775(19)	0.01518(15)	−0.00030(11)	0.00418(11)	0.00049(13)
Hg2	0.02780(19)	0.02693(19)	0.01563(15)	0.00037(12)	0.00324(12)	0.00213(14)
Se	0.0197(4)	0.0156(4)	0.0147(3)	0.0011(3)	0.0070(3)	0.0016(3)
O1	0.021(3)	0.025(3)	0.033(3)	−0.012(3)	0.004(3)	0.001(2)
O2	0.021(3)	0.016(3)	0.018(3)	−0.001(2)	−0.004(2)	−0.003(2)
O3	0.021(3)	0.033(3)	0.018(3)	0.008(2)	0.009(2)	0.012(3)
<i>β-Hg₂SeO₃</i>						
Hg1	0.0134(12)	0.0305(13)	0.0493(16)	−0.004(3)	0.0209(15)	−0.0010(10)
Hg2	0.0191(13)	0.0355(13)	0.0447(15)	−0.002(2)	0.0259(15)	0.0019(11)
<i>γ-Hg₂SeO₃</i>						
Hg	0.02833(17)	0.01545(14)	0.03186(17)	0.00086(15)	0.00112(11)	0.00112(10)
Se	0.0159(4)	0.0149(4)	0.0207(4)	0	0	−0.0006(3)
O1	0.026(3)	0.027(4)	0.021(3)	0	0	−0.017(3)
O2	0.027(2)	0.024(3)	0.027(3)	−0.001(2)	−0.009(2)	0.008(2)

up of six-membered rings built of four mercury atoms and two selenite(IV) groups. In case of β - and γ -Hg₂SeO₃, the size of the channels is larger due to formation of eight-membered rings (four Hg atoms, four

SeO₃ groups), and the direction of the channels is parallel to the *c*-axis for both modifications. The formation of six-membered rings in the α -modification and eight-membered rings in the two others corresponds

Table 4

Coordination around Hg and Se atoms with interatomic distances (Å) and angles (deg), as well as bond valence sums (BVS) (v.u.).

