

# Hydrothermal Crystal Growth and Crystal Structures of the Mercury(II) Chromates(VI) $\alpha$ -HgCrO<sub>4</sub>, $\beta$ -HgCrO<sub>4</sub>, and HgCrO<sub>4</sub>·H<sub>2</sub>O

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*Dedicated to Professor Wolfgang Jeitschko on the occasion of his 70<sup>th</sup> birthday*

Single crystals of  $\alpha$ -HgCrO<sub>4</sub>,  $\beta$ -HgCrO<sub>4</sub> and HgCrO<sub>4</sub>·H<sub>2</sub>O were obtained by reacting yellow HgO in chromic acid of various concentrations under hydrothermal conditions at 200 °C (4 d). All crystal structures were solved and refined from single crystal diffractometer data sets [ $\alpha$ -HgCrO<sub>4</sub>:  $P2_1/n$ ,  $Z = 4$ ,  $a = 5.5079(8)$ ,  $b = 8.5266(12)$ ,  $c = 7.3503(10)$  Å,  $\beta = 94.022(3)^\circ$ , 955 structure factors,  $R[F^2 > 2\sigma(F^2)] = 0.0296$ ;  $\beta$ -HgCrO<sub>4</sub>:  $Cmcm$ ,  $Z = 4$ ,  $a = 5.7187(9)$ ,  $b = 9.0169(14)$ ,  $c = 7.0114(11)$  Å, 361 structure factors,  $R[F^2 > 2\sigma(F^2)] = 0.0275$ ; HgCrO<sub>4</sub>·H<sub>2</sub>O:  $P\bar{1}$ ,  $Z = 2$ ,  $a = 5.6157(15)$ ,  $b = 6.1115(16)$ ,  $c = 7.590(2)$  Å,  $\alpha = 108.850(5)$ ,  $\beta = 91.666(5)$ ,  $\gamma = 116.569(5)^\circ$ , 1235 structure factors,  $R[F^2 > 2\sigma(F^2)] = 0.0316$ ]. The previously reported structure of  $\alpha$ -HgCrO<sub>4</sub> has been re-determined. It contains distorted [HgO<sub>7</sub>] pentagonal bipyramids in which the short bonds are directed towards the apices. The new polymorph  $\beta$ -HgCrO<sub>4</sub> adopts the CrVO<sub>4</sub> ( $\beta$ -CrPO<sub>4</sub>) structure type and is composed of slightly distorted [HgO<sub>6</sub>] octahedra. The previously unknown monohydrate HgCrO<sub>4</sub>·H<sub>2</sub>O crystallizes in a unique structure and is composed of one nearly regular [HgO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] octahedron and one considerably distorted [HgO<sub>6</sub>] octahedron. All three structures contain tetrahedral chromate anions CrO<sub>4</sub><sup>2-</sup> as the second building units with average Cr-O distances of ca. 1.65 Å.

*Key words:* Mercury(II), Chromates(VI), Crystal Structure, Hydrothermal Synthesis

## Introduction

Synthesis and crystal chemistry of mercury oxocompounds of group VI B elements (Cr, Mo, W) have attracted much attention in the past few years. For the corresponding molybdates(VI) the following compounds have been structurally characterized: HgMoO<sub>4</sub> [1], two modifications of Hg<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> [2, 3], Hg<sub>2</sub>Mo<sub>5</sub>O<sub>16</sub> [4], and two modifications of Hg<sub>2</sub>MoO<sub>4</sub> [5]. Representatives of tungstates(VI) are restricted to mercurous Hg<sub>2</sub>WO<sub>4</sub> [5] and mercuric HgWO<sub>4</sub> [6, 7]. Crystallographically well-characterized compounds in the system Hg-Cr-O-(H) include the mercury(II) chromates(VI) in the form of the double basic salt HgCrO<sub>4</sub>·2HgO [8], the neutral salt HgCrO<sub>4</sub> [9], the hemihydrate HgCrO<sub>4</sub>·1/2H<sub>2</sub>O [10], the spinel-type mercury(II) chromate(III) HgCr<sub>2</sub>O<sub>4</sub> [11], as well as the mineral *wattersite*, Hg<sub>5</sub>CrO<sub>6</sub> [12]. The latter compounds were synthesized either by solid state reactions (HgCrO<sub>4</sub>·2HgO and HgCr<sub>2</sub>O<sub>4</sub>), or by evap-

