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# The Mixed-Metal Oxochromates(VI) $\text{Cd}(\text{Hg}^{\text{I}}_2)_2(\text{Hg}^{\text{II}})_3\text{O}_4(\text{CrO}_4)_2$ , $\text{Cd}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$ and $\text{Zn}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$ —Examples of the Different Crystal Chemistry within the Zinc Triad

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**Abstract:** The three mixed-metal oxochromates(VI)  $\text{Cd}(\text{Hg}^{\text{I}}_2)_2(\text{Hg}^{\text{II}})_3\text{O}_4(\text{CrO}_4)_2$ ,  $\text{Cd}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$ , and  $\text{Zn}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$  were grown under hydrothermal conditions. Their crystal structures were determined from single-crystal X-ray diffraction data. The crystal-chemical features of the respective metal cations are characterised, with a linear coordination for mercury atoms in oxidation states +I and +II, octahedral coordination spheres for the divalent zinc and cadmium cations and a tetrahedral configuration of the oxochromate(VI) anions. In the crystal structures the formation of two subunits is apparent, viz. a mercury-oxygen network and a network of cadmium (zinc) cations that are directly bound to the oxochromate(VI) anions. An alternative description of the crystal structures based on oxygen-centred polyhedra is also given.

**Keywords:** zinc; cadmium; mercury; oxochromates(VI); crystal chemistry; oxo-centred polyhedra

## 1. Introduction

The three elements of the zinc triad have a closed-shell  $nd^{10}(n+1)s^2$  electronic configuration with  $n = 3, 4,$  and  $5$  for zinc, cadmium, and mercury, respectively. In compounds of these elements with ionic or predominantly ionic character, zinc exclusively exhibits oxidation state +II, cadmium with very few exceptions has an oxidation state of +II ( $\text{Cd}_2(\text{AlCl}_4)_2$  being one of them with an oxidation state of +I [1,2]), whereas a multitude of mercuric (oxidation state +II), mercurous (oxidation state +I) and mixed-valent mercury compounds are known. The crystal-chemical features of all three elements are remarkably different. The most frequently observed coordination numbers for zinc in its compounds are 4, 5, and 6 with (distorted) tetrahedral, trigonal-bipyramidal, and octahedral coordination environments, respectively. The larger cadmium cation has a coordination number of four only in combination with larger anions (like in CdS), and in the majority of cases exhibits coordination numbers of six, or higher. For most of the latter cases, the coordination spheres are considerably distorted and difficult to derive from simple polyhedra. In many aspects, including structural characteristics, zinc and cadmium compounds resemble their alkaline earth congeners magnesium and calcium, respectively, which likewise have a closed shell electronic configuration. Mercury, on the other hand, is unique amongst all metals (*cf.* the low melting point) and has a peculiar crystal chemistry, showing a preference for linear coordination by more electronegative elements (coordination number of two). To a certain extent, these features can be related to relativistic effects that are pronounced for this element [3,4]. While a number of review articles devoted to the crystal chemistry of mercury have been published over the years [5–11], to the best of the author's knowledge, apart from chapters in a compendium on coordination chemistry [11,12], special reviews on the crystal chemistry of zinc or cadmium did not appear thus far.

During previous crystal growth experiments it was successfully shown that mixed-metal compounds of the zinc triad can be prepared under hydrothermal conditions in form of their sulfate or selenate salts, viz.  $\text{CdXO}_4(\text{HgO})_2$  ( $X = \text{S, Se}$ ) [13],  $(\text{MXO}_4)_2(\text{HgO})_2(\text{H}_2\text{O})$  ( $X = \text{S, Se}$ ;  $M = \text{Cd, Zn}$ ),  $\text{CdSeO}_4(\text{Hg}(\text{OH})_2)$ , and  $(\text{ZnSe}^{\text{IV}}\text{O}_3)(\text{ZnSe}^{\text{VI}}\text{O}_4)\text{Hg}^{\text{I}}_2(\text{OH})_2$  [14]. In the present study it was intended to replace the sulfate ( $\text{SO}_4^{2-}$ ) or selenate ( $\text{SeO}_4^{2-}$ ) anions with chromate anions ( $\text{CrO}_4^{2-}$ ) to search for new mixed-metal compounds of the zinc triad. Chromates, in particular, appeared to be promising candidates for formation of new compounds because they show pH-dependent chromate  $\rightleftharpoons$  dichromate equilibria and are able to stabilize different oxidation states for mercury. Mercurous chromates(VI) are scarce and known only for dimorphic  $\text{Hg}_2\text{CrO}_4$  [15] and  $\text{Hg}_6\text{Cr}_2\text{O}_9$  [16], whereas mercuric chromates are more frequent with structure determinations reported for dimorphic  $\text{HgCrO}_4$  [17,18], for  $\text{Hg}_3\text{O}_2\text{CrO}_4$  [19],  $\text{HgCr}_2\text{O}_7$  [20],  $\text{HgCrO}_4(\text{H}_2\text{O})_{0.5}$  [21], and  $\text{HgCrO}_4(\text{H}_2\text{O})$  [18]. In addition to these mercurous and mercuric chromates(VI), the mixed-valent  $\text{Hg}(\text{I}/\text{II})$  compounds  $(\text{Hg}^{\text{I}}_2)_2\text{O}(\text{CrO}_4)(\text{Hg}^{\text{II}}\text{O})$  (mineral name wattersite [22]) and  $\text{Hg}_6\text{Cr}_2\text{O}_{10}$  ( $=2\text{Hg}_2\text{CrO}_4 \cdot 2\text{HgO}$ ) [16] are also known. The two lead(II) mercury(II) chromates(VI)  $\text{Pb}_2\text{HgCrO}_6$  [23] and  $\text{Pb}_2(\text{Hg}_3\text{O}_4)(\text{CrO}_4)$  [24] served as a proof of concept that additional metal ions can be incorporated into mercury oxochromates(VI). Crystallographic data for zinc and cadmium chromates, on the other hand, are restricted to  $\text{CrVO}_4$ -type  $\text{ZnCrO}_4$  [25],  $\text{Zn}_2(\text{OH})_2\text{CrO}_4$  [26], and to dimorphic  $\text{CdCrO}_4$  (low-temperature form,  $Cmcm$ ; high-temperature form,  $C2/m$ ) and  $\text{Cd}_2\text{CrO}_5$  [27], respectively.