α -Hg ₂ SeO ₃ ^a						
Hg1	O3 ⁱ	O3 ⁱⁱ	O2 ⁱⁱ	Hg2		
O3 ⁱ	2.152(5)	3.056(6)	3.314(7)	4.683(5)		
O3 ⁱⁱ	79.08(14)	2.612(5)	3.288(8)	4.141(5)		
O2 ⁱⁱ	84.64(17)	75.98(16)	2.726(5)	3.975(5)		
Hg2	173.71(16)	107.06(12)	98.03(10)	2.5379(5)		
Hg2	O2 ⁱⁱⁱ	O1	O1 ^{iv}	O1 ^v	Hg1	
O2 ⁱⁱⁱ	2.215(5)	3.225(8)	3.352(7)	2.609(7)	4.605(5)	
O1	85.87(18)	2.509(5)	3.205(7)	5.0224(4)	4.127(5)	
O1 ^{iv}	89.27(19)	78.71(14)	2.545(5)	3.205(7)	4.268(6)	
O1 ^v	57.44(16)	130.6(2)	69.82(16)	3.014(6)	4.754(6)	
Hg1	153.51(14)	109.72(14)	114.22(12)	117.54(10)	2.5379(5)	
Se	O1 ^{vi}	O2 ^{vii}	O3			
O1 ^{vi}	1.675(5)	2.609(7)	2.629(7)			
O2 ^{vii}	101.2(3)	1.701(5)	2.655(8)			
O3	101.7(3)	102.0(3)	1.715(5)			
<i>BVS</i>						
Hg1: 1.02	Hg2: 1.06	Se: 4.09	O1: 1.84	O2: 1.85	O3: 1.91	
β -Hg ₂ SeO ₃ ^{b,c}						
Hg1	O2	O2 ⁱ	O3 ⁱⁱ	O1	O2 ⁱⁱ	Hg1 ⁱⁱⁱ
O2	2.24(4)	3.17(4)	3.46(6)	2.53(5)	3.17(4)	4.72(4)
O2 ⁱⁱ	80.2(11)	2.66(4)	3.44(6)	4.42(6)	5.037(1)	4.24(4)
O3 ⁱⁱⁱ	87.6(13)	79.3(12)	2.73(5)	5.34(5)	2.65(6)	4.22(4)
O1	56.9(12)	105.3(12)	141.8(12)	2.92(4)	4.44(6)	4.39(4)
O2 ⁱⁱⁱ	73.7(13)	127.3(13)	55.2(12)	97.3(11)	2.96(4)	4.44(4)
Hg1 ⁱⁱⁱ	163.5(9)	109.8(8)	106.8(10)	107.0(7)	107.7(7)	2.527(5)
Hg2	O3 ^{iv}	O1 ^v	O1	O1 ^{iv}	Hg2 ⁱⁱⁱ	
O3 ^{iv}	2.37(5)	3.41(5)	3.16(6)	2.54(6)	4.83(5)	
O1 ^v	86.3(13)	2.50(5)	3.39(5)	5.037(1)	4.11(4)	
O1	78.3(15)	82.9(12)	2.65(4)	3.41(5)	4.20(4)	
O1 ^{iv}	57.5(12)	141.3(15)	77.8(13)	2.84(5)	4.33(4)	
Hg2 ⁱⁱⁱ	162.7(10)	110.1(9)	108.8(8)	107.5(9)	2.520(5)	
Se	O1	O3	O2			
O1	1.63(4)	2.53(5)	2.54(5)			
O3	100(2)	1.67(4)	2.65(6)			
O2	100.1(19)	104(2)	1.68(4)			
<i>BVS</i>						
Hg1: 1.04	Hg2: 1.02	Se: 4.52	O1: 2.08	O2: 2.02	O3: 1.80	
γ -Hg ₂ SeO ₃ ^d						
Hg	O2 ⁱ	O2	O1	O1 ⁱⁱ	Hg ⁱⁱⁱ	
O2 ⁱ	2.208(5)	2.794(9)	3.074(6)	2.607(7)	4.681(5)	
O2	72.64(18)	2.493(4)	3.646(7)	4.966(7)	4.372(5)	
O1	80.44(18)	92.93(19)	2.537(4)	4.004(3)	4.082(5)	
O1 ⁱⁱ	57.23(17)	128.02(16)	91.66(9)	3.026(5)	4.457(6)	
Hg ⁱⁱⁱ	162.69(11)	121.16(11)	107.47(15)	106.42(12)	2.5267(7)	
Se	O1 ^{iv}	O2	O2 ^v			
O1 ^{iv}	1.690(6)	2.607(7)	2.607(7)			
O2	100.3(2)	1.705(4)	2.628(9)			
O2 ^v	100.3(2)	100.8(3)	1.705(4)			
<i>BVS</i>						
Hg: 1.09	Se: 4.05	O1: 1.82	O2: 1.93			

^aSymmetry transformations used to generate equivalent atoms: (i) $-x+1, -y+1, -z+1$; (ii) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $x+1, y, z$; (iv) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (v) $x, y-1, z$; (vi) $x-1, y, z$; (vii) $x, y+1, z$.

^bSymmetry transformations used to generate equivalent atoms: (i) $2-x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $-x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $1-x, y, z$; (iv) $x, -y, z-\frac{1}{2}$; (v) $x, -y, z+\frac{1}{2}$.

^cDistances and angles were calculated using the lattice parameters from the cell refinement of the powder data

^dSymmetry transformations used to generate equivalent atoms: (i) $1-x+\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $x+0, -y+0, -z+\frac{1}{2}$; (iii) $-x+1, y+0, -z+\frac{1}{2}$; (iv) $x-\frac{1}{2}, -y+\frac{1}{2}, z$; (v) $x, y, -z$.

