

Hydrothermal Single Crystal Growth and Crystal Structures of the Mercury(II) Selenates(VI) HgSeO_4 , $\text{HgSeO}_4 \cdot \text{HgO}$ and $\text{HgSeO}_4 \cdot 2\text{HgO}$

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Z. Naturforsch. **57 b**, 1043–1050 (2002); received April 22, 2002

Mercury(II), Selenates(VI), Hydrothermal Synthesis

Colourless single crystals of HgSeO_4 were prepared under hydrothermal conditions by reacting yellow HgO in concentrated selenic acid at 250 °C (10 d); yellow crystals of $\text{HgSeO}_4 \cdot \text{HgO}$ and red-brown crystals of $\text{HgSeO}_4 \cdot 2\text{HgO}$ were obtained during hydrolysis of the so prepared HgSeO_4 in demineralized water at 200 °C (7 d). All crystal structures were solved and refined from single crystal diffractometer data sets. The structures of HgSeO_4 and $\text{HgSeO}_4 \cdot 2\text{HgO}$ are isotypic with the corresponding sulphates. They are based on $[\text{HgO}_7]$ polyhedra with a [4+3] coordination around the mercury atom and isolated SeO_4^{2-} tetrahedra for HgSeO_4 , as well as hexagonal $[\text{Hg}_3\text{O}_2]^{2+}$ nets perpendicular to [001] and disordered SeO_4^{2-} tetrahedra in the interstices of the nets for $\text{HgSeO}_4 \cdot 2\text{HgO}$. The hitherto unknown compound $\text{HgSeO}_4 \cdot \text{HgO}$ crystallizes in a new structure type. The main structural features of this compound are $\frac{1}{\infty}[\text{O}-\text{Hg}-\text{O}]$ zigzag chains which extend parallel to [010] and are built of two crystallographically independent Hg and O atoms, isolated SeO_4^{2-} tetrahedra situated between the chains and $[\text{HgO}_x]$ polyhedra ($x = 6$ and 7) connecting both building units *via* common oxygen atoms.

Introduction

In standard handbooks about mercury and its compounds nearly twenty different phases are reported for the system Hg-Se-O-(H) [1], but only a few representatives are structurally and crystallographically well-characterized. Full structure analyses have been performed on the mercury(II) selenites(IV) HgSeO_3 [2], $\text{Hg}_3(\text{HSeO}_3)_2(\text{SeO}_3)_2$ [3] and $\text{HgSeO}_3 \cdot 1/2\text{H}_2\text{O}$ [4], the hydrated form of mercury(II) selenate(VI) $\text{HgSeO}_4 \cdot \text{H}_2\text{O}$ [5], and the mercury(I) selenate(VI) Hg_2SeO_4 [6]. The compounds with composition $\text{Hg}(\text{XO}_4) \cdot 2\text{HgO}$ ($X = \text{S}, \text{Cr}$ and Se) and the compounds CdSO_4 , HgSO_4 and HgSeO_4 respectively, are reported to be isotypic [7]*. The crystal structures of both structure types have been solved from intensity data of synthetic MSO_4 ($M = \text{Cd}, \text{Hg}$) [9] and $\text{HgSO}_4 \cdot 2\text{HgO}$ [10] crystals (mineral name: *schuetteite*), and have later been re-investigated to obtain improved accuracies of atomic coordinates and interatomic distances for MSO_4 ($M = \text{Cd}, \text{Hg}$) [11] and $\text{Hg}(\text{XO}_4) \cdot 2\text{HgO}$ ($X = \text{S}$ [12] and Cr [13]). During these studies it turned

out for both $\text{HgSO}_4 \cdot 2\text{HgO}$ and $\text{HgCrO}_4 \cdot 2\text{HgO}$ that the XO_4 tetrahedra are disordered around the two-fold axis. Additionally, in the original investigation the determined atomic coordinates were reported to be only provisional, because no absorption correction had been applied to the single crystal Weissenberg X-ray diffraction data of the highly absorbing $\text{HgSO}_4 \cdot 2\text{HgO}$ crystal [10].

For a more detailed understanding of the crystal chemistry of mercuric selenates(VI), and since $\text{HgSeO}_4 \cdot 2\text{HgO}$ is formed as an intermediate during the thermal decomposition [14] of different modifications of the mercury selenites(IV) Hg_2SeO_3 , HgSeO_3 and the acidic $\text{Hg}_3(\text{HSeO}_3)_2(\text{SeO}_3)_2$, it seemed desirable to refine the structures of both HgSeO_4 and $\text{HgSeO}_4 \cdot 2\text{HgO}$ from single crystal data. Experiments were therefore started to grow single crystals of both compounds under hydrothermal conditions. Besides crystals of the desired products single crystals of the mixed-valent mercury(II) selenite(IV) selenate(VI), $\text{Hg}_3\text{Se}_3\text{O}_{10}$ [15], and the hitherto unknown basic mercury(II) selenate(VI), $\text{HgSeO}_4 \cdot \text{HgO}$, were formed during these studies. In this article preparation conditions and single crystal structure analyses of the com-

* HgCrO_4 is monoclinic [8] and crystallizes in a structure type different from that of the mentioned neutral salts MXO_4 .