## 2. Results and Discussion

Three mixed-metal oxochromates(VI) were obtained under the given hydrothermal conditions, viz.  $\text{Cd}(\text{Hg}^{\text{I}}_2)_2(\text{Hg}^{\text{II}})_3\text{O}_4(\text{CrO}_4)_2$ ,  $\text{Cd}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$  and  $\text{Zn}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$ . Although the educt ratio  $\text{Hg}:\text{Cd}(\text{Zn}):\text{Cr}$  was 2:1:1, the ratio in the solid reaction products was different with a much higher mercury content, namely 7:1:2 for  $\text{Cd}(\text{Hg}^{\text{I}}_2)_2(\text{Hg}^{\text{II}})_3\text{O}_4(\text{CrO}_4)_2$ , 4:1:1 for  $\text{Cd}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$  and  $\text{Zn}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$ , and 5:0:1 for wattersite crystals. The formation of mixed-valent mercury(I,II) compounds, i.e., wattersite in both batches and  $\text{Cd}(\text{Hg}^{\text{I}}_2)_2(\text{Hg}^{\text{II}})_3\text{O}_4(\text{CrO}_4)_2$  in the cadmium-containing batch, indicates that complex redox equilibria between different mercury species ( $\text{Hg}(0) \rightleftharpoons \text{Hg}(\text{I}) \rightleftharpoons \text{Hg}(\text{II})$ ) must have been present under the chosen hydrothermal reaction conditions. Such redox equilibria are easily influenced by the presence of additional redox partners, here, for example  $\text{Cr}(\text{VI}) \rightleftharpoons \text{Cr}(\text{III})$ , and other interacting parameters like temperature, pressure, pH, concentration of the reactants, etc. Such a complex interplay between different adjustable parameters not only makes a prediction of solid products difficult, but can also lead to multi-phase formation and the presence of element species with different oxidation states in one batch. This kind of behaviour is not only exemplified by the three title compounds but also for other mixed-valent mercury oxocompounds that were obtained under similar hydrothermal conditions [16,28–30].

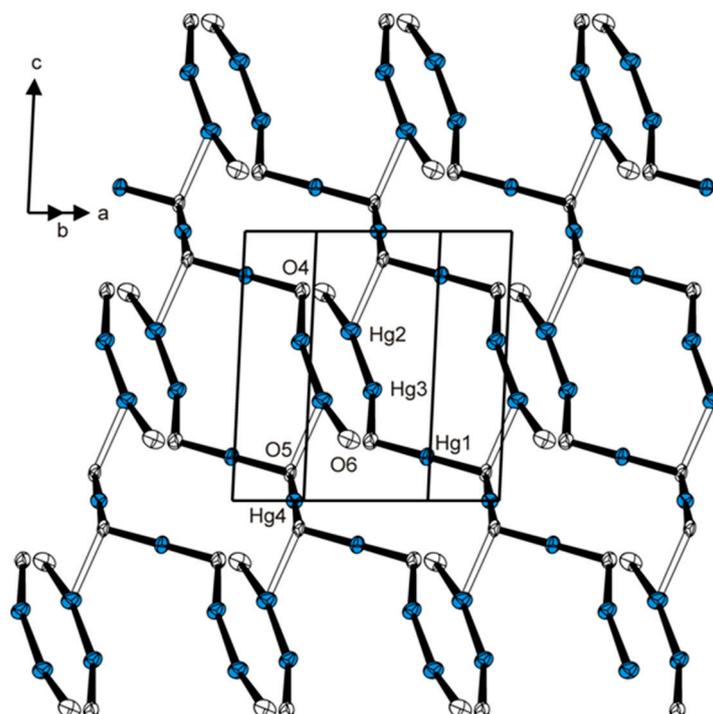
The strong preference for linear coordination of mercuric and mercurous cations is confirmed in the crystal structures of the three title compounds where O–Hg–O and/or Hg–Hg–O units with Hg–O bond lengths less than 2.2 Å are present. Representative bond lengths of the three title compounds are listed in Table 1.

**Table 1.** Selected bond lengths (Å) and angles (°).

$\text{Cd}(\text{Hg}^{\text{I}}_2)_2(\text{Hg}^{\text{II}})_3\text{O}_4(\text{CrO}_4)_2$			$\text{Zn}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$		
Hg1	O4	2.002(8)	Hg1	O3	2.030(7)
Hg1	O5	2.016(8)	Hg1	O4	2.045(6)
Hg1	O3	2.732(11)	Hg1	O8	2.703(7)
Hg1	O2	2.734(13)	Hg1	O1	2.805(8)
Hg2	O6	2.192(8)	Hg1	O4	2.819(7)
Hg2	O5	2.528(8)	Hg1	O7	2.840(7)
Hg2	Hg3	2.5301(6)	Hg2	O1	2.043(6)
Hg2	O4	2.692(9)	Hg2	O2	2.069(6)
Hg3	O4	2.098(8)	Hg2	O4	2.728(7)

