

Preparation and Crystal Structures of the Isotypic Compounds $\text{CdXO}_4 \cdot 2 \text{HgO}$ ($X = \text{S}, \text{Se}$)

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Colourless single crystals of the compounds $\text{CdXO}_4 \cdot 2 \text{HgO}$ ($X = \text{S}, \text{Se}$) were obtained under hydrothermal conditions (250 °C, 5 d), starting from stoichiometric amounts of HgO , $\text{CdSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{CdSeO}_4 \cdot 2\text{H}_2\text{O}$, respectively. The crystal structures were determined from X-ray diffraction data sets. The $\text{CdXO}_4 \cdot 2\text{HgO}$ compounds crystallise isotypically with two formula units in space group $P\bar{1}$ (# 2) [$\text{CdSO}_4 \cdot 2\text{HgO}$ ($\text{CdSeO}_4 \cdot 2\text{HgO}$): $a = 6.793(2)$ ($6.9097(5)$) Å, $b = 7.205(2)$ ($7.1786(6)$) Å, $c = 7.359(2)$ ($7.4556(6)$) Å, $\alpha = 73.224(6)$ ($74.586(2)$)°, $\beta = 66.505(6)$ ($68.229(1)$)°, $\gamma = 63.054(5)$ ($63.886(1)$)°, 1670 (1786) structure factors, 92 parameters, $R[F^2 > 2\sigma(F^2)] = 0.0379$ (0.0244)] and are made up from *zig-zag* $[\text{O}-\text{Hg}-\text{O}]_\infty$ chains with very short bonds of $\bar{d}(\text{Hg}-\text{O})$ 2.025 Å, distorted $[\text{CdO}_6]$ octahedra ($\bar{d}(\text{Cd}-\text{O}) = 2.297$ Å), and XO_4 tetrahedra ($\bar{d}(\text{S}-\text{O}) = 1.458$ Å, $\bar{d}(\text{Se}-\text{O}) = 1.633$ Å) as the main building blocks. The $\text{CdXO}_4 \cdot 2\text{HgO}$ compounds reveal no structural relationship with the corresponding $\text{HgXO}_4 \cdot 2\text{HgO}$ phases.

Key words: Mercury, Cadmium, Sulfate, Selenate, Hydrothermal Synthesis, Crystal Structure

Introduction

The preparation of anhydrous cadmium and mercury sulfates and selenates has been known for long and the corresponding crystal structures are well documented. All neutral $M^{\text{II}}\text{XO}_4$ compounds crystallise isotypically in the corresponding low-temperature modification in space group $Pmn2_1$ (# 31) (CdSO_4 [1], CdSeO_4 [2], HgSO_4 [1], HgSeO_4 [3]); additionally, two high-temperature modifications of CdSO_4 have been described to crystallise in $P\bar{3}m1$ (# 164) and $Cmcm$ (# 63) [4, 5]. The only condensed compound structurally characterised so far is the disulfate CdS_2O_7 [6], whereas three basic mercury compounds, $\text{HgSeO}_4 \cdot \text{HgO}$ [3] and the isotypic $\text{HgXO}_4 \cdot 2\text{HgO}$ ($X = \text{S}$ [7, 8], Se [3]), are known.

Nearly 40 years ago, the reaction of HgO with solutions of sulfates and selenates of various divalent metals, including cadmium, has been investigated. From X-ray powder data of the polycrystalline reaction products it was suggested that the obtained compounds $\text{CdSO}_4 \cdot 2\text{HgO}$ [9] and $\text{CdSeO}_4 \cdot 2\text{HgO}$ [10] show a structural relationship to the above mentioned phases $\text{HgXO}_4 \cdot 2\text{HgO}$. Since no crystal data or structural details for the compounds $\text{CdXO}_4 \cdot 2\text{HgO}$ ($X = \text{S}, \text{Se}$)

have been published so far, experiments intended to lead to hydrothermal crystal growth were started. During this project single crystals of both $\text{CdXO}_4 \cdot 2\text{HgO}$ phases were obtained and the crystal structures determined from X-ray diffraction data.