Table 1. Details of data collection and structure refinement*.

Compound	HgSeO ₄	HgSeO ₄ ·HgO	HgSeO ₄ ·2HgO
Temperature [°C]	22(2)	22(2)	22(2)
Radiation; λ [Å]		— Mo-K α_1 ; 0.71073 —	
Diffractometer	CAD4 (Nonius)	— SMART CCD detector (Siemens) —	
Formula weight [g·mol ⁻¹]	343.55	560.14	776.73
Crystal system	orthorhombic	monoclinic	trigonal
Space group (no.)	<i>Pmn</i> 2 ₁ (31)	<i>P</i> 2 ₁ / <i>c</i> (14)	<i>P</i> 3 ₁ 21 (152)
Formula units <i>Z</i>	2	8	3
Crystal dimensions [mm ³]	0.55 · 0.48 · 0.15	0.12 · 0.10 · 0.038	0.06 · 0.036 · 0.03
Crystal description	colourless column	yellow fragment	dark red parallelepiped
<i>a</i> [Å]	6.7311(9)	9.6247(12)	7.1643(15)
<i>b</i> [Å]	4.9308(6)	7.1313(9)	
<i>c</i> [Å]	4.989(2)	14.8713(18)	10.101(4)
β [°]		109.811(2)	
<i>V</i> [Å ³]	165.58(8)	960.3(2)	449.0(4)
μ [cm ⁻¹]	573.02	713.71	827.87
X-ray density [g·cm ⁻³]	6.891	7.749	8.618
Range θ_{\min} - θ_{\max}	5.09 - 34.92	2.25 - 30.21	3.28 - 30.11
Range <i>h</i>	-10 → 10	-10 → 10	-9 → 10
<i>k</i>	-7 → 7	-10 → 10	-10 → 10
<i>l</i>	-8 → 8	-20 → 20	-14 → 12
Structure solution and refinement		— SHELX97 [16] —	
Measured reflections	2744	12413	5027
Independent reflections	766	2501	891
Obs. reflections [<i>I</i> > 2 σ (<i>I</i>)]	718	2019	846
<i>R</i> _i	0.0601	0.0577	0.0532
Absorption correction		— HABITUS [18] —	
<i>T</i> _{min} ; <i>T</i> _{max}	0.0586; 0.1928	0.0261; 0.1913	0.0611; 0.1372
Number of parameters	36	146	45
Ext. coef. (SHELXL97)	0.132(6)	0.00205(5)	0.00191(11)
Δe_{\max} ; Δe_{\min} [e ⁻ ·Å ⁻³] with distance [Å] to atom	2.02 [0.73, Hg]; -4.43 [0.64, Hg]	2.10 [0.87, Hg4]; -2.33 [0.80, Hg3]	1.68 [0.79, Hg1]; -1.22 [0.58, Hg1]
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.0267	0.0234	0.0209
<i>wR</i> 2 (<i>F</i> ² all)	0.0599	0.0527	0.0451
Flack parameter [19]	0.15(2)	—	0.43(3)
Goof	1.101	1.005	1.049
CSD number	412403	412404	412405

* Additional crystallographic information on each compound can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, e-mail: crystdata@FIZ-karlsruhe.de, on quoting the name of the author, the literature citation and the CSD number listed at the end of the table.

pounds HgSeO₄, HgSeO₄·HgO, and HgSO₄·2HgO are reported.

Experimental Section

Sample preparation

Crystals of all compounds were prepared under hydrothermal conditions. For this purpose a steel autoclave equipped with teflon-lined tubes (volume 5 cm³, filling degree *ca.* 70%) was heated in a conventional laboratory furnace. Crystals obtained from the different batches were filtered from the remaining solution, washed with purified ethanol and acetone, and finally dried in a desiccator.

Colourless, highly refracting crystals up to several mm in length of HgSeO₄ were prepared by reacting yellow

HgO (Merck, p.A) with a concentrated 80%_wt H₂SeO₄ solution (Merck, p.A) at 250 °C (10 d). Treatment of the so obtained HgSeO₄ at 200 °C (7 d) in demineralized water yielded different crystalline products which were separated under a polarizing microscope. Besides small dark red or red brown crystals with mostly columnar habit of HgSeO₄·2HgO, yellow crystals of HgSeO₄·HgO and colourless crystals of Hg₃Se₃O₁₀ [15] were obtained under these conditions.