oration of aqueous solutions (HgCrO<sub>4</sub> and HgCrO<sub>4</sub>·1/2H<sub>2</sub>O). In the course of systematic investigations on hydrothermal phase formation of mercury sulfates(VI) [13], selenates(VI) [14] and tellurates(VI) [15], the related system Hg-Cr<sup>VI</sup>-O-(H) was re-investigated. The compounds obtained during that work are the subject of the present communication. Also given is a comparative discussion of the crystal structures of the obtained chromates and the corresponding sulfate and selenate compounds of the same formula type.

## Experimental Section

### Preparation

All chemicals used were of high purity. Freshly precipitated HgO, prepared by adding NaOH to an aqueous HgCl<sub>2</sub> solution, was reacted with CrO<sub>3</sub> under hydrothermal conditions at 200 °C for 4 days (Teflon-lined steel containers with 8 ml filling capacity). Representative experiments are given in Table 1. Obtained solid phases were filtered off, washed with mother liquor and an ethanol/acetone mixture. They

HgO [mg]	CrO <sub>3</sub> [mg]	H <sub>2</sub> O [ml]	HgO:CrO <sub>3</sub> ratio	Identified solid phases	Method and amount
317	52	3	3.0 : 1.0	HgCrO <sub>4</sub> · 2HgO, unknown phase	single crystal and powder powder (minor amounts)
1000	52	3	9.2 : 1.0	HgO, HgCrO <sub>4</sub> · 2HgO, unknown phase	powder single crystal and powder powder (minor amounts)
322	1061	3	1.0 : 7.1	HgCrO <sub>4</sub> · H <sub>2</sub> O, unknown phase	powder powder (minor amounts)
1015	1079	3	1.0 : 2.3	HgCrO <sub>4</sub> · 2HgO, HgCrO <sub>4</sub> · H <sub>2</sub> O, unknown phase	powder (main phase) powder and single crystal powder (minor amounts)
500	1500	1	1.0 : 6.5	$\alpha$ -HgCrO <sub>4</sub> , $\beta$ -HgCrO <sub>4</sub>	powder powder
500	1700	1	1.0 : 7.4	$\alpha$ -HgCrO <sub>4</sub> , $\beta$ -HgCrO <sub>4</sub>	single crystal single crystal

Table 1. Experimental parameters for hydrothermal crystal growth of HgO-CrO<sub>3</sub>-(H<sub>2</sub>O) phases.

Table 2. Details of data collection and structure refinement.