Experimental Section

Syntheses: Stoichiometric amounts of 2 HgO (Merck, p. A.), $\text{CdSeO}_4 \cdot 2\text{H}_2\text{O}$ (obtained from CdO (Fluka, 99%) and diluted H_2SeO_4 (Merck, p. A.)) and $\text{CdSO}_4 \cdot 7\text{H}_2\text{O}$ (Merck, p. A.), respectively, were charged in Teflon inlays with 10 ml capacity which were two-thirds filled with demineralised water and then sealed in a steel autoclave. This device was heated up to 250 °C within 3 h, kept at that temperature for 5 d and cooled down to RT in the course of 2 d. After filtering and washing with mother liquor, water and ethanol, colourless parallelepipeds of the title compounds with an edge-length up to 0.2 mm could be isolated. Besides the title compounds, colourless single crystals of the hydrous phases $\text{CdSeO}_4 \cdot \text{Hg}(\text{OH})_2 \cdot \text{H}_2\text{O}$ and the isotypic $(\text{CdXO}_4 \cdot \text{HgO})_2 \cdot \text{H}_2\text{O}$ ($X = \text{S}, \text{Se}$) were obtained during these experiments. The description of their crystal structures will be given elsewhere.

Single crystal diffraction intensities of the crystals were collected in the ω -scan technique with 0.3° rotation width and 30 s exposure time per frame using a SMART three-

Table 1. Details of data collection and refinement.

Compound	$\text{CdSO}_4 \cdot 2\text{HgO}$	$\text{CdSeO}_4 \cdot 2\text{HgO}$
Diffractometer	— SMART (Siemens) —	
Radiation	— Mo- K_α —	
Wavelength λ [Å]	— 0.71073 —	
Temperature [°C]	— 22(2) —	
Crystal dim. [mm]	0.150×0.030×0.012	0.150×0.020×0.018
Crystal description	Colorless rod	Colorless rod
Space group	— $P\bar{1}$ (# 2) —	
Formula units	— 2 —	
a [Å]	6.793(2)	6.9097(5)
b [Å]	7.205(2)	7.1786(6)
c [Å]	7.359(2)	7.4556(6)
α [°]	73.224(6)	74.586(2)
β [°]	66.505(6)	68.229(1)
γ [°]	63.054(5)	63.886(1)
Volume [Å ³]	291.85(15)	306.04(4)
Formula weight	641.64	688.55
[g·mol ⁻¹]		
μ [mm ⁻¹]	56.404	59.395
X-ray density [g·cm ⁻³]	7.302	7.472
Range $\theta_{\min} - \theta_{\max}$	3.05, 30.52	2.96, 30.49
Range $h; k; l$	−9, 9; −10, 10; −9, 10	−9, 9; −10, 10; −10, 10
Solution and refinement	— SHELX-97 [13] —	
Measured reflections	3258	3522
Independent reflections	1670	1786
Observed reflections	1338	1369
[$I > 2\sigma(I)$]		
R_i	0.0302	0.0450
Absorption correction	SADABS [11]	HABITUS [12]
Coeff. of Transm.	0.0432; 0.4850	0.0881; 0.4489
$T_{\min}; T_{\max}$		
Number of parameters	— 92 —	
Extinction coefficient	0.0037(4)	0.0068(2)
(SHELXL97)		
Difference electron density [e·Å ⁻³]	4.00 (0.84 Hg2)	2.29 (0.80 Hg2)
with distance to atom [Å]	−4.18 (0.78 Hg1)	−1.31 (1.77 O2)
$R[F^2 > 2\sigma(F^2)];$ $wR(F^2 \text{ all})$	0.0379; 0.0944	0.0244, 0.0510
Goof	1.021	0.910
CSD-number	413287	413288

circle diffractometer (Siemens) equipped with a CCD camera. Three independent sets of 606 frames were recorded thus scanning the whole reciprocal sphere. The measured intensities were corrected for Lorentz and polarization effects, and due to the high linear absorption coefficients absorption corrections were applied using the programs SADABS [11] and HABITUS [12], respectively. The crystal structures were solved by direct methods and refined with the SHELX97 program package [13]. The displacement parameters of all atoms were refined anisotropically. The final difference Fourier maps did not indicate any additional atomic sites, and the highest difference peaks were located close to the metal positions. Further details of the data collections and refinements are summarized in Table 1, atomic parameters

Table 2. Atomic coordinates and equivalent isotropic displacement parameters [\AA^2] of $\text{CdSO}_4 \cdot 2\text{HgO}$ (first row) and $\text{CdSeO}_4 \cdot 2\text{HgO}$ (second row).