X-ray analyses

X-ray powder diffraction (XRPD) analyses of separated crystals were in good agreement with the PDF entries #14-0485 for HgSeO₄ and #14-0486

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	s.o.f.
HgSeO₄						
Hg	2 <i>a</i>	0	0.85409(6)	0	0.01497(14)	1
Se	2 <i>a</i>	0	0.34047(15)	0.4806(7)	0.0089(3)	1
O1	4 <i>b</i>	0.6924(7)	0.8096(11)	0.8338(11)	0.0163(9)	1
O2	2 <i>a</i>	0	0.6670(12)	0.4164(17)	0.0184(13)	1
O3	2 <i>a</i>	0	0.2996(17)	0.8072(14)	0.0179(13)	1
HgSeO₄·HgO						
Hg1	4 <i>e</i>	0.00865(3)	0.13512(4)	0.12558(2)	0.01496(8)	1
Hg2	4 <i>e</i>	0.33534(3)	0.38026(3)	0.14665(2)	0.01329(8)	1
Hg3	4 <i>e</i>	0.35891(3)	0.13508(4)	0.37772(2)	0.02004(9)	1
Hg4	4 <i>e</i>	0.66553(3)	0.38013(3)	0.35650(2)	0.01462(8)	1
Se1	4 <i>e</i>	0.03994(8)	0.15122(9)	0.38975(5)	0.01156(14)	1
Se2	4 <i>e</i>	0.65939(8)	0.15274(10)	0.11865(5)	0.01212(14)	1
O1	4 <i>e</i>	0.0265(6)	0.8144(6)	0.0592(4)	0.0183(11)	1
O2	4 <i>e</i>	0.0630(6)	0.2326(8)	0.2937(4)	0.0298(13)	1
O3	4 <i>e</i>	0.0666(6)	0.4695(7)	0.1268(4)	0.0273(14)	1
O4	4 <i>e</i>	0.2105(5)	0.0882(7)	0.4583(4)	0.0221(12)	1
O5	4 <i>e</i>	0.2281(5)	0.5998(7)	0.4412(4)	0.0185(11)	1
O6	4 <i>e</i>	0.2468(5)	0.1271(6)	0.1668(4)	0.0173(11)	1
O7	4 <i>e</i>	0.3712(6)	0.4626(7)	0.3287(4)	0.0239(12)	1
O8	4 <i>e</i>	0.5036(6)	0.2303(9)	0.0451(4)	0.0361(15)	1
O9	4 <i>e</i>	0.5583(5)	0.1298(6)	0.3509(4)	0.0201(12)	1
O10	4 <i>e</i>	0.7359(7)	0.3123(7)	0.1985(4)	0.0280(13)	1
HgSeO₄·2HgO						
Hg1	6 <i>c</i>	0.81048(5)	0.49524(8)	0.69174(3)	0.01686(11)	1
Hg2	3 <i>a</i>	0.29993(7)	0	2/3	0.01576(13)	1
Se	3 <i>a</i>	0.77942(19)	0	2/3	0.0149(2)	1
O1	6 <i>c</i>	0.8430(10)	0.5137(9)	0.9500(6)	0.0178(11)	1
O2A	6 <i>c</i>	0.716(2)	0.764(2)	0.7386(13)	0.025(2) [#]	0.5
O2B	6 <i>c</i>	0.904(3)	0.891(3)	0.7441(13)	0.025(2) [#]	0.5
O3A	6 <i>c</i>	0.588(3)	0.930(3)	0.5516(15)	0.025(2) [#]	0.5
O3B	6 <i>c</i>	0.606(3)	0.839(3)	0.5582(15)	0.025(2) [#]	0.5

Table 2. Atomic coordinates and isotropic displacement parameters [Å²].

restrained.

for HgSeO₄·2HgO, respectively. XRPD of the yellow crystals revealed an unknown phase; the obtained powder pattern is in good agreement with the simulation calculated from the structural parameters of the subsequently refined compound, HgSeO₄·HgO.

The quality of the single crystals of all three compounds used for structure analyses was checked under a polarizing microscope. Intensity data were then measured in the $\omega/2\theta$ technique on a CAD4 four-circle diffractometer for HgSeO₄, and in the ω -scan mode on a SMART-CCD three-circle diffractometer for the other compounds. All data sets were corrected for Lorentz and polarization effects. The crystal structure of HgSeO₄·HgO was solved by direct methods and refined with the SHELX97 program package [16], the structures of HgSeO₄ and HgSeO₄·2HgO were refined with the same program using the atomic coordinates of the corresponding isotopic sulphates as starting parameters in the given non-centrosym-

metric space groups. All crystals of the latter compounds examined were systematically twinned, but no additional symmetry was found by the PLATON program [17]. Under consideration of racemic twinning a twin ratio of approximately 5.5:1 for HgSeO₄ and 1:1 for HgSeO₄·2HgO was determined. Due to high absorption coefficients an absorption correction was applied to all data sets using the program HABITUS [18] by minimizing the internal *R* value and optimizing the crystal shape. The so derived habit was the basis of the numerical absorption correction. In the final least-squares cycles for HgSeO₄ and HgSeO₄·HgO all atoms were refined anisotropically. As with the sulphate(VI) and the chromate(VI) analogues of HgSeO₄·2HgO the XO₄ tetrahedron is disordered in this structure. Therefore a split atom model was considered for the selenate(VI) group with occupation factors constrained to 0.5 for the O atoms and the corresponding displacement parameters refined isotropically. The distance between the split oxygen atom positions became