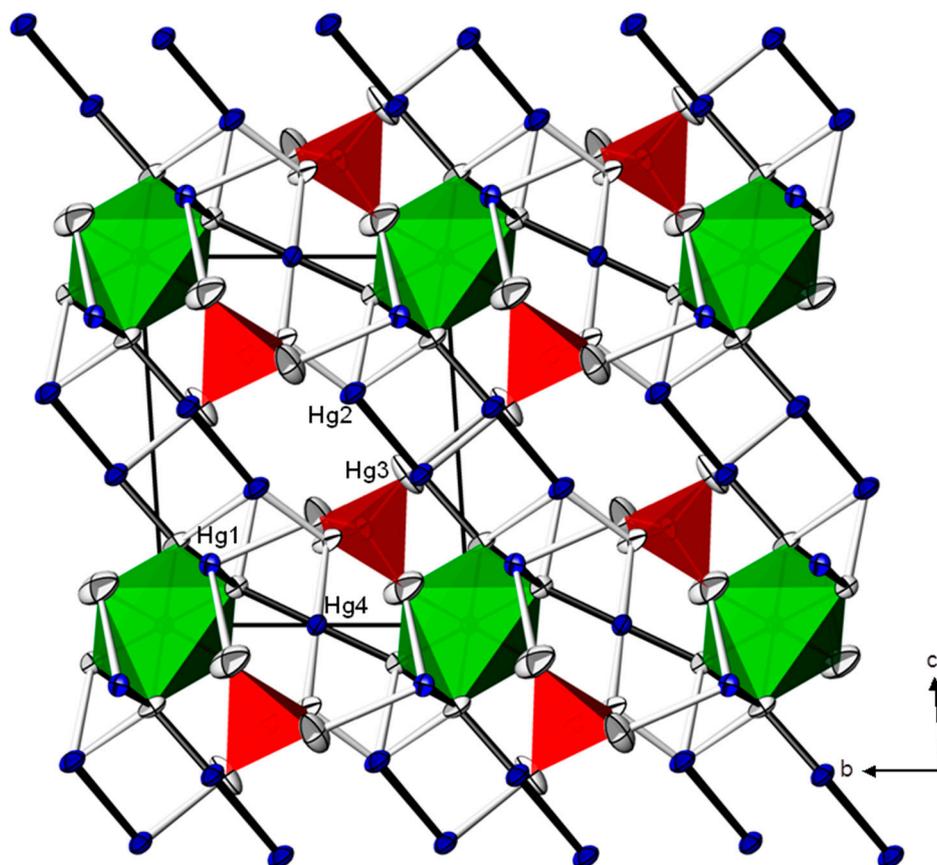


a distance of 2.002(8) and 2.016(8) Å with a nearly linear O4–Hg1–O5 angle of 175.2(3)°. Hg4, located on an inversion centre, shows two short distances of 2.037(8) Å to O5, and due to the symmetry restriction a linear O5–Hg4–O5(−x + 1, −y + 1, −z) angle. The Hg<sub>2</sub><sup>2+</sup> dumbbell exhibits a Hg2–Hg3 distance of 2.5301(6) Å, which is slightly above the arithmetic mean of 2.518(25) Å calculated for more than one hundred different Hg<sub>2</sub><sup>2+</sup> dumbbells that are present in crystal structures of various inorganic oxocompounds [30]. The two O atoms tightly bonded to the Hg2–Hg3 dumbbell have distances of Hg2–O6 = 2.192(8) Å and Hg3–O4 = 2.098(8) Å but only one of them has an arrangement approaching linearity with respect to the dumbbell (O6–Hg2–Hg3 = 165.6(2)°) while the other is virtually vertical to the dumbbell (O4–Hg2–Hg3 = 94.91(17)°). Under consideration of one longer Hg3–O5 bond of 2.528(8) Å, the mercuric and mercurous cations and the three oxygen sites O4–O6 are fused into strings with the composition {(Hg<sup>I</sup><sub>2</sub>)<sub>2</sub>(Hg<sup>II</sup>)<sub>3</sub>O<sub>6</sub>}<sup>2−</sup> that are aligned into sheets extending parallel to (01 $\bar{1}$ ) (Figure 1).



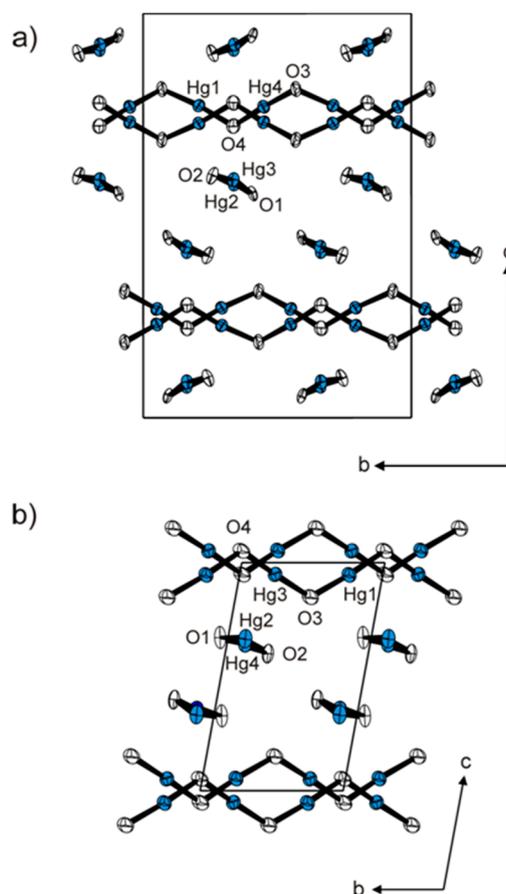
**Figure 1.** The Hg–O network in the structure of Cd(Hg<sup>I</sup><sub>2</sub>)<sub>2</sub>(Hg<sup>II</sup>)<sub>3</sub>O<sub>4</sub>(CrO<sub>4</sub>)<sub>2</sub> in a projection along  $[130]$ . Displacement ellipsoids are drawn at the 74% probability level. Short Hg–O bonds < 2.2 Å are given as solid lines, and longer Hg–O bonds as open lines.

The Cd<sup>2+</sup> cation (located on an inversion centre) and the Cr(VI) atom are situated between the sheets. They are bound to six and four oxygen sites in form of slightly distorted polyhedra with octahedral and tetrahedral configurations, respectively. The [CdO<sub>6</sub>] octahedron is flanked by two [CrO<sub>4</sub>] tetrahedra sharing two corner O atoms (O2 and its symmetry-related counterpart). The range of Cd–O bond lengths in the [CdO<sub>6</sub>] octahedron is narrow (2.252(7)–2.322(11) Å), with a mean of 2.29 Å; the corresponding values for the [CrO<sub>4</sub>] tetrahedron are 1.611(11)–1.677(8) and 1.65 Å, in good agreement with typical values for oxochromates(VI) comprising isolated [CrO<sub>4</sub>]<sup>2−</sup> anions (1.646(25) Å) [31]. By sharing some of the oxygen sites of the resulting {CdO<sub>4</sub>(CrO<sub>4</sub>)<sub>2</sub>} groups with the {(Hg<sup>I</sup><sub>2</sub>)<sub>2</sub>(Hg<sup>II</sup>)<sub>3</sub>O<sub>6</sub>} network and also by additional Hg–O interactions > 2.2 Å, the three-dimensional framework structure of Cd(Hg<sup>I</sup><sub>2</sub>)<sub>2</sub>(Hg<sup>II</sup>)<sub>3</sub>O<sub>4</sub>(CrO<sub>4</sub>)<sub>2</sub> is established (Figure 2).



