

Crystal chemistry of new descloizite-type compounds containing mercury

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Abstract: Up to date the only mercury-containing phase with a descloizite-type of structure was synthetic $\text{HgZn}(\text{OH})[\text{AsO}_4]$. During phase formation studies under hydrothermal conditions, six new synthetic phases with composition $\text{HgM}^{\text{II}}(\text{OH})[\text{AsO}_4]$ ($M^{\text{II}} = \text{Mg}, \text{Co}, \text{Ni}, \text{Cu}$) or $\text{HgM}^{\text{III}}(\text{O})[\text{AsO}_4]$ ($M^{\text{III}} = \text{Mn}, \text{Fe}$) could be obtained. All phases adopt the descloizite-type of structure, as revealed by crystal-structure analysis using single-crystal X-ray diffraction data (space group $Pnma$, $Z = 4$, $a \approx 7.8$, $b \approx 6.2$, $c \approx 8.6$ Å). Whereas the crystal structures of the Mg-, Co- and Ni-members show a high degree of similarity with the known Zn-member, the crystal structures of the Cu-, Mn- and Fe-members show much higher displacements of atoms relative to the Zn-member. In case of the Cu-member and to a minor extent in the Mn-member, this is ascribed to Jahn-Teller distortions of the $[\text{MO}_6]$ octahedra, and, in case of the Mn- and Fe-members, to missing hydrogen bonding interactions. The replacement of OH^- by an O^{2-} anion in the two $\text{HgM}^{\text{III}}(\text{O})[\text{AsO}_4]$ ($M^{\text{III}} = \text{Mn}, \text{Fe}$) structures is unprecedented for descloizite-type phases and represent rare examples where an $\text{OH}^- \rightarrow \text{O}^{2-}$ substitution does not change the adopted structure family and/or the space-group type.

Key-words: descloizite-adelite group; mercury; arsenates; crystal structure; crystal chemistry; structural similarity; isotypism.

1. Introduction

Descloizite is a rare mineral with idealized composition $\text{PbZn}(\text{OH})[\text{VO}_4]$ (Qurashi & Barnes, 1964; Hawthorne & Faggiani, 1979) named in honour of Alfred Des Cloizeaux, Professor of Mineralogy at the University of Paris. Since the large Pb^{II} cation, the smaller Zn^{II} cation and the tetrahedral orthovanadate group VO_4^{3-} can be replaced by ions and tetrahedral groups with similar sizes, numerous minerals and synthetic compounds with general formula $M1^{\text{I,II}}M2^{\text{II,III}}(\text{OH},\text{O})[\text{X}^{\text{V,VII}}(\text{O}_4,\text{O}_3\text{OH})]$ ($M1 = \text{Cd}^{\text{II}}, \text{Hg}^{\text{II}}, \text{Pb}^{\text{II}}, \text{Na}^{\text{I}}; M2 = \text{Mn}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}; X = \text{As}^{\text{V}}, \text{V}^{\text{V}}, \text{Mo}^{\text{VI}}$) are presently known to crystallize in the orthorhombic descloizite structure family in space-group type $Pnma$. A recent compilation of these compounds and their structures together with the relationship to the isoformular adelite (= $\text{CaMg}(\text{OH})[\text{AsO}_4]$) structure family (space-group type $P2_12_12_1$) has been given by Đorđević *et al.* (2016).

Only one of the descloizite-type members has been reported so far to contain mercury, viz. synthetic $\text{HgZn}(\text{OH})[\text{AsO}_4]$ (Weil, 2004a). To possibly expand the number of $\text{HgM}^{\text{II}}(\text{OH})[\text{AsO}_4]$ phases and to investigate which of the two structure types (descloizite or adelite) would eventually be adopted by corresponding phases, hydrothermal phase formation studies with other divalent metal cations and a similar ionic radius (Shannon, 1976) than that of Zn^{II} were started. Next to the size of the $M2$ cation in question, another precondition was the relative stability of precursor compounds in aqueous solution, ruling out divalent titanium,

vanadium and chromium. Eventually, $\text{Mg}^{\text{II}}, \text{Mn}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}$, and Cu^{II} were chosen as appropriate cations for the experiments.