HgSeO₄							
Hg-	O1	2.241(5) (2×)	Se- O3	1.642(8)	O3-Se-O2	108.3(5)	
	O2	2.273(8)		O2	1.642(6)	O3-Se-O1	112.5(3) (2×)
	O3	2.398(8)		O1	1.662(5) (2×)	O2-Se-O1	110.5(3) (2×)
	O1	2.683(5) (2×)			<1.652>	O1-Se-O1	102.4(4)
	O3	2.898(8)					
	O2	3.054(9)					
		(2.559)					
HgSeO₄·HgO							
Hg1-O6	2.163(5)	Hg2-O9	2.047(5)	Hg3-O9	2.089(5)		
	O5	2.170(5)	O6	2.061(4)	O4	2.179(5)	
	O3	2.448(5)	O3	2.582(5)	O7	2.462(5)	
	O2	2.475(5)	O4	2.657(5)	O8	2.589(5)	
	O1	2.520(5)	O7	2.675(5)	O10	2.591(6)	
	O1	2.677(5)		<2.405>	O2	2.783(6)	
		(2.355)			O6	2.952(6)	
						<2.521>	
O6-Hg1-O5	166.92(18)	O9-Hg2-O6	171.0(2)	O9-Hg3-O4	156.7(2)		
Hg4-O6	2.033(4)	Se1-O3	1.619(5)	Se2-O8	1.625(5)		
	O9	2.049(4)	O2	1.624(5)	O10	1.629(5)	
	O7	2.701(5)	O1	1.633(5)	O7	1.642(5)	
	O10	2.783(5)	O4	1.674(5)	O5	1.661(5)	
	O5	2.834(5)		<1.638>		<1.639>	
	O1	2.839(5)					
		(2.450)					
O6-Hg4-O9	168.6(2)	O3-Se1-O2	114.9(3)	O8-Se2-O10	109.8(3)		
		O3-Se1-O1	108.2(3)	O8-Se2-O7	109.2(3)		
		O2-Se1-O1	110.2(3)	O10-Se2-O7	109.8(3)		
		O3-Se1-O4	108.5(3)	O8-Se2-O5	109.7(3)		
		O2-Se1-O4	103.5(3)	O10-Se2-O5	109.5(3)		
		O1-Se1-O4	111.5(3)	O7-Se2-O5	108.8(3)		
HgSeO₄·2HgO							
Hg1-O1	2.150(6)	Hg2-O1	2.111(7) (2×)	Se- O3B	1.625(15)		
	O1	2.165(6)	O3A	2.626(16) (2×)	O2B	1.647(13)	
	O2A	2.391(15)	O2B	2.656(15) (2×)	O3A	1.673(15)	
	O3B	2.408(16)	O2A	2.673(13) (2×)	O2A	1.678(14)	
	O3A	2.577(15)	O2B	2.948(14) (2×)		<1.656>	
	O1	2.617(6)		<2.603>			
	O2B	2.622(15)					
	O3B	2.623(15)	O1-Hg2-O1	171.5(3)	O3B-Se-O2B	112.9(8)	
	O2A	2.704(15)			O3B-Se-O3A	110.6(8)	
	O3A	2.821(16)			O2B-Se-O3A	107.4(7)	
		(2.508)			O3B-Se-O2A	109.7(7)	
					O3A-Se-O2A	103.2(8)	
O1-Hg1-O1	166.02(7)				O2B-Se-O2A	112.6(8)	

Table 3. Selected interatomic distances [Å] and angles [°].

1.19(2) Å for d (O2A-O2B) and 0.72(2) Å for d (O3A-O3B). The final difference Fourier maps for all compounds did not indicate any additional atomic sites, and the highest difference peaks were located close to the mercury positions. Further details of data collections and structure refinements are listed in Table 1. Final atomic coordinates, selected distances and angles, and displacement parameters for all compounds are given in Tables 2 - 4. The structure representations were produced with the program ATOMS [20].

Discussion

The crystal structure of **HgSeO₄** is based on [HgO₇] polyhedra and SeO₄²⁻ tetrahedra. The connection to the three-dimensional network is achieved by sharing common edges and corners (Fig. 1a). Previous authors [9, 11] have reported that the metal atom is tetrahedrally coordinated. Indeed, the Hg atom is surrounded by four closely bonded O atoms forming a considerably distorted