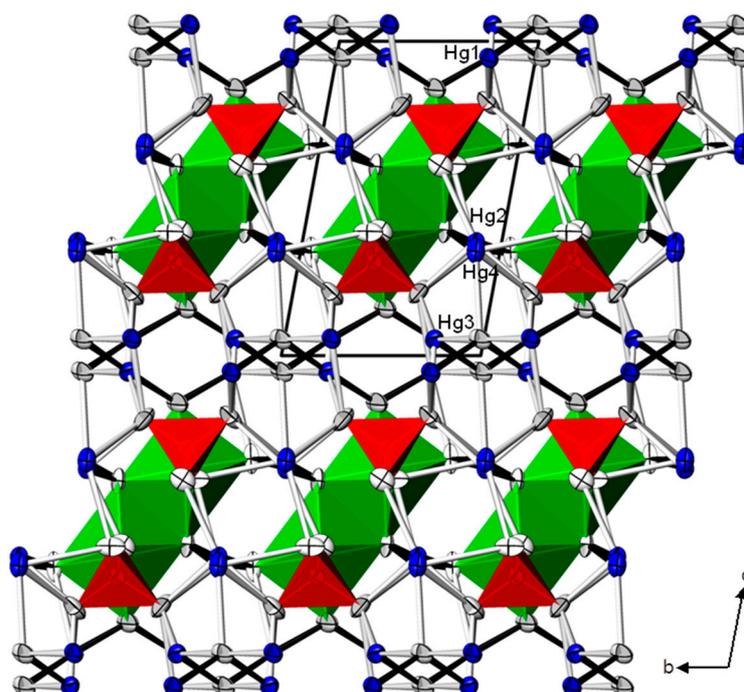
**Figure 2.** Crystal structure of  $\text{Cd}(\text{Hg}^{\text{I}})_2(\text{Hg}^{\text{II}})_3\text{O}_4(\text{CrO}_4)_2$  emphasizing the layered arrangement of the Hg–O network and the  $[\text{CdO}_6]$  (green) and  $\text{CrO}_4$  (red) polyhedra. Displacement ellipsoids are as in Figure 1.

The second cadmium-containing phase,  $\text{Cd}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$ , and the zinc-containing phase,  $\text{Zn}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$ , have the same formula type but are not isotypic. The cadmium compound shows orthorhombic symmetry (space group  $Pbca$ , eight formula units) whereas the symmetry of the zinc compound is triclinic (space group  $P\bar{1}$ , two formula units). Nevertheless, the general set-up of the two structures is very similar. Both structures contain two types of Hg–O chains defined by short Hg–O distances between 2.01 and 2.05 Å and more or less linear O–Hg–O angles ( $164$ – $177^\circ$ ). The Hg–O–Hg angles in all these chains are around  $120^\circ$ , thus defining a zigzag arrangement. In the  $\text{Cd}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$  structure one of the chains,  $[\text{Hg}4\text{–O}4\text{–Hg}1\text{–O}3]^\infty$ , runs parallel  $[010]$ , the other,  $[\text{Hg}3\text{–O}2\text{–Hg}2\text{–O}1]^\infty$ , runs parallel  $[100]$  (Figure 3a). In the  $\text{Zn}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$  structure the directions of propagation of the Hg–O chains are  $[100]$  for  $[\text{Hg}2\text{–O}1\text{–Hg}4\text{–O}2]^\infty$  and  $[110]$  for  $[\text{Hg}3\text{–O}4\text{–Hg}1\text{–O}3]^\infty$  (Figure 3b).

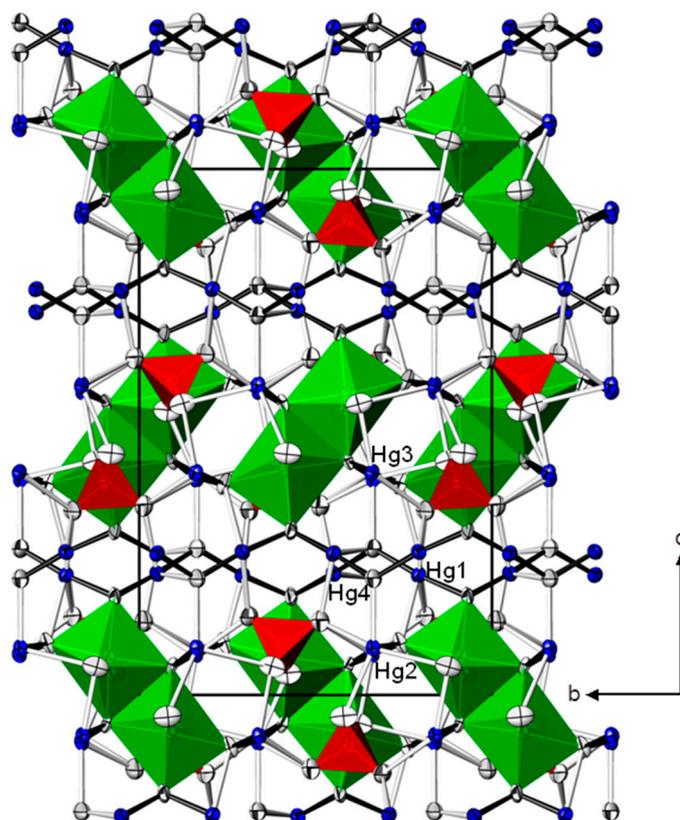


**Figure 3.** The two different Hg–O chains in the structures of (a) Cd(Hg<sup>II</sup>)<sub>4</sub>O<sub>4</sub>(CrO<sub>4</sub>) and (b) Zn(Hg<sup>II</sup>)<sub>4</sub>O<sub>4</sub>(CrO<sub>4</sub>). Displacement ellipsoids are drawn at the 90% probability level.