Compound	$\alpha$ -HgCrO <sub>4</sub>	$\beta$ -HgCrO <sub>4</sub>	HgCrO <sub>4</sub> · H <sub>2</sub> O
Temperature [°C]		- 22(1) -	
Crystal dimensions [mm]	0.030 × 0.024 × 0.012	0.036 × 0.030 × 0.015	0.036 × 0.024 × 0.012
Crystal colour; shape	dark orange; prism	yellow; plate	orange; fragment
Crystal system	monoclinic	orthorhombic	triclinic
Space group	$P2_1/n$	$Cmcm$	$P\bar{1}$
Formula units $Z$	4	4	2
$a$ [Å]	5.5079(8)	5.7187(9)	5.6157(15)
$b$ [Å]	8.5266(12)	9.0169(14)	6.1115(16)
$c$ [Å]	7.3503(10)	7.0114(11)	7.590(2)
$\alpha$ [°]	90	90	108.850(5)
$\beta$ [°]	94.022(3)	90	91.666(5)
$\gamma$ [°]	90	90	116.569(5)
$V$ [Å <sup>3</sup> ]	344.35(8)	361.54(10)	215.80(10)
$V/Z$ [Å <sup>3</sup> ]	86.09	90.39	107.90
Formula weight [g · mol <sup>-1</sup> ]	316.59	316.59	334.61
$\mu$ [mm <sup>-1</sup> ]	47.522	45.262	37.947
X-ray density [g · cm <sup>-3</sup> ]	6.107	5.816	5.150
Range $\theta_{\min} - \theta_{\max}$ [°]	3.66 - 29.49	4.22 - 31.96	2.90 - 30.03
Range $h$	-7 → 7	-7 → 8	-7 → 6
$k$	-11 → 11	-13 → 12	-8 → 8
$l$	-10 → 10	-10 → 10	-10 → 10
Measured reflections	3338	2178	2438
Independent reflections	955	361	1235
Obs. reflections [ $I > 2\sigma(I)$ ]	645	322	773
$R_i$	0.0654	0.0392	0.0515
Trans. Coef. $T_{\min}; T_{\max}$	0.3263; 0.6629	0.2173; 0.6797	0.3955; 0.7021
Number of parameters	55	21	67
Diff. elec. dens. max.; min [e <sup>-</sup> · Å <sup>-3</sup> ] ( $d$ [Å], atom)	1.61 (0.02, Hg); -1.27 (0.76, Cr)	1.42 (0.75, Hg) -2.69 (1.96, O2)	2.53 (1.47, O2); -1.31 (1.69, O4)
$R[F^2 > 2\sigma(F^2)]$	0.0296	0.0275	0.0316
$wR2(F^2 \text{ all})$	0.0398	0.0551	0.0625
Goof	0.720	1.155	0.822
CSD number	416148	416147	416146
Structure type	own type	CrVO <sub>4</sub> ( $\beta$ -CrPO <sub>4</sub> )	own type

were either investigated by single crystal and/or powder X-ray diffraction. HgCrO<sub>3</sub> · 2HgO crystallizes as red, mostly plate-like crystals, whereas HgCrO<sub>4</sub> · H<sub>2</sub>O crystallizes as orange blocks up to 1 mm in length,  $\beta$ -HgCrO<sub>4</sub> as small yellow rods, and  $\alpha$ -HgCrO<sub>4</sub> as dark orange prisms.

#### X-ray powder diffraction

Measurements of ground bulk products were performed on a Philips X'Pert Pro diffractometer system (Cu-K $\alpha_{1,2}$  radiation ( $\lambda = 1.54060, 1.54439$  Å), Bragg-Brentano ge-

Table 3. Atomic coordinates and isotropic displacement parameters [Å<sup>2</sup>].

Atom	Wyckoff Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
<b><math>\alpha</math>-HgCrO<sub>4</sub></b>					
Hg	4e	0.25251(7)	0.03660(5)	0.15817(6)	0.01983(10)
Cr	4e	0.2773(3)	0.18907(16)	0.6641(2)	0.0147(3)
O1	4e	0.4117(11)	0.3588(8)	0.6066(9)	0.0242(16)
O2	4e	0.4392(11)	0.1098(7)	0.8438(8)	0.0207(15)
O3	4e	0.2662(12)	0.0711(7)	0.4925(9)	0.0274(18)
O4	4e	0.0023(10)	0.2229(8)	0.7189(8)	0.0224(16)
<b><math>\beta</math>-HgCrO<sub>4</sub></b>					
Hg	4a	0	0	0	0.02036(14)
Cr	4c	0	0.3727(2)	1/4	0.0215(4)
O1	8f	0	0.2725(8)	0.0618(10)	0.0343(15)
O2	8g	0.254(2)	-0.0217(8)	1/4	0.055(3)
<b>HgCrO<sub>4</sub> · H<sub>2</sub>O</b>					
Hg1	1b	0	0	1/2	0.02009(17)
Hg2	1a	0	0	0	0.02245(18)
Cr	2i	0.6367(3)	0.2192(3)	0.3294(2)	0.0181(3)
O1	2i	0.2237(16)	0.5180(14)	0.7208(11)	0.0303(19)
O2	2i	0.2446(19)	0.4466(15)	0.0690(12)	0.042(2)
O3	2i	0.3348(16)	0.0125(15)	0.1945(12)	0.040(2)
O4	2i	0.6025(17)	0.2980(17)	0.5455(10)	0.037(2)
O5	2i	0.8431(16)	0.0667(14)	0.2922(9)	0.0236(16)

ometry, silicon single crystal sample holder, 5–70°/2 $\theta$ , 0.02°/step, 5 s/step).