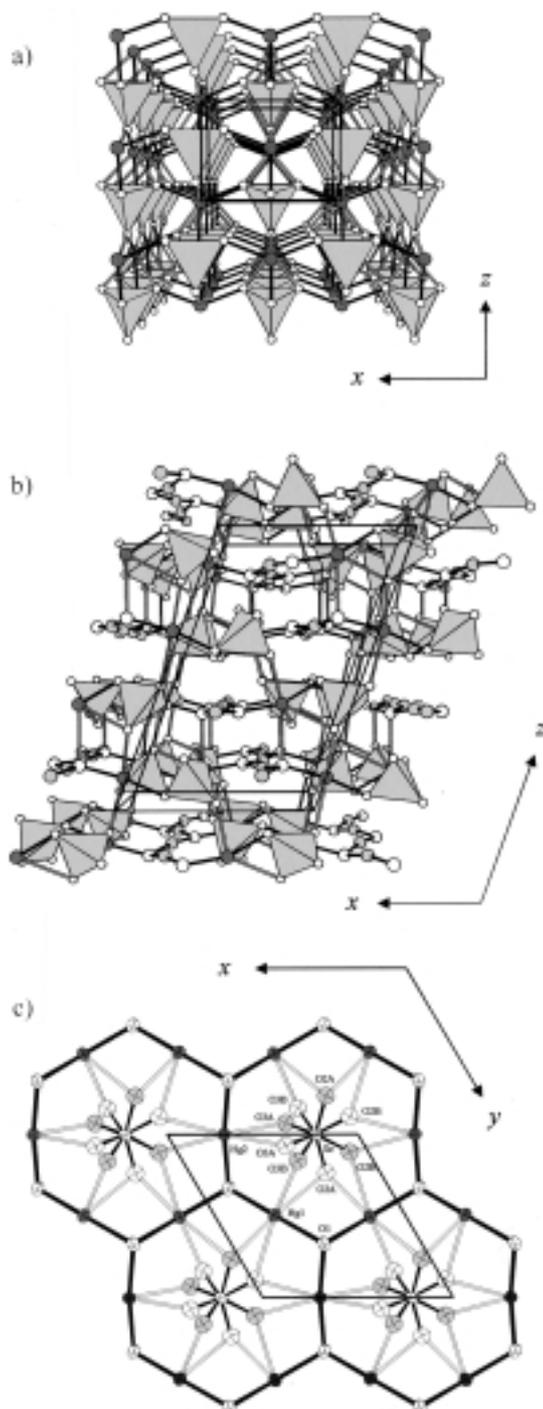
Table 4. Anisotropic displacement parameters [\AA^2].

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
HgSeO₄						
Hg	0.01212(15)	0.01520(15)	0.0176(2)	0.0036(2)	0	0
Se	0.0083(3)	0.0067(3)	0.0116(10)	0.0012(3)	0	0
O1	0.0098(17)	0.021(2)	0.018(2)	0.0042(16)	0.0017(15)	-0.0033(15)
O2	0.033(4)	0.004(3)	0.019(3)	0.004(2)	0	0
O3	0.024(3)	0.018(3)	0.011(3)	0.005(2)	0	0
HgSeO₄·HgO						
Hg1	0.01133(15)	0.01636(14)	0.01619(15)	-0.00218(10)	0.00333(10)	-0.00117(10)
Hg2	0.01327(16)	0.01251(13)	0.01388(14)	0.00031(9)	0.00433(10)	-0.00157(9)
Hg3	0.01848(17)	0.01718(15)	0.03015(18)	-0.00272(11)	0.01568(13)	-0.00295(11)
Hg4	0.01458(16)	0.01290(13)	0.01652(14)	-0.00039(10)	0.00544(11)	-0.00290(10)
Se1	0.0109(3)	0.0131(3)	0.0113(3)	-0.0019(3)	0.0045(2)	-0.0022(3)
Se2	0.0127(4)	0.0132(3)	0.0112(3)	0.0005(3)	0.0050(3)	0.0018(3)
O1	0.025(3)	0.016(2)	0.018(3)	-0.001(2)	0.013(2)	-0.005(2)
O2	0.039(4)	0.037(3)	0.017(3)	0.000(3)	0.015(3)	-0.007(3)
O3	0.015(3)	0.013(3)	0.056(4)	0.003(2)	0.015(3)	0.006(2)
O4	0.013(3)	0.036(3)	0.016(3)	-0.003(2)	0.003(2)	0.002(2)
O5	0.010(3)	0.037(3)	0.010(3)	0.005(2)	0.005(2)	0.003(2)
O6	0.016(3)	0.008(2)	0.029(3)	-0.0001(19)	0.010(2)	0.0005(18)
O7	0.038(3)	0.017(3)	0.022(3)	-0.002(2)	0.017(3)	0.003(2)
O8	0.032(3)	0.056(4)	0.018(3)	0.011(3)	0.006(3)	0.027(3)
O9	0.013(3)	0.013(2)	0.040(4)	-0.002(2)	0.016(2)	-0.0032(19)
O10	0.046(4)	0.021(3)	0.019(3)	-0.006(2)	0.015(3)	-0.007(3)
HgSeO₄·2HgO						
Hg1	0.01301(17)	0.01592(17)	0.02071(16)	-0.00035(16)	-0.00166(12)	0.00652(15)
Hg2	0.0144(2)	0.0127(2)	0.0196(2)	0.0020(2)	0.00098(10)	0.00633(12)
Se	0.0140(4)	0.0123(7)	0.0177(5)	0.0000(5)	0.0000(2)	0.0062(3)
O1	0.017(3)	0.013(3)	0.022(3)	0.000(2)	0.001(2)	0.006(3)