The Cd<sup>2+</sup> and Zn<sup>2+</sup> cations, respectively, are located between the Hg–O chains and have the function as bridging groups between adjacent Hg–O chains. Under consideration of other oxygen atoms (O5, O6) that are not part of the Hg–O chains, both metal sites have a distorted octahedral coordination environment. The Cd–O bond lengths are in a greater range than those of the [CdO<sub>6</sub>] octahedron in the structure of Cd(Hg<sup>I</sup>)<sub>2</sub>(Hg<sup>II</sup>)<sub>3</sub>O<sub>4</sub>(CrO<sub>4</sub>)<sub>2</sub>, 2.237(6)–2.421(6) Å, but have the same mean value of 2.29 Å. The Zn–O bond lengths in Zn(Hg<sup>II</sup>)<sub>4</sub>O<sub>4</sub>(CrO<sub>4</sub>) are expectedly shorter (2.045(8)–2.325(7) Å; mean 2.12 Å). In both *M*(Hg<sup>II</sup>)<sub>4</sub>O<sub>4</sub>(CrO<sub>4</sub>) structures (*M* = Cd, Zn) two [MO<sub>6</sub>] octahedra are fused via edge-sharing into a [M<sub>2</sub>O<sub>10</sub>] double octahedron. These double octahedra are aligned in layers parallel (001) and have the same orientation in each layer in the structure of Zn(Hg<sup>II</sup>)<sub>4</sub>O<sub>4</sub>(CrO<sub>4</sub>) (Figure 4), whereas their orientations alternate in the structure of Cd(Hg<sup>II</sup>)<sub>4</sub>O<sub>4</sub>(CrO<sub>4</sub>) due to the presence of the *a* glide plane (Figure 5).



**Figure 4.** The crystal structure of  $\text{Zn}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$ .  $[\text{CrO}_4]$  tetrahedra are red,  $[\text{ZnO}_6]$  octahedra are green. Displacement ellipsoids are as in Figure 3.

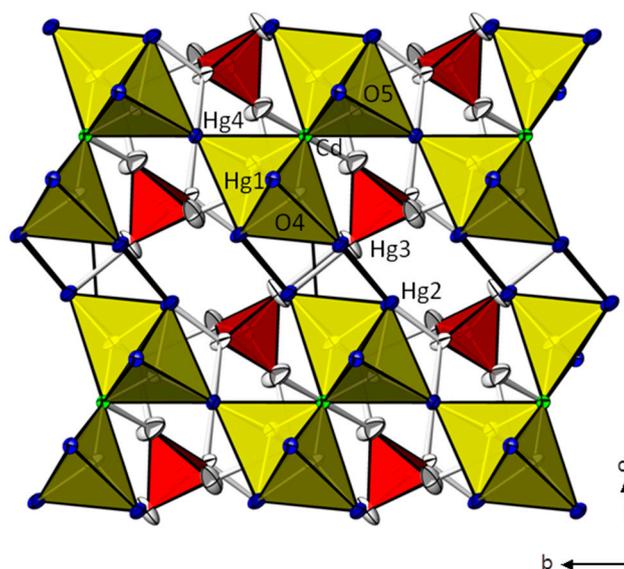


**Figure 5.** The crystal structure of  $\text{Cd}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$ .  $[\text{CrO}_4]$  tetrahedra are red, and  $[\text{CdO}_6]$  octahedra are green. Displacement ellipsoids are as in Figure 3.

The Cr(VI) atoms sit above and below the  $[M_2O_{10}]$  double octahedra and link them through two bridging vertex O atoms into “ $M\text{CrO}_4$ ” ( $M = \text{Cd}$  ( $\text{Zn}$ )) slabs extending parallel  $[100]$ . The structural characteristics of the tetrahedral  $[\text{CrO}_4]$  groups in the two structures follow the general trend [31] and in direct comparison show subtle differences. A somewhat greater distortion for the cadmium-containing structure (1.620(7)–1.658(7) Å, 108.8(4)–111.0(4)°) is observed compared to the zinc-containing structure (1.634(7)–1.657(6) Å, 108.5(4)–110.9(4)°).

The presence of two distinct structural subunits in each of the  $\text{Cd}(\text{Hg}^{\text{I}}_2)_2(\text{Hg}^{\text{II}})_3\text{O}_4(\text{CrO}_4)_2$  and  $M(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$  structures, viz., a mercury-oxygen network and cadmium/zinc cations bound directly to  $[\text{CrO}_4]^{2-}$  anions, allows to reformulate them as  $\{(\text{Hg}^{\text{I}}_2)_2(\text{Hg}^{\text{II}})_3\text{O}_4\}^{2+}\{\text{Cd}(\text{CrO}_4)_2\}^{2-}$  and  $M\text{CrO}_4 \cdot 4\text{HgO}$  ( $M = \text{Cd}, \text{Zn}$ ), respectively. The alternative formulae also emphasize the “basic” character (in an acid/base sense) of these compounds which is associated with the presence of oxygen atoms that are exclusively bonded to metal cations, here, those of mercury, cadmium (zinc), or mixtures thereof. Since these oxygen atoms do not belong to a chromate anion they are defined as “basic”. In the vast majority of cases, such “basic” oxygen atoms are surrounded by four metal cations in the form of distorted tetrahedra. Krivovichev and co-workers have resumed the use of such oxygen-centred  $[\text{OM}_4]$  tetrahedra for a rational structure description and classification of mineral and synthetic lead(II) oxo-compounds [32]. A general review of anion-centred  $[\text{OM}_4]$  tetrahedra in the structures of inorganic compounds with different metals  $M$  has been published some time ago, including  $[\text{OHg}_4]$  tetrahedra [33]. However, mixed  $[\text{OM}_4]$  tetrahedra with  $M = \text{Hg}$  and  $\text{Cd}$  or  $\text{Zn}$  are unknown so far.