The results of these investigations and a comparative discussion of the resulting crystal structures with the first member (= Zn) of the $\text{HgM}^{\text{II}}(\text{OH})[\text{AsO}_4]$ series, with the eponymous descloizite structure (Hawthorne & Faggiani, 1979), and with related mineral families are reported in this article.

2. Experimental

2.1. Preparation

Hydrothermal phase formation studies were conducted in a similar fashion as described for $\text{HgZn}(\text{OH})[\text{AsO}_4]$ (Weil, 2004a). The corresponding metal nitrates, $\text{Hg}(\text{NO}_3)_2(\text{H}_2\text{O})$ or HgO , and Na_2HAsO_4 were mixed in the molar ratio 1:1:1 (overall load about 300 mg) and placed in a Teflon container that was subsequently filled up to two-thirds of its volume with water (ca. 6 mL). After sealing with a Teflon lid, the container was placed in a steel autoclave and heated at 220 °C for five to ten days. In case of the Fe-batch, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ was used as the iron(II) source. An alternative route was also applied for a Co-batch. Here 200 mg of the amorphous product that was obtained by reaction of an aqueous suspension of CoCO_3 with half-concentrated H_3AsO_4 (ca. 40 wt%) was mixed with 180 mg HgO and treated hydrothermally in the same way as described above.

After reaction time, the solid material was filtered off, washed with mother liquor, water and ethanol and dried in a flow of air. All batches resulted in multi-phase products as revealed by optical microscopy. Dependent on the batch, mercury droplets were present next to polycrystalline material and crystals with different forms and colours. Single crystals were manually selected and their unit cells determined by single-crystal X-ray diffraction. The bulk material was investigated by X-ray powder diffraction measurements.

2.2. X-ray diffraction and single-crystal structure analysis

Ground bulk samples were characterized at room temperature by X-ray powder diffraction on a PanAlytical X'Pert Pro diffractometer (Bragg-Brentano geometry, Cu $K\alpha_{1,2}$ radiation (1.54060 Å, 1.54439 Å), using an X'Celerator multi-channel detector that was recently calibrated with a LaB₆ NIST standard.

The quality of single crystals was pre-checked under a polarising microscope. Suitable crystals were mounted on the tip of thin glass fibres and fixed with epoxy glue. Diffraction data were measured at room temperature with high redundancy either on a Siemens SMART-CCD three-circle diffractometer or on a Bruker APEX-II CCD four-circle diffractometer, both equipped with Mo $K\alpha$ radiation (Bruker, 2013). Correction of absorption effects were performed with the semi-empirical multi-scan method using SADABS (Krause *et al.*, 2015) or numerically with the program HABITUS (Herrendorf, 1993). For all six data sets the indexation procedure resulted in primitive orthorhombic cells with lattice parameters similar to those of HgZn(OH)[AsO₄] (Weil, 2004a). Likewise, inspection of reflection conditions revealed space-group type *Pnma* for all measurements thus indicating descloizite-type structures. The current refinements and descriptions of the six descloizite-type structures relate to the standard setting of space group type *Pnma* (No. 62) that has also been used for structure analysis of the eponymous structure of descloizite, PbZn(OH)[VO₄] (Hawthorne & Faggiani, 1979), and the mercury-containing member HgZn(OH)[AsO₄] (Weil, 2004a). Note that alternative settings of this space-group type in the setting *Pnam* were used by Đorđević *et al.* (2016) for better comparison between descloizite- and adelite-type structures. For standardisation of all structures reported herein, the atomic coordinates and labelling of HgZn(OH)[AsO₄] were used as starting parameters for refinement with the SHELXL program (Sheldrick, 2008). For the crystal structures of the Co-, Cu-, Mg- and Zn-members, hydrogen atom positions of the hydroxyl group were discernible from difference Fourier maps. The H atoms were refined with restraints on the O–H bond length using a value of 0.85(1) Å. For the Fe- and Mn-structures, difference Fourier maps did not indicate the presence of H atoms, thus revealing the presence of an oxidic group instead of a hydroxyl group.