[HgO₄] tetrahedron with Hg-O bonds < 2.40 Å. However, more remote O atoms with distances 2.40 Å < $d(\text{Hg-O})$ < 3 Å cannot be excluded from bonding interactions with the mercury atom which is also confirmed by a bond-valence analysis performed with the parameters provided by Brese and O'Keefe [21]. The bond-valence sums (BVS) calculated under consideration of a tetrahedrally coordinated Hg atom are equal to 1.73 (Hg), 5.78 (Se), 1.89 (O1), 1.93 (O2), and 1.80 (O3). More reasonable BVS of 2.10 (Hg), 5.78 (Se), 2.04 (O1), 1.93 (O2) and 1.89 (O3) are obtained if all distances $d(\text{Hg-O})$ < 3 Å are considered as bonding interactions. Therefore, the Hg atom is better described as [4+3] coordinated (Fig. 2a), with an average Hg-O distance of $\bar{d}(\text{Hg-O}) = 2.488$ Å. This is in good agreement with $\bar{d}(\text{Hg-O}) = 2.445$ Å calculated for the likewise sevenfold coordinated Hg atom in the hydrated selenate(VI), HgSeO₄·H₂O [5]. The SeO₄²⁻ tetrahedron shows a slight distortion; the

observed bond length distribution with a mean of $\bar{d}(\text{Se-O}) = 1.652$ Å is within the typical range for a selenate(VI) group and similar to those found in the hydrated form ($\bar{d}(\text{Se-O}) = 1.641$ Å) and the other structures reported in this article.

HgSeO₄·HgO crystallizes in a new structure type. The main structural features are $\frac{1}{2}$ [O-Hg-O] chains extending parallel to [010], two isolated SeO₄²⁻ groups and two [HgO_x] polyhedra ($x = 6$ and 7) which connect both building units *via* common oxygen atoms (Fig. 1b). The chains are made up of two crystallographically independent mercury atoms, Hg2 and Hg4, with two short bonds ($\bar{d}(\text{Hg-O})_{\text{short}} = 2.048$ Å) to the bridging oxygen atoms and a virtually linear mean (O-Hg-O) angle of 169.8°; the mean (Hg-O-Hg) angle of 121.1° reflects the zigzag orientation of the chain. Distances > 2.6 Å from the mercury atoms of the chain to the remote oxygen atoms make the crystal chemical situation comparable to the orthorhombic modification of HgO with



its planar $\infty[\text{O}-\text{Hg}-\text{O}]$ zigzag chain arrangement ($\bar{d}(\text{Hg}-\text{O})_{\text{short}} = 2.038$ and 2.067 Å, $\angle(\text{O}-\text{Hg}-\text{O}) = 178.3^\circ$, $\angle(\text{Hg}-\text{O}-\text{Hg}) = 108.6^\circ$)*. In $\text{HgSeO}_4 \cdot \text{HgO}$

*HgO is polymorphic and crystallizes in three modifications,

Fig. 1. Crystal structures of a) HgSeO_4 , b) $\text{HgSeO}_4 \cdot \text{HgO}$ and c) $\text{HgSeO}_4 \cdot 2\text{HgO}$. For all representations short Hg-O bonds < 2.4 Å are given in black. For clarity in b) the long bonds (> 2.4 Å) of the (Hg-O)-chain mercury atoms to the more distant O atoms are omitted. In a) and b) the polyhedral representation for the selenate(VI) groups (SeO_4^{2-} tetrahedra are light grey, Hg atoms are grey, O atoms are white) and a perspective view along [010] was chosen; c) shows a part of an $[\text{Hg}_3\text{O}_2]^{2+}$ net with disordered SeO_4^{2-} tetrahedra located inside the interstices in projection parallel to [001] and displacement ellipsoids [29] drawn at the 74% probability level. One orientation of the disordered selenate(VI) group is given in white, the other in grey.

both coordination figures around the mercury atoms Hg1 and Hg3 deviate significantly from ideal polyhedra. Two $[\text{Hg}1\text{O}_6]$ polyhedra, which can be described as distorted octahedra, form an edge-sharing dimer $[\text{Hg}_2\text{O}_{10}]$, whereas the $[\text{Hg}3\text{O}_7]$ polyhedron is difficult to derive from a simple polyhedral description (Fig. 2b). Like many other $[\text{HgO}_x]$ polyhedra observed in various mercury(II) oxo-compounds [22 - 24] both polyhedra show a $[2 + x]$ coordination with two short Hg-O bonds ($\bar{d}(\text{Hg}-\text{O})_{\text{short}} = 2.167$ Å for $[\text{Hg}1\text{O}_6]$ and 2.134 Å for $[\text{Hg}1\text{O}_7]$, respectively); the angle between the short bonded O atoms and the Hg atom is nearly linear for Hg1, whereas a noticeable deviation from linearity is observed for Hg3. In both polyhedra the more distant oxygen atoms have bond lengths 2.45 Å $< d(\text{Hg}-\text{O})_{\text{long}} < 3$ Å. Both independent selenate groups show a similar bond length distribution ($\bar{d}(\text{Se}-\text{O}) = 1.639$ Å), but the angular distortion for the $\text{Se}1\text{O}_4^{2-}$ tetrahedron is more pronounced than in $\text{Se}2\text{O}_4^{2-}$.