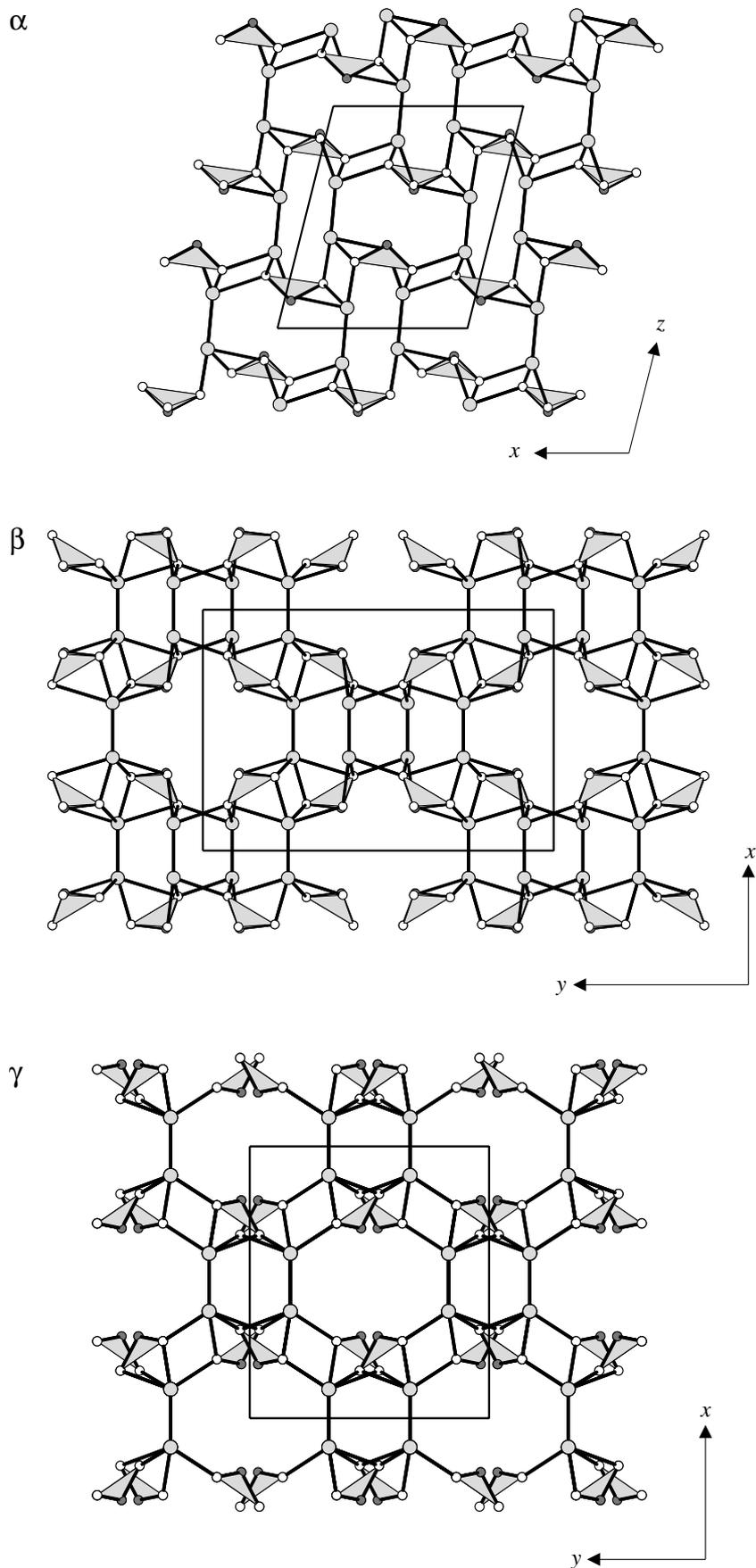


Fig. 2. Projection of the crystal structures parallel to the b -axis (α - Hg_2SeO_3), and parallel to the c -axis (β - Hg_2SeO_3 and γ - Hg_2SeO_3), respectively. The mercury atoms are plotted as gray spheres and the selenite(IV) groups are represented as polyhedra.

with the reaction conditions. While the densest α -modification is formed hydrothermally under comparatively high pressure, β - and γ -modification show a lower density and were grown during a diffusion process under normal laboratory conditions.