Atom	x	y	z	U_{eq}^a
Hg1	0.15855(7)	0.35929(6)	0.78080(6)	0.01468(15)
	0.15599(5)	0.35595(5)	0.78993(5)	0.01537(9)
Hg2	0.33926(7)	0.63714(6)	0.21961(6)	0.01385(15)
	0.34184(5)	0.64092(5)	0.20951(5)	0.01420(9)
Cd	0.33147(12)	0.13142(11)	0.22170(11)	0.0122(2)
	0.33410(10)	0.13766(9)	0.21137(8)	0.01228(13)
S	0.7936(5)	0.1360(4)	0.3021(5)	0.0129(5)
Se	0.79841(13)	0.13362(12)	0.31165(11)	0.01172(17)
O1	0.0290(14)	0.1091(14)	0.1761(13)	0.030(2)
	0.0575(10)	0.0783(10)	0.1681(9)	0.0251(15)
O2	0.1510(12)	0.4689(11)	0.2635(13)	0.0182(17)
	0.1538(9)	0.4786(9)	0.2406(9)	0.0197(13)
O3	0.1999(16)	0.0631(12)	0.5636(13)	0.028(2)
	0.2204(11)	0.0780(9)	0.5463(8)	0.0231(14)
O4	0.5502(12)	0.7993(11)	0.1364(11)	0.0136(15)
	0.5511(9)	0.8008(9)	0.1403(8)	0.0144(11)
O5	0.6642(13)	0.1748(14)	0.1710(12)	0.0252(19)
	0.6377(10)	0.2057(10)	0.1688(9)	0.0254(14)
O6	0.6858(15)	0.3098(13)	0.4186(13)	0.0279(19)
	0.7203(12)	0.3244(10)	0.4311(9)	0.0301(16)

$$^a U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

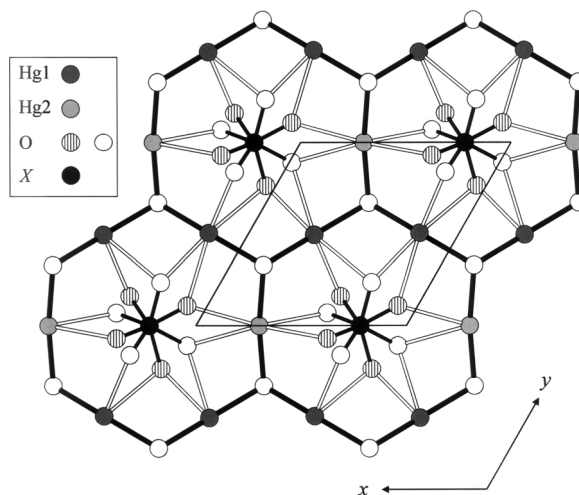


Fig. 1. $\text{HgXO}_4 \cdot 2\text{HgO}$. View down the c axis of a part of an $[\text{Hg}_3\text{O}_2]^{2+}$ net with disordered XO_4^{2-} tetrahedra located in the interstices. Short Hg-O bonds are given in black, longer Hg-O bonds are represented as open lines.

and selected distances are listed in Tables 2 and 3, respectively. Additional crystallographic information on the structures are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, email: 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. Drawings of structural details were produced using the program ATOMS [13].

Table 3. Selected interatomic distances [Å], angles [°] and bond valence sums (BVS) [v. u.].

$\text{CdSO}_4 \cdot 2\text{HgO}$						$\text{CdSeO}_4 \cdot 2\text{HgO}$					
Hg1	O2		2.004(7)	Hg1	O2		2.006(6)	Hg2	O2		2.015(7)
	O4		2.025(7)		O4		2.024(5)		O4		2.049(7)
	O6		2.825(8)		O6		2.717(6)		O6		2.726(8)
	O3		2.873(9)		O3		2.832(6)		O5		2.806(8)
	O1		2.975(9)		O1		3.028(7)		O1		2.995(9)
Hg2	O2		2.015(7)	Hg2	O2		2.016(5)	Cd	O2		2.223(7)
	O4		2.049(7)		O4		2.066(5)		O5		2.286(7)
	O6		2.726(8)		O6		2.614(6)		O1		2.289(8)
	O5		2.806(8)		O5		2.716(6)		O4		2.290(8)
	O6		2.995(9)		O1		2.884(7)		O3		2.294(8)
Cd	O5		3.081(9)	Cd	O5		2.907(7)		O4		2.399(7)
	O1		3.086(9)		O1		2.233(5)		O5		2.251(6)
	O2		2.223(7)		O5		2.251(6)		O1		2.277(6)
	O4		2.286(7)		O1		2.277(6)		O4		2.297(5)
	O1		2.289(8)		O4		2.297(5)		O3		2.304(6)
S	O5		1.442(8)	Se	O6		1.613(6)		O4		2.418(5)
	O1		1.448(8)		O3		1.632(6)		O6		1.613(6)
	O6		1.458(9)		O1		1.639(6)		O3		1.632(6)
	O3		1.482(8)		O5		1.648(6)		O1		1.639(6)
	O2		1.442(8)		O5		1.648(6)		O6		1.613(6)
O2	Hg1	O4	171.9(3)	O2	Hg1	O4	171.9(2)	O2	Hg1	O4	172.3(3)
O2	Hg2	O4	172.3(3)	O2	Hg2	O4	172.6(2)	Hg1	O2	Hg2	114.1(3)
Hg1	O2	Hg2	114.1(3)	Hg1	O2	Hg2	116.9(3)	Hg1	O4	Hg2	114.3(3)
Hg1	O4	Hg2	114.3(3)	Hg1	O4	Hg2	116.7(3)	O5	S	O1	106.6(5)
O5	S	O1	106.6(5)	O5	Se	O1	106.2(3)	O5	S	O6	110.1(5)
O5	S	O6	110.1(5)	O5	Se	O6	108.7(4)	O1	S	O6	112.3(5)
O1	S	O6	112.3(5)	O1	Se	O6	111.5(3)	O5	S	O3	109.1(5)
O5	S	O3	109.1(5)	O5	Se	O3	108.8(3)	O1	S	O3	108.2(5)
O1	S	O3	108.2(5)	O1	Se	O3	108.8(3)	O6	S	O3	110.4(5)
O6	S	O3	110.4(5)	O6	Se	O3	112.7(3)				
BVS: Hg1 2.04, Hg2 2.10, Cd 2.10, S 6.28, O1 2.08, O2 2.23, O3 1.90, O4 2.30, O5 2.14, O6 1.86.						BVS: Hg1 2.07, Hg2 2.14, Cd 2.10, Se 6.09, O1 2.00, O2 2.21, O3 1.96, O4 2.24, O5 2.07, O6 1.92.					