It has to be noted that the crystal qualities of the two HgM^{III}2(O)[AsO₄] phases were much poorer compared with those of the HgM^{II}2(OH)[AsO₄] phases. This became noticeable, for example, in high R_{int} values (Table 1) and

displacement parameters for some oxygen atoms that deviate from being spherical. However, structure refinements of the HgM^{III}2(O)[AsO₄] phases in space-group types with lower symmetry than *Pnma* did not achieve any improvements.

Details of the data collections and structure refinements are listed in Table 1. Selected bond lengths and angles are collated in Table 2. Further details of the crystal-structure investigations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (e-mail: crysdata@fiz-karlsruhe.de, <https://www.fiz-karlsruhe.de/en/leistungen/kristallographie/icsd.html>) on quoting the appropriate CSD number listed at the end of Table 1.

Bond valence calculations (Brown, 2002) were performed by using the parameters provided by Brese & O'Keeffe (1991) to verify the derived oxidation states of the metal cations, *i.e.* +II for the hydroxyl compounds HgM^{II}2(OH)[AsO₄] (M^{II} = Co, Cu, Mg, Ni) and +III for the oxidic compounds HgM^{III}2(O)[AsO₄] (M^{III} = Fe, Mn). Results are compiled in Table 3. Drawings of structural details were produced with the program ATOMS (Dowty, 2008).

3. Discussion

3.1. Preparation

From all batches, descloizite-type phases containing mercury could be isolated in form of single crystals, but only as minor by-products. Structure analysis revealed that four of them show the same formula type HgM^{II}2(OH)[AsO₄] (M^{II} = Mg, Co, Ni, Cu) and have retained their oxidation states for M^{II} , whereas for the Mn- and Fe-members an oxidation to trivalent M^{III} was observed, resulting in phases with composition HgM^{III}2(O)[AsO₄], *i.e.* without the presence of a hydroxyl group.

Other phases obtained after hydrothermal treatment were graphtonite-type Hg₃(AsO₄)₂ (Larsson *et al.*, 1993) as the main phase in all batches, sometimes accompanied by recrystallized HgO, HgAs₂O₆ (Mormann & Jeitschko, 2000; Weil, 2000), α -(Hg₂)₃(AsO₄)₂ or β -(Hg₂)₃(AsO₄)₂ (Weil, 2004b), the mixed-valent mercury(I,II) phase Hg₆As₂O₁₀ (Weil, 2014), the cluster cationic phase (Hg₃)₃(AsO₄)₄ (Wessels *et al.*, 1997), and droplets of mercury. Dependent on the type of metal, other phases identified by single-crystal X-ray diffraction included the basic arsenates Mg_{6.75}(OH)₃(H_{0.166}AsO₄)₃(HAsO₄) (Weil, 2013), Co₂(AsO₄)(OH) (Riffel *et al.*, 1975), Co_{6.75}(OH)₃(H_{0.166}AsO₄)₃(HAsO₄) (Hughes *et al.*, 2003), Ni_{6.49}(OH)₃(H_{0.34}AsO₄)₃(HAsO₄) (Hughes *et al.*, 2003), Ni₅(AsO₄)₂(OH)₄ (Barbier, 1996), and Mn₅(H₂O)₄(AsO₃(OH))₂(AsO₄)₂ (Kampf, 2009). For all batches, the X-ray powder diffraction pattern of the respective bulk material revealed additional reflections that could not be assigned to phases mentioned above or to any other known phases deposited in the Powder Diffraction File (Faber & Fawcett, 2002).

Multi-phase formation is rather common as a result of hydrothermal preparation methods. Apart from various reaction parameters (temperature, pressure, concentration,

Table 1. Details of data collections and structure refinements.