The structure of $\text{HgSeO}_4 \cdot 2\text{HgO}$ consists of layers perpendicular to [001] (Fig. 1c). The layers are composed of slightly corrugated hexagonal $[\text{Hg}_3\text{O}_2]^{2+}$ nets with a short distance of $\bar{d}(\text{Hg}-\text{O})_{\text{short}} = 2.134$ Å and nearly linear (O-Hg-O) angles with a mean of 168.8° . The Hg-O distances within the nets are substantially shorter than the distance $\bar{d}(\text{Hg}-\text{O})_{\text{long}} = 2.660$ Å to the oxygen atoms of the disordered SeO_4^{2-} tetrahedra located inside the interstices of the nets and to the oxygen atoms of adjacent layers. All distances $d(\text{Hg}-\text{O})$ within the isotypic $\text{HgXO}_4 \cdot 2\text{HgO}$ ($X = \text{S}, \text{Se}, \text{Cr}$) structures are in the same range. The SeO_4^{2-} group is disordered around the two-fold axis and is only slightly

an orthorhombic form, also known as the mineral *montroydite* [25], a trigonal form [26] and a rare triclinic form [27].

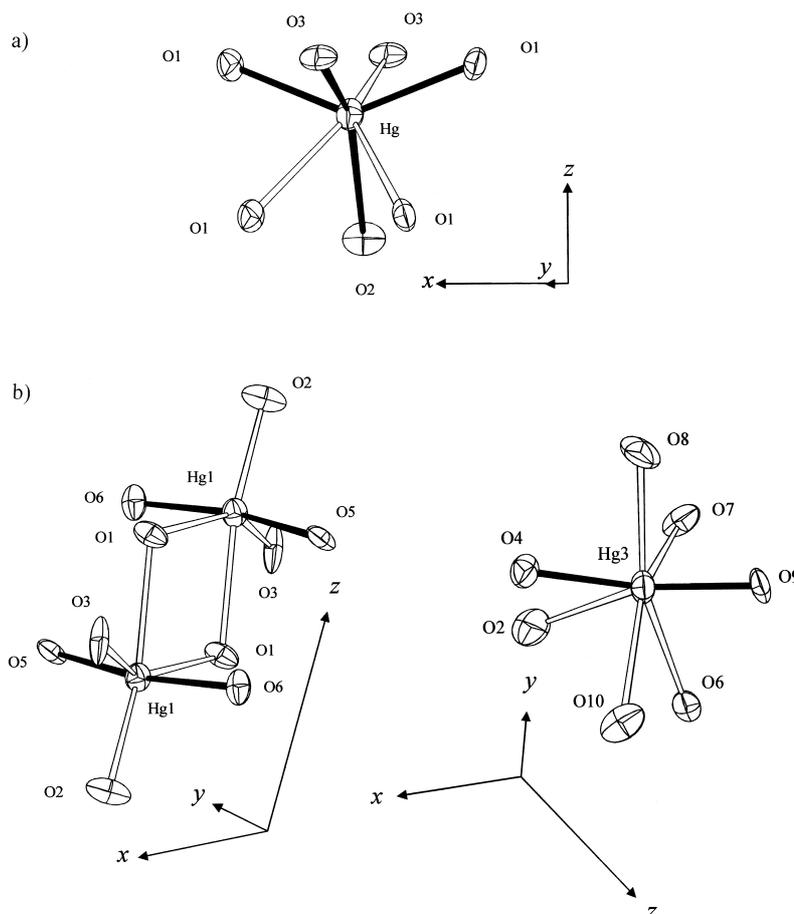


Fig. 2. a) HgSeO_4 and b) $\text{HgSeO}_4 \cdot \text{HgO}$. Coordination polyhedra around the Hg atoms with distances $< 3 \text{ \AA}$ and anisotropic displacement ellipsoids drawn at the 74% probability level [29]; short Hg-O bonds ($< 2.4 \text{ \AA}$) are given in black.

distorted from the geometry of an ideal tetrahedron ($\bar{d}(\text{Se-O}) = 1.656 \text{ \AA}$, mean angle 109.4°). Recently, a reinvestigation of the crystal structure of $\text{HgSO}_4 \cdot 2\text{HgO}$ on the basis of neutron powder diffraction data was published [28] which reports a lowering of the symmetry from space group $P3_121$ (152) to $P3_1$ (144). Due to the symmetry reduction (loss of the twofold axis) the SO_4 tetrahedron is then ordered in the given model*. Refinements carried out in the lower symmetry space group on the basis of the present single crystal data for both $\text{HgSeO}_4 \cdot 2\text{HgO}$ and $\text{HgSO}_4 \cdot 2\text{HgO}$ [12] resulted in considerably higher residuals and high correlations between the atomic coordinates. In addition, unlikely atomic distances for the XO_4 tetrahedra and large displacement parameters for

some oxygen atoms were observed which led to the conclusion that the presented model in $P3_121$ with a disorder of the XO_4 tetrahedron is essentially correct.