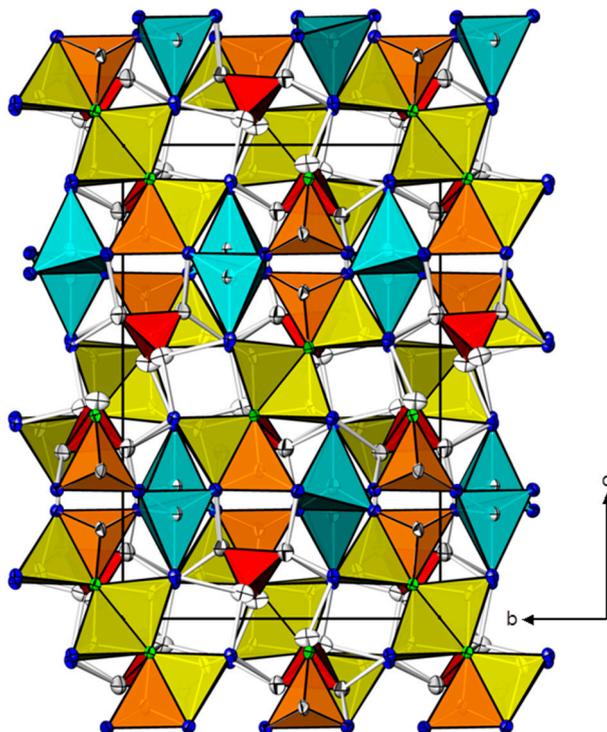
In the structure of  $\text{Cd}(\text{Hg}^{\text{I}}_2)_2(\text{Hg}^{\text{II}})_3\text{O}_4(\text{CrO}_4)_2$ , the “basic” oxygen atoms are represented by O4 and O5, both being bound to three mercury cations and one cadmium cation. The two types of  $[\text{OHg}_3\text{Cd}]$  tetrahedra are considerably distorted, with O–M distances between 2.002(8) and 2.692(9) Å and M–O–M angles ranging from 98.6(3) to 123.5(4)°. Based on the alternative description by using oxygen-centred polyhedra, the  $[\text{OHg}_3\text{Cd}]$  tetrahedra are linked through common edges (Cd–Hg2) and corners (Cd, Hg1, Hg4) into sheets with a width of two tetrahedra parallel (001). Adjacent sheets are connected along  $[001]$  through the Hg–Hg bond of the Hg2–Hg3 dumbbell. The remaining  $[\text{CrO}_4]$  tetrahedra are situated in the voids of this arrangement and connected to the “basic” metal-oxygen network through additional Cd–O and Hg–O bonds (Figure 6).



**Figure 6.** Crystal structure of  $\text{Cd}(\text{Hg}^{\text{I}}_2)_2(\text{Hg}^{\text{II}})_3\text{O}_4(\text{CrO}_4)_2$  using oxygen-centred  $[\text{OHg}_3\text{Cd}]$  tetrahedra (yellow) for visualisation. Displacement ellipsoids are as in Figure 1.

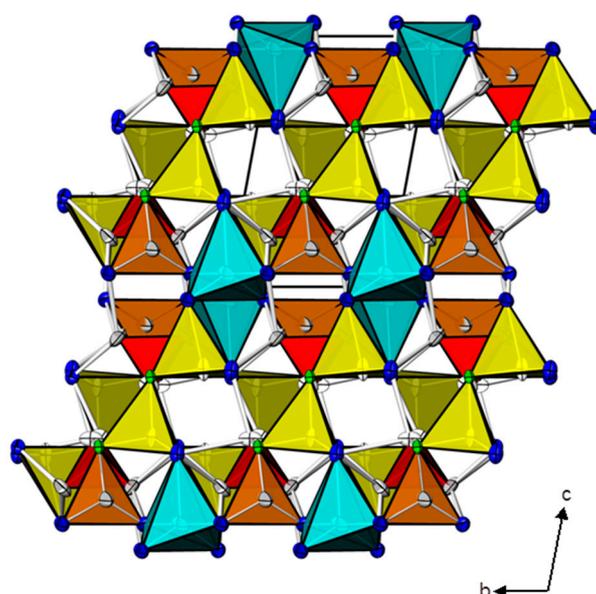
The “basic” O atoms in the crystal structures of  $\text{Cd}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$  and  $\text{Zn}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$  are atoms O1–O4. In the cadmium-containing structure, O1 is surrounded distorted tetrahedrally

by two  $\text{Hg}^{2+}$  and two  $\text{Cd}^{2+}$  cations (bond lengths range 2.045(7)–2.421(6) Å, bond angles range 96.3(2)–118.6(3)°),  $\text{O}_2$  from one  $\text{Cd}^{2+}$  and three  $\text{Hg}^{2+}$  cations (2.062(6)–2.667(6) Å; 88.8(2)–117.8(3)°) and  $\text{O}_4$  from four  $\text{Hg}^{2+}$  cations (2.014(7)–2.838(8) Å; 93.1(3)–122.2(3)°). With two  $\text{Hg}^{2+}$  and one  $\text{Cd}^{2+}$  cation,  $\text{O}_3$  has only three bonding partners (2.026(6)–2.237(6) Å; 107.9(3)–119.6(3)°) that form a distorted trigonal-pyramidal polyhedron. The different types of  $[\text{OM}_4]$  tetrahedra ( $M = \text{Hg}, \text{Cd}$ ) and the  $[\text{OHg}_2\text{Cd}]$  trigonal pyramid are linked by sharing vertices and edges into a three-dimensional framework. Like in the structure of  $\text{Cd}(\text{Hg}^{\text{I}})_2(\text{Hg}^{\text{II}})_3\text{O}_4(\text{CrO}_4)_2$ , the tetrahedral  $[\text{CrO}_4]$  groups in the  $\text{Cd}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$  structure are located in the voids of this arrangement and are connected with the framework through additional  $M\text{--O}$  bonds (Figure 7).



**Figure 7.** Crystal structure of  $\text{Cd}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$  using oxygen-centred tetrahedra for visualisation.  $[\text{OHg}_2\text{Cd}_2]$  and  $[\text{OHg}_3\text{Cd}]$  tetrahedra are yellow,  $[\text{OHg}_2\text{Cd}]$  trigonal pyramids are orange and  $[\text{OHg}_4]$  tetrahedra are turquoise. Displacement ellipsoids are as in Figure 3.