Compound	HgMg(OH)[AsO ₄]	HgMn(O)[AsO ₄]	HgFe(O)[AsO ₄]	HgCo(OH)[AsO ₄]	HgNi(OH)[AsO ₄]	HgCu(OH)[AsO ₄]
M_R	380.83	410.45	411.36	415.45	415.23	420.06
Temp./°C	23	23	23	23	23	23
Radiation; $\lambda/\text{\AA}$			– Mo $K\alpha$; 0.71073 –			
Diffractometer	SMART CCD	APEXII CCD	APEXII CCD	APEXII CCD	SMART CCD	APEXII CCD
Crystal size/ μm^3	60 × 20 × 10	40 × 10 × 10	60 × 10 × 10	80 × 40 × 20	120 × 40 × 30	70 × 60 × 20
Crystal colour; form	Colourless; pinacoid	Red-brown; needle	Red-brown; lath	Brownish; plate	Green; needle	Green-blue; platy
Space group, no.	<i>Pnma</i> , 62	<i>Pnma</i> , 62	<i>Pnma</i> , 62	<i>Pnma</i> , 62	<i>Pnma</i> , 62	<i>Pnma</i> , 62
<i>Z</i>	4	4	4	4	4	4
<i>a</i> / $\text{\AA}$	7.7172 (4)	8.121 (4)	8.025 (2)	7.6793 (12)	7.63250 (10)	7.7336 (9)
<i>b</i> / $\text{\AA}$	6.2282(3)	6.129 (3)	6.1411 (16)	6.2766 (9)	6.17710 (10)	6.1867 (8)
<i>c</i> / $\text{\AA}$	8.6295(5)	8.435 (4)	8.484 (2)	8.6312 (12)	8.6147 (2)	8.5418 (10)
<i>V</i> / $\text{\AA}^3$	414.77(4)	419.9 (3)	418.13 (19)	416.02 (11)	406.155 (13)	408.69 (9)
μ/mm^{-1}	45.083	47.256	47.902	48.645	50.378	50.663
X-ray density/g cm ^{−3}	6.099	6.493	6.535	6.633	6.791	6.827
Range $\theta_{\min} - \theta_{\max}$	3.54–32.71	3.48–28.03	3.49–38.04	3.55–39.84	3.57–40.085	3.55–40.23
Range						
<i>h</i>	−11 → 11	−10 → 10	−13 → 13	−13 → 11	−13 → 12	−12 → 14
<i>k</i>	−9 → 9	−8 → 8	−10 → 10	−11 → 11	−10 → 10	−11 → 11
<i>l</i>	−12 → 13	−11 → 11	−14 → 14	−15 → 15	−15 → 15	−15 → 15
Meas. reflections	6575	16094	20388	35817	8164	18083
Indep. reflections	804	555	1206	1358	1316	1361
Obs. reflections	702	422	876	1071	1082	1196
[$I > 2\sigma(I)$]						
R_i	0.0412	0.1988	0.1200	0.1027	0.0385	0.0593
Absorption corr.	HABITUS	SADABS	HABITUS	HABITUS	SADABS	SADABS
Transm. coeff. $T_{\min}$; $T_{\max}$	0.225; 0.641	0.534; 0.746	0.220; 0.745	0.121; 0.458	0.062; 0.279	0.037; 0.328
Parameters	48	46	47	49	49	49
Ext. coef. (SHELXL97)	–	–	0.00167 (13)	0.00093 (11)	0.00062 (17)	0.0019 (3)
Diff. elec. dens. max; min/e [−] $\text{\AA}^{-3}$ (dist./ $\text{\AA}$, atom)	1.66 (0.09, Hg); −1.32 (0.93, O4)	2.15 (0.85, O3); −3.22 (0.97, O3)	3.37 (0.53, Hg1); −3.62 (0.04, Hg1)	2.11 (0.25, Hg1); −1.68 (0.61, Hg1)	2.60 (0.77, Hg1); −2.13 (0.34, Hg1)	3.41 (0.66, Hg1); −1.84 (0.97, Hg1)
$R[F^2 > 2\sigma(F^2)]$	0.0180	0.0377	0.0265	0.0186	0.0251	0.0226
$wR2(F^2 \text{ all})$	0.0306	0.0822	0.0526	0.0330	0.0502	0.0589
Goof	0.934	1.120	0.899	0.914	1.035	1.087
CSD number	1856567	1856565	1856566	1856569	1856568	1856570

Table 2. Selected bond lengths/Å, angles/° with estimated standard deviations in parentheses.