The relationship between HgSeO_4 and $\text{HgSeO}_4 \cdot 2\text{HgO}$ and their corresponding sulphate analogues is not only restricted to crystal chemical considerations, but also to the chemical behaviour. Both neutral salts are formed under strongly acidic conditions by reacting HgO with concentrated H_2XO_4 ($X = \text{S}, \text{Se}$) solutions. Hydrolysis of the neutral salts by diluting the acid or by reaction of the solids with demineralized water under normal laboratory conditions (room temperature, normal pressure) yields the double basic salts. Under moderate hydrothermal conditions ($T \approx 200^\circ\text{C}$, $\text{pH} \approx 5$) HgSO_4 converts likewise to $\text{HgSO}_4 \cdot 2\text{HgO}$ [12], whereas hydrothermal treatment of HgSeO_4 leads to a mixture of the double and the single basic salts, as well as the

*The authors had to incorporate soft distance restraints to retain acceptable S-O distances.

mixed-valent Hg₃Se₃O₁₀. This is an indication for a more complex interplay of different redox, pro-

tolysis and precipitation equilibria for the selenium compounds.

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- [1] Gmelins Handbuch der anorganischen Chemie. 8th ed., Vol 34, Part B4, Quecksilber, 1094 f., Verlag Chemie Weinheim (1969).
- [2] M. Koskenlinna, J. Valkonen, *Acta Crystallogr.* **C51**, 1040 (1995).
- [3] M. Koskenlinna, J. Valkonen, *Acta Crystallogr.* **C52**, 491 (1996).
- [4] M. Koskenlinna, J. Valkonen, *Acta Crystallogr.* **C52**, 1070 (1996).
- [5] C. Stålhandske, *Acta Crystallogr.* **B34**, 1408 (1978).
- [6] E. Dorm, *Acta Chem. Scand.* **23**, 1607 (1969).
- [7] K. Aurivillius, B. Malmros, *Acta Chem. Scand.* **15**, 1932 (1961).
- [8] C. Stålhandske, *Acta Crystallogr.* **B34**, 1968 (1978).
- [9] P. A. Kokkoros, P. J. Rentzeperis, *Z. Kristallogr.* **119**, 234 (1963).
- [10] G. Nagorsen, S. Lyng, A. Weiss, A. Weiss, *Angew. Chem.* **74**, 119 (1962).
- [11] K. Aurivillius, C. Stålhandske, *Z. Kristallogr.* **153**, 121 (1980).
- [12] M. Weil, *Acta Crystallogr.* **E57**, i98 (2001).
- [13] T. Hansen, Hk. Müller-Buschbaum, L. Walz, *Z. Naturforsch* **50b**, 47 (1995).
- [14] M. Weil, *J. Solid State Chem.*, submitted.
- [15] M. Weil, U. Kolitsch, *Acta Crystallogr.* **C58**, i47 (2002).
- [16] G. M. Sheldrick, SHELX97. Program for Crystal Structure Solution and Refinement, University of Göttingen, Germany (1997).
- [17] A. L. Spek, PLATON. A multipurpose crystallographic tool, Utrecht Technical University, Utrecht, The Netherlands (2001).
- [18] W. Herrendorf, HABITUS. Program for Optimization of the Crystal Shape for the Numerical Absorption Correction, Universities of Karlsruhe and Gießen, Germany (1993-1997).
- [19] H. D. Flack, *Acta Crystallogr.* **A39**, 876 (1983).
- [20] E. Dowty. ATOMS for Windows. Version 5.1. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA (1999).
- [21] N. E. Brese, M. O'Keefe, *Acta Crystallogr.* **B47**, 192 (1991).
- [22] K. Aurivillius, *Ark. Kemi* **24**, 151 (1965).
- [23] D. Grdenić, *Q. Rev. Chem. Soc.* **19**, 303 (1965).
- [24] Hk. Müller-Buschbaum, *J. Alloys Compd.* **229**, 107 (1995).
- [25] K. Aurivillius, *Acta Chem. Scand.* **18**, 1305 (1964).
- [26] K. Aurivillius, I. B. Carlsson, *Acta Chem. Scand.* **12**, 1297 (1958).
- [27] D. J. Benjamin, *Mater. Res. Bull.* **17**, 179 (1982).
- [28] M. A. K. Ahmed, H. Fjellvåg, A. Kjekshus, *Thermochim. Acta* **390**, 113 (2002).
- [29] C. K. Johnson, ORTEPII. Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA (1976).