The Hg–Hg distances of the Hg_2^{2+} dumbbells (α : 2.5379(5) Å; β : 2.527(5) and 2.520(5) Å; γ : 2.5267(7) Å) differ only slightly from the average distance $\bar{d}(\text{Hg–Hg}) = 2.514$ Å calculated as the arithmetic mean of nearly 60 different Hg_2^{2+} dumbbells observed for various mercury(I) oxo compounds. The dumbbells in β - and γ - Hg_2SeO_3 consist of crystallographically equivalent Hg atoms, and a symmetrical oxygen environment around the dumbbells is observed, whereas in α - Hg_2SeO_3 the dumbbell is built of two inequivalent Hg atoms which results in an asymmetrical oxygen coordination sphere around these atoms (Fig. 3). Besides the neighboring mercury atom, Hg atoms are bonded to three (Hg1, $\bar{d}(\text{Hg1–O}) = 2.497$ Å) and four (Hg2, 2.571 Å) oxygen atoms in α - Hg_2SeO_3 , five (Hg1, 2.70 Å) and four (Hg2, 2.59 Å) oxygen atoms in β - Hg_2SeO_3 , and four oxygen atoms in the γ -modification ($\bar{d}(\text{Hg–O}) = 2.566$ Å). Normally, interactions between an oxygen atom and a mercury atom are considered as bonding, if the distance $d(\text{Hg–O})$ is < 3 Å, which has empirically been derived from the van der Waals radii of the Hg and O atoms [23]. Some of the Hg–O distances are very close to this value ($d(\text{Hg2–O1}) = 3.014(6)$ Å in α - Hg_2SeO_3 , and $d(\text{Hg–O1}) = 3.026(5)$ Å in γ - Hg_2SeO_3), and bond-valence units for the distances are not negligible (Table 4);² this leads to the conclusion that these oxygen atoms also belong to the first coordination sphere. More remote oxygen atoms are located at distances $d(\text{Hg–O}) > 3.3$ Å. For all modifications, the angles $\angle(\text{Hg–Hg–O})$ between the closely bonded oxygen atoms and the mercury dumbbells are virtually linear ranging from 153.5° to 173.7° which is in accordance with the data for $\angle(\text{Hg–Hg–O})$ angles observed for other mercury(I) oxo compounds [25]. The Hg–O distances of these linear bonded oxygen atoms are considerably shorter than the Hg–O distances of the remaining O atoms.

The selenite(IV) groups display the well-known trigonal pyramidal geometry with a similar distribution of bond length $\bar{d}(\text{Se–O})$ and mean angles $\angle(\text{O–Se–O})$, respectively (α - Hg_2SeO_3 : 1.697 Å, 101.6°; β - Hg_2SeO_3 : 1.66 Å, 101.4°; γ - Hg_2SeO_3 : 1.700 Å, 100.5°). Like in other metal selenites(IV) (10), the lone-pairs of the Se^{IV} ions are stereochemically active and protrude into the cavities of the structure. As well, the arrangement of the