HgMg(OH)[AsO ₄]					HgMn(O)[AsO ₄]					HgFe(O)[AsO ₄]				
Mg1	–	O4	2.031 (2)	2x	Mn1	–	O4	1.904 (8)	2x	Fe1	–	O4	1.947 (3)	2x
	–	O1	2.087 (2)	2x		–	O1	1.980 (9)	2x		–	O1	2.040 (3)	2x
	–	O3	2.109 (2)	2x		–	O3	2.156 (8)	2x		–	O3	2.092 (3)	2x
		∅	2.07				∅	2.01				∅	2.03	
Hg1	–	O2	2.078 (3)		Hg1	–	O2	2.016 (13)		Hg1	–	O4	2.038 (4)	
	–	O4	2.104 (3)			–	O4	2.056 (13)			–	O2	2.043 (4)	
	–	O1	2.628 (2)	2x		–	O1	2.744 (9)	2x		–	O1	2.684 (3)	2x
	–	O1	2.765 (2)	2x		–	O1	2.853 (9)	2x		–	O1	2.893 (3)	2x
	–	O3	2.799 (3)				∅	2.54				∅	2.54	
		∅	2.54				∅	2.54				∅	2.54	
As1	–	O1	1.681 (2)	2x	As1	–	O1	1.690 (9)	2x	As1	–	O1	1.681 (3)	2x
	–	O3	1.697 (3)			–	O3	1.692 (12)			–	O2	1.686 (4)	
	–	O2	1.715 (3)			–	O2	1.694 (14)			–	O3	1.708 (4)	
		∅	1.69				∅	1.69				∅	1.69	
O2–Hg1–O4			161.68 (13)		O2–Hg1–O4			172.8 (6)		O2–Hg1–O4			175.61 (19)	
HgCo(OH)[AsO ₄]					HgNi(OH)[AsO ₄]					HgCu(OH)[AsO ₄]				
Co1	–	O4	2.0501 (16)	2x	Ni1	–	O4	2.012 (2)	2x	Cu1	–	O4	1.9524 (16)	2x
	–	O1	2.0919 (18)	2x		–	O1	2.075 (2)	2x		–	O1	1.987 (2)	2x
	–	O3	2.1263 (18)	2x		–	O3	2.096 (2)	2x		–	O3	2.348 (2)	2x
		∅	2.09				∅	2.06				∅	2.10	
Hg1	–	O2	2.093 (3)		Hg1	–	O2	2.106 (4)		Hg1	–	O4	2.156 (3)	
	–	O4	2.099 (3)			–	O4	2.121 (3)			–	O3	2.305 (3)	
	–	O1	2.6342 (19)	2x		–	O1	2.584 (2)	2x		–	O2	2.355 (4)	
	–	O3	2.753 (3)			–	O1	2.730 (2)	2x		–	O1	2.652 (2)	2x
	–	O1	2.761 (2)	2x		–	O3	2.766 (4)			–	O1	2.687 (2)	2x
		∅	2.53				∅	2.52				∅	2.50	
As1	–	O1	1.6812 (18)	2x	As1	–	O1	1.682 (2)	2x	As1	–	O2	1.678 (3)	
	–	O3	1.698 (3)			–	O3	1.702 (3)			–	O1	1.689 (2)	2x
	–	O2	1.715 (3)			–	O2	1.709 (4)			–	O3	1.692 (3)	
		∅	1.69				∅	1.69				∅	1.69	
O2–Hg1–O4			160.35 (10)		O2–Hg1–O4			161.68 (13)		O2–Hg1–O4			141.75 (10)	

Table 3. Calculation of bond valence sums/v.u.

<i>M</i>	Mg	Mn	Fe	Co	Ni	Cu
Hg	2.13	2.12	2.12	2.12	2.12	1.98
<i>M2</i>						
Considered as <i>M</i> ^{II}	2.14	3.41	2.76	2.06	2.01	2.16
Considered as <i>M</i> ^{III}	–	3.14	2.95	2.13	2.60	–
As	4.88	4.90	4.94	4.88	4.88	4.96
O1	1.89	2.00	1.95	1.89	1.89	1.97
O2	1.90	2.11	2.07	1.87	1.87	1.63
O3	1.96	1.91	1.99	1.94	1.92	1.96
O4						
Considered with H	2.24	–	–	2.21	2.17	2.30
Considered without H	1.56	2.15	2.04	1.59	1.55	1.40