The above discussed similarities between the  $\text{Cd}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$  and  $\text{Zn}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$  crystal structures are also valid by using oxygen-centred polyhedra as an alternative description. The general structural set-up of  $\text{Zn}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$  is likewise accomplished by edge- and vertex-sharing of oxygen-centred polyhedra with  $[\text{CrO}_4]$  tetrahedra in the free space and completion of the cohesion through additional  $M\text{--O}$  bonds (Figure 8). However, one of the oxygen-centered polyhedra is distinctly different. While  $\text{O}_1$  and  $\text{O}_2$  are again surrounded tetrahedrally by  $\text{Hg}^{2+}$  and  $\text{Zn}^{2+}$  cations (2.009(6)–2.805(8) Å, 87.0(2)–123.8(3)°; 2.027(6)–2.325(7) Å, 98.8(3)–116.7(3)°), and  $\text{O}_3$  in the form of a trigonal pyramid by two  $\text{Hg}^{2+}$  and one  $\text{Zn}^{2+}$  cations (2.015(6)–2.045(8) Å, 112.5(3)–123.2(4)°),  $\text{O}_4$  has increased the number of Hg cations to which it is bound from four to five. The resulting coordination polyhedron is that of a distorted trigonal bipyramid, with the  $\tau_5$  index [34] being 0.90 [35]. The  $\text{O}_4\text{--Hg}_{\text{equatorial}}$  bond lengths and corresponding angles range between 2.024(6) and 2.728(7) Å and 117.8(3)–121.6(3)°, respectively; the  $\text{O}_4\text{--Hg}_{\text{axial}}$  bond lengths are 2.819(7) and 2.933(7) Å with an angle  $\text{Hg}_1\text{--O}_4\text{--Hg}_3$  of 175.5(2)°.



**Figure 8.** Crystal structure of  $\text{Zn(Hg}^{\text{II}}\text{)}_4\text{O}_4(\text{CrO}_4)$  using oxygen-centred tetrahedra for visualisation.  $[\text{OHg}_2\text{Cd}_2]$  and  $[\text{OHg}_3\text{Cd}]$  tetrahedra are yellow,  $[\text{OHg}_2\text{Cd}]$  trigonal pyramids are orange and  $[\text{OHg}_5]$  trigonal bipyramids are turquoise. Displacement ellipsoids are as in Figure 3.

Bond valence sums (BVS) [36], using the bond valence parameters of Brese and O’Keeffe [37], were calculated for the three structures. The results are reasonably close to the expected values (in valence sums) of 1 for mercurous Hg, 2 for mercuric Hg, 2 for Cd and Zn, 6 for Cr and 2 for O (Table 2). The global instability index GII was used as a measure of the extent to which the valence sum rule is violated [36]. The resultant GII values of 0.14 v.u. for  $\text{Cd(Hg}^{\text{I}}\text{)}_2(\text{Hg}^{\text{II}}\text{)}_3\text{O}_4(\text{CrO}_4)_2$ , 0.14 v.u. for  $\text{Cd(Hg}^{\text{II}}\text{)}_4\text{O}_4(\text{CrO}_4)$  and 0.11 v.u. for  $\text{Zn(Hg}^{\text{II}}\text{)}_4\text{O}_4(\text{CrO}_4)$  indicate stable structures with some lattice-induced strain [38].

**Table 2.** Results of bond valence calculations/valence units <sup>(1)</sup>.

<b><math>\text{Cd(Hg}^{\text{I}}\text{)}_2(\text{Hg}^{\text{II}}\text{)}_3\text{O}_4(\text{CrO}_4)_2</math></b>
Hg1 2.07, Hg2 1.03, Hg3 1.04, Hg4 2.05, Cd1 2.13, Cr1 5.99, O1 1.82 [2 Hg, 1 Cr], O2 1.87 [1 Hg, 1 Cd, 1 Cr], O3 1.75 [1 Hg, 1 Cr], O4 1.94 [3 Hg, 1 Cd], O5 2.29 [3 Hg, 1 Cd], O6 1.91 [1 Cr, 2 Hg].
<b><math>\text{Cd(Hg}^{\text{II}}\text{)}_4\text{O}_4(\text{CrO}_4)</math></b>
Hg1 2.13, Hg2 2.21, Hg3 2.13, Hg4 2.18, Cd1 2.12, Cr1 6.16, O1 2.21 [2 Hg, 2 Cd], O2 2.20 [3 Hg, Cd], O3 2.08 [2 Hg, Cd], O4 2.07 [4 Hg], O5 2.12 [Cr, Cd, 2 Hg], O6 2.02 [Cr, Cd, Hg], O7 1.97 [Cr, 3 Hg], O8 1.96 [Cr, 3 Hg].
<b><math>\text{Zn(Hg}^{\text{II}}\text{)}_4\text{O}_4(\text{CrO}_4)</math></b>
Hg1 2.12, Hg2 2.00, Hg3 2.11, Hg4 2.19, Zn1 1.99, Cr1 5.96, O1 2.20 [3 Hg, Zn], O2 2.18 [2 Hg, 2 Zn], O3 2.15 [2 Hg, Zn], O4 1.98 [5 Hg], O5 1.99 [Cr, Zn, 2 Hg], O6 1.94 [Cr, Zn, Hg], O7 1.98 [Cr, 4 Hg], O8 1.98 [Cr, 4 Hg].

(1) For oxygen atoms the type and number of atoms they are bound to are indicated in brackets.