#### Single crystal diffraction

Intensities of all single crystals were collected using the  $\omega$ -scan technique with 0.3° rotation width and 30 s exposure times per frame on a SMART APEX three-circle diffractometer (Bruker AXS; Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å) equipped with a CCD camera. Three independent sets of 600 frames were measured thus scanning the whole reciprocal sphere. The measured intensities were corrected for Lorentz and polarization effects and a numerical absorption correction was applied using the program HABITUS [16]. All crystal structures were solved by direct methods and refined with the SHELXTL program package [17]. In the last least-squares cycles 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 mercury positions. The hydrogen atoms in HgCrO<sub>4</sub> · H<sub>2</sub>O were not located. Further details of data collection and structure refinement are summarized in Table 2. Final atomic coordinates and equivalent isotropic displacement parameters are listed in Table 3, and selected interatomic distances, angles as well as bond-valence sums [18], using the parameters by Brese & O’Keeffe [19], are given in Table 4. Anisotropic displacement parameters are gathered in Table 5. Additional crystallographic information on all structures is available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, email:

crysdata@fiz-karlsruhe.de, by quoting the literature citation, the name of the authors and the depository number listed at the end of Table 2. Drawings of structural details were produced using the program ATOMS [20].

## Results and Discussion

### Preparation conditions

The hydrothermal formation of the different mercury(II) chromates(IV) from aqueous solutions depends primarily on the adjusted *pH*. While only slightly acidic solutions (*pH*  $\approx$  5) yield the double basic salt HgCrO<sub>4</sub> · 2HgO, moderate increase of the chromic acid concentration to *pH*  $\approx$  3 led also to a crystal growth of the monohydrate phase HgCrO<sub>4</sub> · H<sub>2</sub>O. Further decrease of the *pH* to  $\approx$  1 yields both forms of anhydrous HgCrO<sub>4</sub>. Under the chosen experimental conditions it was not possible to obtain single-phase products, which made it difficult to measure other physical properties of the bulk (thermal behaviour, vibrational spectroscopy *etc.*). Besides small amounts of yet unidentified microcrystalline products, mixtures of the chromates as listed in Table 1 were obtained in each run. It is noteworthy that under hydrothermal conditions no hemihydrate HgCrO<sub>4</sub> · 1/2H<sub>2</sub>O [10] was observed, whereas crystal growth experiments under slow evaporation of a mercury chromate solution (205 mg HgO and 205 mg CrO<sub>3</sub> dissolved in 10 ml H<sub>2</sub>O) yielded this compound as a single-phase product in form of large red crystals.

### Crystal structures

The crystal structure of the first modification of mercury(II) chromate(VI) was determined some years ago by Stålhandske [9], and is subsequently denoted as  **$\alpha$ -HgCrO<sub>4</sub>**. We decided to re-determine the crystal structure because the lattice parameters determined during our study (Table 2) are more disparate from

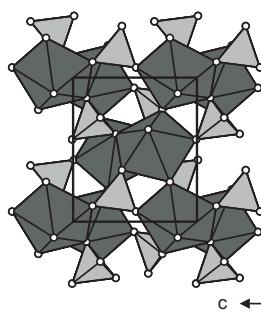


Fig. 1.  $\alpha$ -HgCrO<sub>4</sub>. Projection of the crystal structure along the *a*-axis. [HgO<sub>7</sub>] polyhedra are dark-grey, CrO<sub>4</sub> tetrahedra are light-grey.