pH, *etc.*) that could have an impact on solubility products and product formation, different redox equilibria must particularly be considered. For example, mercury can exist in aqueous solution in form of the mercuric cation Hg^{II}, in form of the mercurous dumbbell (Hg₂)²⁺ and in form of the cluster cation (Hg₃)⁴⁺, as shown for preparation of (Hg₃)₃(PO₄)₄ (Weil & Glaum, 2001) and (Hg₃)₃(AsO₄)₄ (Wessels *et al.*, 1997). The underlying equilibria Hg²⁺_(aq) + Hg⁰_(l) ⇌ (Hg₂)²⁺_(aq); (Hg₂)²⁺_(aq) + Hg²⁺_(aq) ⇌ (Hg₃)⁴⁺_(aq) and also the solubility products of corresponding phases can be influenced by various parameters defined above or,

in particular, by the presence of additional redox partners. In the current formation studies of mercury-containing descloizite phases, this involves first-row transition metal cations that (could) act as reducing agents. Starting from mercuric and divalent transition metal sources, this explains the presence of reduced mercury phases (elementary mercury, mercurous (Hg₂)₃(AsO₄)₂, mixed-valent Hg₆As₂O₁₀ and (Hg₃)₃(AsO₄)₄) and also of oxidized transition metal phases (HgFe(O)[AsO₄] and HgMn(O)[AsO₄]) where the oxidation state of Fe and Mn has changed from +II to +III. Unfortunately, such interdependent redox equilibria and the high number of adjustable reaction parameters that need to be considered for hydrothermal reaction conditions make the (reproducible) formation of a single-phase product very difficult.

The formation of the two HgM^{III}2(O)[AsO₄] members (*M*^{III} = Mn, Fe), *i.e.* containing a trivalent metal and without an OH group, is unprecedented in descloizite-type compounds. Whereas the absence of the H atom is difficult to prove unambiguously for such highly absorbing crystals on the basis of X-ray diffraction methods alone¹, the results of bond-valence calculations clearly revealed a trivalent oxidation state for the Mn and Fe members (Table 3), and

¹ $\mu \approx 50 \text{ mm}^{-1}$. Note that the H atom could nevertheless be located from difference Fourier maps for all HgM²⁺2(OH)[AsO₄] structures.

a divalent oxidation state for all $M2$ cations in the series comprising hydroxyl groups.

3.2. Crystal structures and crystal chemistry

The descloizite-type structures of the six title compounds are made up from edge-sharing $[M2(OH)_2O_4]$ octahedra for OH^- -bearing compounds ($M = Mg, Co, Ni, Cu$) or $[M2O_6]$ octahedra for the Fe- and Mn-members, forming infinite chains parallel to $[010]$. The chains are linked by $[AsO_4]$ tetrahedra through common corners into a three-dimensional framework structure. The crystal structures of $HgM2^{II}(OH)[AsO_4]$, $HgM2^{III}(O)[AsO_4]$ and $HgCu(OH)[AsO_4]$ are displayed in Figs. 1a–1c.

The divalent mercury cations are situated in the voids of this arrangement. With the exception of the Cu-member, they show the characteristic (pseudo)linear coordination by two shortly bonded O atoms (Breitinger, 2004; Weil *et al.*, 2005), here with variations of the $O2-Hg-O4$ angles between 160° and 176° . For the Cu-member a more pronounced bending of the $O2-Hg-O4$ angle is observed with 142° . In the corresponding $[HgO_2]$ group, one O atom ($O2$) belongs also to an arsenate group and the other ($O4$) to an OH^- group or an oxidic O atom for the $HgM2^{II}(OH)[AsO_4]$ members or the two $HgM2^{III}(O)[AsO_4]$ members, respectively. The distorted coordination spheres of the mercury cations in the two types of structures are completed by additional O atoms (four O atoms for $HgM2^{III}(O)[AsO_4]$ structures and five for $HgM2^{II}(OH)[AsO_4]$ structures) with remote $Hg-O$ distances ranging between 2.6 and 2.9 Å, and with very similar average $Hg-O$ distances for each of the six structures (Table 2). The corresponding coordination polyhedra around the divalent mercury cations are difficult to derive from simple geometric shapes. They might be best described as distorted octahedra for the $[2 + 4]$ coordination sets with the two shortly bound O atoms in axial positions, and as monocapped octahedra for the $[2 + 5]$ coordination sets, likewise with the axial positions occupied by the shortly bonded O atoms. In comparison with the two Cd-compounds adopting the descloizite structure type, *viz.* $CdCo(OH)(AsO_4)$ and $CdCu(OH)(AsO_4)$ (Đorđević *et al.*, 2016), and with the structure of descloizite itself (Hawthorne & Faggiani, 1979), the average $Hg-O$ distances in the title structures (≈ 2.53 Å; Table 2) are intermediate between the average $Cd-O$ (2.44 Å; $Cd-O$ range: 2.16–2.64 Å) and the average $Pb-O$ distances (2.61 Å, $Pb-O$ range: 2.44–2.73 Å), reflecting the different ionic radii of the three cations, *viz.* $Cd^{II} = 0.95$ Å, $Hg^{II} = 1.02$ Å, $Pb^{II} = 1.19$ Å (all values for CN = 6; Shannon, 1976).