Results and Comment

The main interest in the crystal structure determination of the title compounds arises from the replacement of Hg with Cd atoms and the structural relation of the $\text{HgXO}_4 \cdot 2\text{HgO}$ phases with the corresponding $\text{CdXO}_4 \cdot 2\text{HgO}$ compounds as suggested by Denk *et al.* [9, 10]. Before discussing the crystal structures of the title compounds, a short description of the $\text{HgXO}_4 \cdot 2\text{HgO}$ structure type is therefore appropriate which was solved for the first time in space group $P3_121$ (# 152) from synthetic *schuetteite* crystals, $\text{HgSO}_4 \cdot 2\text{HgO}$ [7]. Subsequent structure refinements of the phases with $X = \text{Cr}$ [15], Se [3] and S [8] led to an improved accuracy of the structural

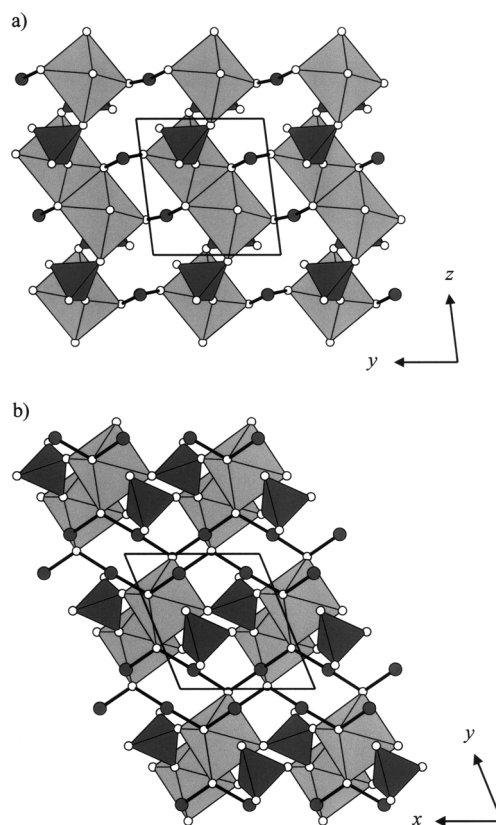


Fig. 2. $\text{CdXO}_4 \cdot 2\text{HgO}$. a) Projection of the crystal structure along [100], and b) along [001]. Hg atoms are plotted as dark grey spheres, O atoms as white spheres; XO_4 tetrahedra (dark-grey) and $[\text{CdO}_6]$ octahedra (light-grey) are given in the polyhedral representation. For clarity, only short Hg-O < 2.10 Å bonds are included.