$\alpha$ -HgCrO<sub>4</sub>

Hg	O1	2.089(6)	O1	Hg	O2	164.9(2)	O3	Cr	O4	108.7(3)
Hg	O2	2.108(6)	O1	Hg	O3	95.4(2)	O3	Cr	O2	110.6(3)
Hg	O3	2.471(6)	O2	Hg	O3	96.3(2)	O4	Cr	O2	109.2(3)
Hg	O4	2.492(6)	O1	Hg	O4	99.1(2)	O3	Cr	O1	109.4(3)
Hg	O1	2.581(6)	O2	Hg	O4	93.1(2)	O4	Cr	O1	110.0(3)
Hg	O2	2.668(6)	O3	Hg	O4	75.3(2)	O2	Cr	O1	108.8(3)
Hg	O4	2.804(6)	O1	Hg	O1	81.4(2)				
			O2	Hg	O1	83.5(2)				
Cr	O3	1.611(6)	O3	Hg	O1	143.6(2)				
Cr	O4	1.621(6)	O4	Hg	O1	141.1(2)				
Cr	O2	1.683(6)	O1	Hg	O2	98.0(2)				
Cr	O1	1.692(6)	O2	Hg	O2	76.9(2)				
	av.	1.652	O3	Hg	O2	147.86(19)				
			O4	Hg	O2	73.82(19)				
			O1	Hg	O2	67.7(2)				
			O1	Hg	O4	86.1(2)				
			O2	Hg	O4	87.5(2)				
			O3	Hg	O4	75.78(19)				
			O4	Hg	O4	150.95(4)				
			O1	Hg	O4	67.81(19)				
			O2	Hg	O4	134.08(18)				

BVS: Hg 2.38, Cr 5.90, O1 2.24, O2 2.04, O3 1.90, O4 1.84

 $\beta$ -HgCrO<sub>4</sub>

Hg	O2	2.286(8) 4×	O2	Hg	O2	180.0 2×	O1	Cr	O1	111.2(6) 2×
Hg	O1	2.495(7) 2×	O2	Hg	O2	101.0(5) 2×	O1	Cr	O2	108.5(2) 4×
			O2	Hg	O2	79.0(5) 2×				
Cr	O1	1.599(7) 2×	O2	Hg	O1	87.2(2) 4×				
Cr	O2	1.698(10) 2×	O2	Hg	O1	92.8(2) 4×				
	av.	1.649	O1	Hg	O1	180.0				

BVS: Hg 2.20, Cr 5.98, O1 1.94, O2 2.15

HgCrO<sub>4</sub> · H<sub>2</sub>O

Hg1	O5	2.021(7) 2×	O5	Hg1	O5	180.000(1)	O2	Hg2	O2	180.0(2)
Hg1	O1	2.702(7) 2×	O5	Hg1	O1	89.5(3) 2×	O2	Hg2	O3	91.9(3) 2×
Hg1	O4	2.983(9) 2×	O5	Hg1	O1	90.5(3) 2×	O2	Hg2	O3	88.1(3) 2×
Hg2	O2	2.300(8) 2×	O1	Hg1	O1	180.0(5)	O3	Hg2	O3	180.0(5)
Hg2	O3	2.314(7) 2×	O5	Hg1	O4	105.8(3) 2×	O2	Hg2	O5	87.8(3) 2×
Hg2	O5	2.390(7) 2×	O5	Hg1	O4	74.2(3) 2×	O2	Hg2	O5	92.2(3) 2×
			O1	Hg1	O4	66.1(2) 2×	O3	Hg2	O5	100.4(3) 2×
Cr	O4	1.597(7)	O1	Hg1	O4	113.9(2) 2×	O3	Hg2	O5	79.6(3) 2×
Cr	O1	1.621(8)	O4	Hg1	O4	180.000(1)	O5	Hg2	O5	180.0(4)
Cr	O3	1.633(8)								
Cr	O5	1.763(7)	O4	Cr	O1	109.5(4)	O4	Cr	O5	110.4(4)
	av.	1.654	O4	Cr	O3	107.9(5)	O1	Cr	O5	109.1(4)
			O1	Cr	O3	110.5(4)	O3	Cr	O5	109.3(4)
O2	O4	2.728(11)								
O2	O1	2.821(11)								