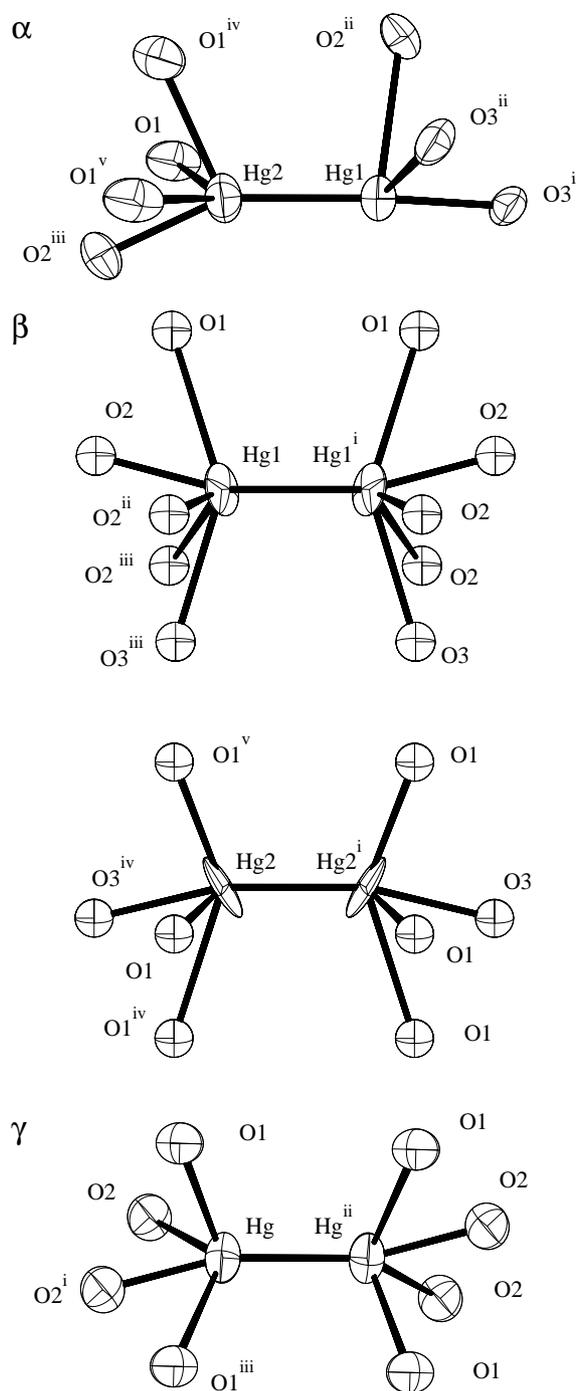


Fig. 3. ORTEP plot [26] of the oxygen coordination sphere around the mercury dumbbells. The ellipsoids are drawn at the 90% probability level. For Symmetry operators, refer Table 4.

SeO_3 pyramids with the apices adjusted to each other within the cavities is a frequently observed structural unit in the crystal chemistry of oxoselenites(IV).

Upon heating in a closed system, β - Hg_2SeO_3 transforms between 320(10)°C and 340(10)°C into the more dense α - Hg_2SeO_3 (Eq. (1)), which in a disproportionation reaction transforms above 370(10)°C into elementary

² Bond-valence sums are in agreement with the expected values and were calculated with the parameters provided by Brese and O'Keeffe [24].

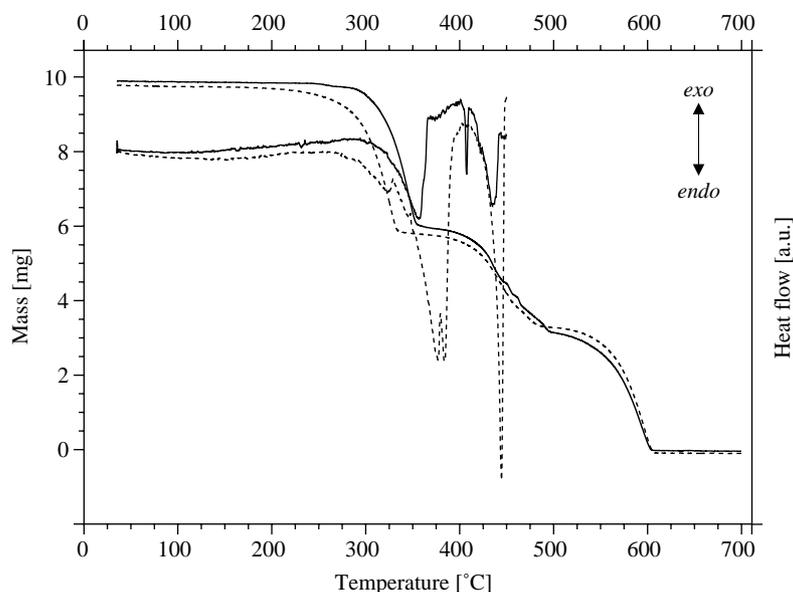
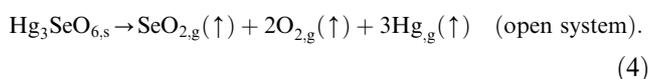
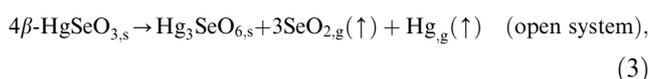
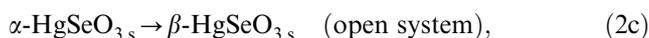
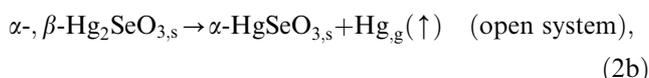
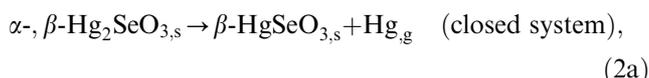