### 3. Materials and Methods

#### 3.1. Preparation

For the hydrothermal experiments, Teflon containers with an inner volume of 5 mL were used. The metal oxides HgO, CrO<sub>3</sub> and ZnO (CdO), all purchased from Merck (Darmstadt, Germany), were used without further purification. 1 mmol HgO, 0.5 mmol CrO<sub>3</sub>, and 0.5 mmol ZnO (CdO) were mixed, placed in a Teflon container and poured with 3 mL water. The container was sealed with a Teflon lid, placed in a steel autoclave, heated at 215 °C for one week and cooled within 12 h to room temperature. In both cases (cadmium- and zinc-containing batches) the final supernatant

solution was colourless ( $\text{pH} \approx 8$ ), and the different crystal colours and forms indicated multi-phase formation. The solid reaction products were filtered off with a glass frit, washed with water, ethanol, and acetone and air-dried. In both the cadmium- and the zinc-containing batch, dark-red crystals of wattersite [22] were identified as the main product. In the cadmium-containing batch the two title compounds,  $\text{Cd}(\text{Hg}^{\text{I}})_2(\text{Hg}^{\text{II}})_3\text{O}_4(\text{CrO}_4)_2$  and  $\text{Cd}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$ , were obtained as dark-red rods and orange plates, respectively, in an estimated ratio of 1:2. In the zinc-containing batch, orange plates of  $\text{Zn}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$  could be isolated as a minor product.

### 3.2. Single Crystal X-ray Diffraction

Prior to the diffraction measurements, crystals were separated from wattersite crystals and checked for optical quality under a polarizing microscope. Selected crystals were fixed with superglue on the tip of thin silica glass fibres. Intensity data were measured at room temperature with Mo-K $\alpha$  radiation, using either a SMART CCD three-circle diffractometer (Bruker, Madison, WI, USA) or a CAD-4 four-circle diffractometer with kappa geometry (Nonius, Delft, The Netherlands). After data reduction, a numerical absorption correction was performed for each data set with the aid of the HABITUS program by optimizing the crystal shape [39]. The crystal structures were solved by Direct Methods [40] and were refined using SHELXL-97 [41].

Numerical details of the data collections and structure refinements are gathered in Table 3, selected bond lengths are given in Table 1. Structure graphics were produced with ATOMS [42]. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum (Karlsruhe, Eggenstein-Leopoldshafen, Germany, Fax: +49-7247-808-666; E-Mail: [crysdata@fiz-karlsruhe.de](mailto:crysdata@fiz-karlsruhe.de), <https://www.fiz-karlsruhe.de/>) on quoting the depository numbers listed at the end of Table 3.

**Table 3.** Details of data collections and structure refinements.

Compound	$\text{Cd}(\text{Hg}^{\text{I}})_2(\text{Hg}^{\text{II}})_3\text{O}_4(\text{CrO}_4)_2$	$\text{Cd}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$	$\text{Zn}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$
Diffractometer	Siemens SMART	Nonius CAD4	Siemens SMART
Formula weight	1812.53	1094.76	1047.73
Crystal dimensions/mm <sup>3</sup>	0.08 × 0.10 × 0.25	0.04 × 0.04 × 0.23	0.01 × 0.05 × 0.10
Crystal description	red, irregular fragment	orange, plate	yellow, plate
Space group	$P\bar{1}$	$Pbca$	$P\bar{1}$
Formula units Z	1	8	2
$a/\text{Å}$	6.1852(5)	6.9848(10)	6.873(3)
$b/\text{Å}$	7.3160(6)	12.8019(15)	6.928(3)
$c/\text{Å}$	8.5038(7)	19.227(3)	10.413(4)
$\alpha/^\circ$	85.5840(10)	90	89.725(7)
$\beta/^\circ$	87.2820(10)	90	70.903(7)
$\gamma/^\circ$	72.0160(10)	90	61.694(7)
$V/\text{Å}^3$	364.80(5)	1719.3(4)	405.7(3)
$\mu/\text{mm}^{-1}$	76.241	74.832	79.606
X-ray density/g·cm <sup>-3</sup>	8.250	8.459	8.576
Range $\theta_{\text{min}}-\theta_{\text{max}}/^\circ$	2.40–30.47	3.18–29.99	3.40–30.58
Range	$h$ −8 → 7	−9 → 9	−9 → 9
	$k$ −10 → 9	−17 → 17	−9 → 9
	$l$ −12 → 12	−27 → 27	−14 → 12
Measured reflections	4245	18,439	4655
Independent reflections	2177	2486	2408
Obs. reflections [ $I > 2\sigma(I)$ ]	2153	1772	1996
$R_i$	0.0450	0.0898	0.0431
Absorption correction		-HABITUS-	
Trans. coeff. $T_{\text{min}}/T_{\text{max}}$	0.004/0.055	0.1393/0.2185	0.0222/0.5407
Ext. coef. (SHELXL97)	0.0057(2)	0.000177(9)	0.00054(7)
Number of parameters	104	128	128
$\Delta e_{\text{max}}; \Delta e_{\text{max}}/e^- \cdot \text{Å}^{-3}$	2.10; −1.78	1.94, −1.94	2.50; −2.24
$R[F^2 > 2\sigma(F^2)]$	0.0336	0.0244	0.0284
$wR2(F^2 \text{ all})$	0.0727	0.0446	0.0570
Goof	1.304	1.021	0.925
CSD number	433,656	433,657	433,658

#### 4. Conclusions

During the present study it was shown that  $\text{SO}_4^{2-}$  or  $\text{SeO}_4^{2-}$  anions could be replaced with isovalent and isoconfigurational  $\text{CrO}_4^{2-}$  anions to prepare new mixed-metal oxocompounds of the zinc triad. The hydrothermally-grown crystals of  $\text{Cd}(\text{Hg}^{\text{I}})_2(\text{Hg}^{\text{II}})_3\text{O}_4(\text{CrO}_4)_2$ ,  $\text{Cd}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$ , and  $\text{Zn}(\text{Hg}^{\text{II}})_4\text{O}_4(\text{CrO}_4)$  each were obtained as minor reaction products in phase mixtures besides the mixed-valent mercury(I/II) compound  $(\text{Hg}_2)_2\text{O}(\text{CrO}_4)(\text{HgO})$  as the major product. All three compounds adopt unique structure types, with characteristic crystal-chemical features of the respective metal cations, namely a linear (or nearly) linear coordination of the  $\text{Hg}_2^{2+}$  and  $\text{Hg}^{2+}$  cations, a distorted octahedral coordination of the  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  cations, and a tetrahedral coordination of Cr in the oxochromate(VI) anions.

**Conflicts of Interest:** The authors declare no conflict of interest.

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