BVS (no hydrogen bonding considered):

Hg1 2.16, Hg2 2.26 Cr 5.93, O1 1.74, O2 0.41, O3 1.94, O4 1.77 O5 2.29

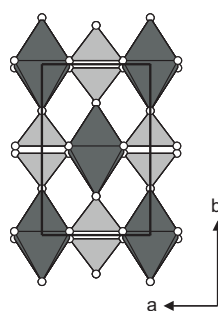
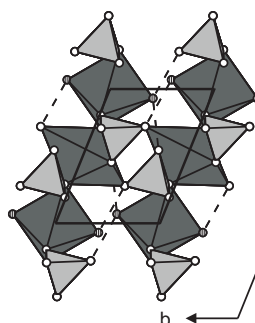
Table 4. Selected distances [Å], angles [°] and bond valence sums (BVS) [v.u.].

the original parameters of  $a = 7.342(1)$ ,  $b = 8.522(1)$ ,  $c = 5.202(1)$  Å,  $\beta = 94.00(2)^\circ$  than one is willing to accept (note that we used a different setting where  $a$  and  $c$  are interchanged). Since the given crystal volume of  $343.4$  Å<sup>3</sup> in [9] is not correct when calculated with the original lattice parameters (which results in  $V = 325.8$  Å<sup>3</sup>), and geometrical data in terms of distances and angles are very similar in both refine-

ments, it appears most likely that the lattice parameter  $c$  was misprinted in the original communication, and it should read  $5.502(1)$  Å instead.

Our refinement basically confirms Stålhandske's results, but provides a model with higher precision and with all atoms refined anisotropically. The Hg atom is almost linearly bonded ( $\angle$ O-Hg-O =  $164.9(2)^\circ$ ) to two O atoms at distances of *ca.* 2.10 Å. The coordi-

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
$\alpha$ -HgCrO <sub>4</sub>						
Hg	0.01661(17)	0.02246(19)	0.02023(18)	-0.0028(2)	-0.00006(12)	0.0030(2)
Cr	0.0138(8)	0.0174(8)	0.0129(7)	0.0021(7)	0.0009(6)	0.0005(7)
O1	0.019(4)	0.023(4)	0.030(4)	0.010(3)	-0.003(3)	-0.009(3)
O2	0.020(4)	0.018(4)	0.024(4)	0.003(3)	0.002(3)	0.002(3)
O3	0.033(4)	0.020(4)	0.029(4)	-0.003(3)	0.002(3)	-0.002(3)
O4	0.011(4)	0.030(4)	0.028(4)	-0.001(3)	0.009(3)	0.001(3)
$\beta$ -HgCrO <sub>4</sub>						
Hg	0.0215(2)	0.0252(2)	0.01439(19)	0.00026(17)	0	0
Cr	0.0273(10)	0.0168(8)	0.0204(8)	0	0	0
O1	0.038(4)	0.033(3)	0.032(3)	-0.012(3)	0	0
O2	0.097(8)	0.042(5)	0.027(4)	0	0	0.041(4)
HgCrO <sub>4</sub> · H <sub>2</sub> O						
Hg1	0.0214(4)	0.0270(4)	0.0194(3)	0.0122(3)	0.0048(3)	0.0154(3)
Hg2	0.0257(4)	0.0286(4)	0.0173(3)	0.0097(3)	0.0056(3)	0.0157(3)
Cr	0.0191(9)	0.0215(8)	0.0179(7)	0.0080(7)	0.0043(6)	0.0126(7)
O1	0.036(5)	0.028(4)	0.037(5)	0.016(4)	0.009(4)	0.021(4)
O2	0.060(6)	0.016(4)	0.037(5)	0.013(4)	0.000(4)	0.006(4)
O3	0.017(4)	0.028(4)	0.058(5)	0.002(4)	-0.018(4)	0.009(4)
O4	0.055(6)	0.052(5)	0.023(4)	0.013(4)	0.020(4)	0.042(5)
O5	0.036(5)	0.033(4)	0.014(3)	0.011(3)	0.008(3)	0.026(4)