parameters and revealed a disorder of the XO_4^{2-} tetrahedra. The crystal structure comprises infinite two-dimensional cationic nets stacked along [001] with an overall composition of $[\text{Hg}_3\text{O}_2]^{2+}$, and the disordered XO_4^{2-} tetrahedra situated in the interstices of the nets, as depicted in Fig. 1. The two short Hg-O distances of *ca.* 2.10 Å within the nets are considerably shorter than the distances to the O atoms of the XO_4 tetrahedra (> 2.65 Å). This arrangement reflects the unique crystal chemistry of mercury(II) with a preference for a more or less linear $[2+x]$ coordination with mostly short Hg-O bonds where x can range from 2 to 6. Explanations of this behaviour and surveys of the crystal chemistry of mercury have been given in the past and are summarized in the most recent review article on the crystal chemistry of mercury and its compounds [16]. It is therefore not astonishing that, although both Hg

and Cd have comparable ionic radii [17] of 1.02 and 0.95 Å, respectively, the crystal chemistry of Hg differs considerably from that of the lighter homologue Cd which itself tends to a more regular coordination environment. This leads one to assume that in a replacement of Hg with Cd either the $\text{HgXO}_4 \cdot 2\text{HgO}$ structure becomes considerably “distorted”, or that a different structure type is formed.

As expected (see above), the crystal structure analyses of the title compounds did not reveal any structural relationship with the $\text{HgXO}_4 \cdot 2\text{HgO}$ phases. Unlike the layered organisation of the latter with its $[\text{Hg}_3\text{O}_2]^{2+}$ nets and the disordered XO_4^{2-} tetrahedra in between, the $\text{CdXO}_4 \cdot 2\text{HgO}$ structure type comprises $[\text{O-Hg-O}]_\infty$ chains, distorted $[\text{CdO}_6]$ octahedra, and ordered XO_4 tetrahedra as the main building blocks. For all atoms in the structures the bond valence sum (BVS) calculations [18] using the parameters of Brese and O’Keeffe [19] are within the range of the expected values (Table 3).

The almost linear $[\text{O-Hg-O}]$ units (O-Hg-O angles of *ca.* 172°) have very short Hg-O distances of $\bar{d}(\text{Hg-O}) = 2.025$ Å and form chains extending parallel to the $[100]$ direction (Fig. 2). The next nearest O atoms are located at considerably longer distances > 2.6 Å. The (Hg-O-Hg) angles between two mercury and the shortly bonded O atoms of *ca.* 115° reflect the *zig-zag* arrangement of the chains which, from a crystal chemical point of view, is comparable to the structure of orthorhombic HgO (*montroydite*) [20] itself ($\angle (\text{O-}$

$\text{Hg-O}) = 178^\circ$, $\angle (\text{Hg-O-Hg}) = 108^\circ$, $\bar{d}(\text{Hg-O})_{\text{short}} = 2.053$ Å, $\bar{d}(\text{Hg-O})_{\text{long}} > 2.8$ Å). This behaviour is also emphasised by choosing the formula $\text{CdXO}_4 \cdot 2\text{HgO}$ (and not *e. g.* CdHgXO_6).

Adjacent $[\text{O-Hg-O}]_\infty$ chains are connected by $[\text{Cd}_2\text{O}_{10}]$ dimers, formed by edge-sharing of distorted $[\text{CdO}_6]$ octahedra, whose Cd-O distances range from 2.22 to 2.42 Å with an average of $\bar{d}(\text{Cd-O}) = 2.297$ Å. This value is in the range typical for Cd atoms with a six-coordination of O atoms. These $[\text{Cd}_2\text{O}_{10}]$ dimers are also linked to the corners of the XO_4 groups. The corresponding XO_4 anions deviate only slightly from the geometry of an ideal tetrahedron. For both compounds, the average M -O distances ($M = \text{Cd}, \text{Hg}$) are very similar and only the X-O distances ($\bar{d}(\text{S-O}) = 1.458$ Å; $\bar{d}(\text{Se-O}) = 1.633$ Å) vary considerably.

The coordination numbers of the O atoms range from 3 to 4. O1 and O5 have CN = 4 and are bonded to X, Cd and two Hg atoms at long distances; O3 and O6 have CN = 3 and are bonded to X, one Cd atom and one Hg atom at long distances, and X and two Hg at long distances, respectively. O4 has CN = 4 with bonds to 2 Hg and 2 Cd atoms. It is the bridging atom of the $[\text{Cd}_2\text{O}_{10}]$ dimer and is also part of the $[\text{O-Hg-O}]_\infty$ chain, which explains the comparatively high bond valence sum. The same applies to the O2 atom with CN = 3 (bonds to two Hg atoms and one Cd atom) which is also a part of the $[\text{O-Hg-O}]_\infty$ chain and shows the shortest Cd-O contact to one corner of the $[\text{Cd}_2\text{O}_{10}]$ dimer (Fig. 2).

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