Fig. 4. Thermoanalytical measurements of α - Hg_2SeO_3 and β - Hg_2SeO_3 (dotted lines).

mercury and β - HgSeO_3 [9] as the only phase detected by XRPD (Eq. (2a)). Above $480(10)^\circ\text{C}$ the capillaries bursted due to the high internal pressure. Therefore no other phases could be identified at higher temperatures with this technique.

Upon heating in an open system, both α - and β - Hg_2SeO_3 decompose in a well-separated three-step mechanism (Fig. 4). No phase transformation between both Hg_2SeO_3 modifications was observed under these conditions; β - Hg_2SeO_3 and α - Hg_2SeO_3 are stable up to ca. 250°C and 290°C , respectively. In the first step, both phases disproportionate into elementary mercury and α - HgSeO_3 (Eq. (2b)) which was identified by XRPD analysis of the material heated to $T = 360^\circ\text{C}$. The decomposition ranges for α - Hg_2SeO_3 (ca. 290 – 350°C) and β - Hg_2SeO_3 (ca. 250 – 330°C) slightly differ due to the different particle sizes of the employed material. In a comparison measurement with ground crystals of α - Hg_2SeO_3 , the decomposition range was considerably lowered and similar to that of the polycrystalline β - Hg_2SeO_3 material. At ca. 380°C (β - Hg_2SeO_3 batch) and 415°C (α - Hg_2SeO_3 batch) α - HgSeO_3 transforms into β - HgSeO_3 (Eq. (2c)), which is accompanied by a strong and narrow endothermic effect and was confirmed by subsequent phase analyses. The obtained phase transformation temperature for the measurement of polycrystalline β - Hg_2SeO_3 is in very good agreement with the value of 376.6°C for the $\alpha \rightarrow \beta$ transformation of polycrystalline α - HgSeO_3 given in Ref. [27].³ In the

second step between ca. 400 and 500°C , β - HgSeO_3 converts in a redox-reaction (Eq. (3)) under loss of Hg and SeO_2 into the basic salt Hg_3SeO_6 [7] which is the only phase detected by XRPD of the material heated up to a temperature of $T = 500^\circ\text{C}$. The third step between 500°C and 600°C is assigned to the complete decomposition of this phase (Eq. (4)). The observed mass losses of ca. 38% after the first, and 67% after the second step, are in agreement with the theoretical mass losses of 37.98% and 63.23%, respectively.



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³ Interestingly, no $\alpha \rightarrow \beta$ transformation has been observed by DSC techniques on heating coarse-crystalline material of α - HgSeO_3 under similar conditions [9].

measurements using the Mettler system. Dr. E. Halwax (TU Wien, Austria) kindly provided valuable comments on the manuscript.

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