Table 5. Anisotropic displacement parameters [ $\text{\AA}^2$ ].fl0Fig. 2.  $\beta$ -HgCrO<sub>4</sub>. Projection of the crystal structure along the  $c$ -axis. [HgO<sub>6</sub>] octahedra are dark-grey, CrO<sub>4</sub> tetrahedra are light-grey.Fig. 3. HgCrO<sub>4</sub> · H<sub>2</sub>O. Projection of the crystal structure along the  $a$ -axis. [Hg1O<sub>6</sub>] and Hg<sub>2</sub>O<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub> octahedra are dark-grey, CrO<sub>4</sub> tetrahedra are light-grey. O atoms of water molecules are represented as hatched spheres. Hydrogen bonding is indicated by dashed lines.

nation sphere around Hg is augmented by five more distant O atoms at distances ranging from 2.471(6) to 2.804(6) Å, which results in a distorted pentagonal bipyramid with the short bonds directed towards the apices. The chromate(VI) tetrahedron is slightly distorted from the ideal geometry, with Cr-O distances ranging from 1.611(6) to 1.692(6) Å. The unique structure of  $\alpha$ -HgCrO<sub>4</sub> can be considered as being built up from *zig-zag* chains of edge-sharing [HgO<sub>7</sub>] polyhedra that extend parallel to the  $a$  axis. Each chain is connected to four adjacent chains by corner-sharing into a three-dimensional framework. The structure is completed by Cr atoms residing in-between the mercury-oxygen nets (Fig. 1). An alternative description of the  $\alpha$ -HgCrO<sub>4</sub> structure, along with a comparative discussion of the crystal chemistry of other mercury chromates, has recently been given by Borisov *et al.* [21].

$\alpha$ -HgCrO<sub>4</sub> is not related to the isotypic salts HgSO<sub>4</sub> [22] and HgSeO<sub>4</sub> [14]. Their crystal structures (or-

thorhombic,  $Pmn2_1$ ) are based on [4 + 3]-oxygen coordinated Hg atoms and XO<sub>4</sub> tetrahedra sharing common edges and corners.

The second modification of mercury(II) chromate(VI), denoted as  $\beta$ -HgCrO<sub>4</sub>, exhibits a slightly lower density than the  $\alpha$ -form (90.39 Å<sup>3</sup> versus 86.09 Å<sup>3</sup> per formula unit) and adopts the CrVO<sub>4</sub> (often also referred to as  $\beta$ -CrPO<sub>4</sub>) structure type. A review on the preparation, crystal chemistry and physicochemical properties of materials belonging to this structure type has been given some years ago [23]. The crystal structure of  $\beta$ -CrPO<sub>4</sub> is displayed in Fig. 2 and is made up of <sup>1</sup><sub>∞</sub>[HgO<sub>4/2</sub>O<sub>2/1</sub>] chains of *trans* edge-sharing [HgO<sub>6</sub>] octahedra running parallel to the  $c$ -axis. These chains are catenated by corner-sharing to CrO<sub>4</sub> tetrahedra into a three-dimensional network. The [HgO<sub>6</sub>] octahedron exhibits two different Hg-O bond lengths. The equatorial bonds to the bridging atoms are shorter (2.286(8) Å) than the axial bonds to the ter-

minal O atoms (2.495(7) Å) of the chain. The shorter (1.599(7) Å) of the two different Cr-O bonds within the CrO<sub>4</sub> tetrahedron are directed to the terminal oxygen atoms of the  $^1_\infty[\text{HgO}_{4/2}\text{O}_{2/1}]$  chains whereas the longer bonds (1.698(10) Å) point to the bridging O atoms of the chain.

**HgCrO<sub>4</sub> · H<sub>2</sub>O** contains two crystallographically distinct Hg atoms, both located on an inversion centre, thus resulting in polyhedra around Hg with  $\bar{1}$  symmetry. The coordination by oxygen atoms for both Hg atoms is very different. Two co-linear short Hg-O bonds of 2.021(7) Å and four long bonds > 2.7 Å result in a considerably distorted octahedral coordination sphere for Hg1, whereas Hg2 exhibits a coordination polyhedron that deviates only slightly from the ideal octahedral geometry with similar Hg-O bond lengths between 2.3 and 2.4 Å. This also includes bonding to two *trans* water molecules (O2) which could unambiguously be assigned due to their low bond valence sum (Table 4).

By corner-sharing an O atom (O5), the [Hg1O<sub>6</sub>] and [Hg2O<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] octahedra form infinite chains which run along the *c*-axis. Medium strong hydrogen bonds between the water molecule and one oxygen atom of the neighbouring octahedron within the chain ( $d(\text{O2-O1}) = 2.821(11)$  Å) are also observed. Adjacent chains are linked together by CrO<sub>4</sub> tetrahedra, and additional hydrogen bonds between the water molecules and O atoms of CrO<sub>4</sub> tetrahedra stabilize this arrangement (Fig. 3). The scattering of the Cr-O contacts within the distorted CrO<sub>4</sub> tetrahedron is quite large and shows bond lengths ranging from 1.597(7) to 1.763(7) Å.

All monohydrates HgXO<sub>4</sub> · H<sub>2</sub>O (*X* = S (orthorhombic, *Pnma*) [24], Se (monoclinic, *P2<sub>1</sub>/c*) [25], Cr (tri-

clinic, *P $\bar{1}$* ) crystallize in their own structure types which differ basically in the formation of varying configurations of the mercury-oxygen chains. In the sulfate, edge-sharing [HgO<sub>5</sub>(H<sub>2</sub>O)] octahedra form  $^1_\infty[\text{HgO}_{4/2}\text{O}_{1/1}(\text{H}_2\text{O})_{1/1}]$  chains, whereas in the selenate  $^1_\infty[\text{HgO}_{4/2}(\text{H}_2\text{O})_{2/2}]$  chains are present which are built of corner-sharing [HgO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] octahedra with water molecules as bridging units.

In most mercuric oxocompounds, Hg atoms show a pronounced 2-coordination with two short Hg-O distances and a linear or roughly linear O-Hg-O angle. Thus, the commonly observed coordination polyhedra show considerably distorted [2 + *x*] coordination spheres, where *x* may range from 2 to 8, with *x* = 4 resulting in flattened octahedra as the most frequently observed coordination polyhedra. The [HgO<sub>6</sub>] octahedron in the structure of HgCrO<sub>4</sub> · H<sub>2</sub>O and the [HgO<sub>7</sub>] pentagonal bipyramid in  $\alpha$ -HgCrO<sub>4</sub> confirm these observations. For all these polyhedra, the tightly bonded oxygen atoms are situated at distances  $\leq 2.10$  Å and more remote oxygen atoms are observed at distances  $2.5 \text{ \AA} < d(\text{Hg}^{\text{II}}\text{-O})_{\text{long}} < 3.0 \text{ \AA}$ . The preference for a linear coordination has been discussed in review articles [26–28] and is attributed to relativistic effects that have a high impact on the crystal chemistry of mercury [29,30]. Only few mercuric oxocompounds show the rarely observed octahedral coordination with only slight distortions from the ideal geometry. As discussed above, this is realized for  $\beta$ -HgCrO<sub>4</sub> and the [HgO<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>] octahedron in HgCrO<sub>4</sub> · H<sub>2</sub>O. Other examples include HgAs<sub>2</sub>O<sub>6</sub> [31,32] and to some extent one [HgO<sub>6</sub>] octahedron in both Hg<sub>2</sub>Te<sub>2</sub>O<sub>7</sub> modifications [33], which might be explained by packing effects within the corresponding structures.

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