The $[M2O_6]$ octahedra in all mercury-containing descloizite structures are more or less distorted, depending on the central metal cation. For a quantitative measure of the distortion, the mean quadratic elongation parameter Δ_{oct} was calculated for each structure according to the formula introduced by Robinson *et al.* (1971) and is as follows (values multiplied by 10^3): Mg = 1.52; Mn = 16.5; Fe = 5.26; Co = 1.33; Ni = 1.80; Cu = 43.7; Zn = 2.13. The low values for the Mg-, Co-, Ni- and Zn-members indicate a small distortion, whereas for the Fe-member a slightly higher

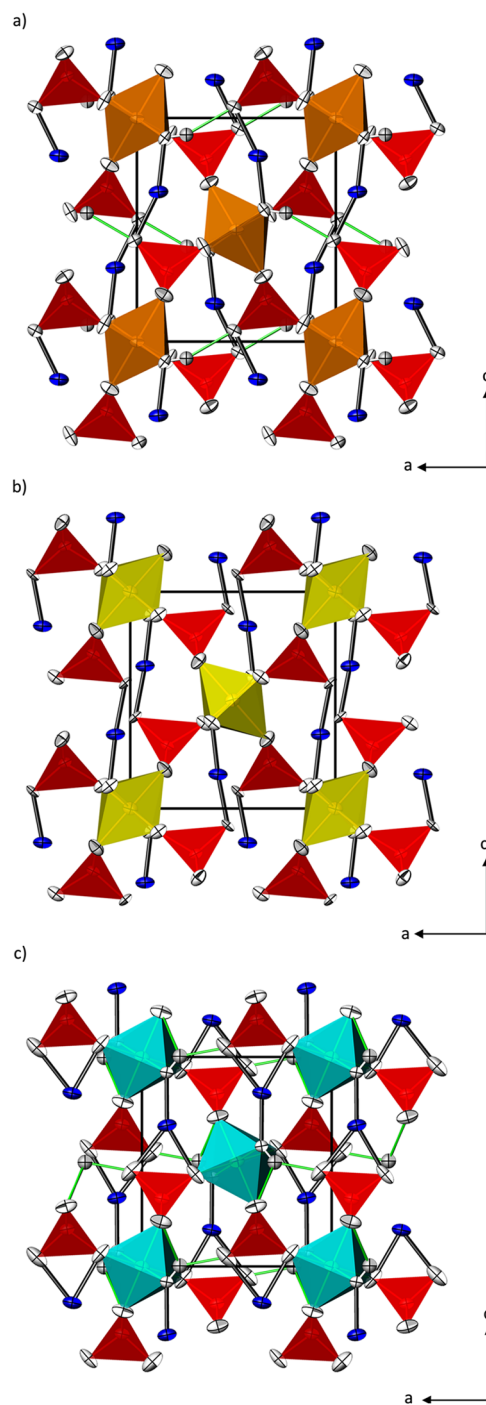


Fig. 1. (a) Representative for the crystal structures of $HgM2^{II}(OH)[AsO_4]$ ($M^{II} = Mg, Co, Ni, Zn$) compounds, the Co-member is given in a projection along $[010]$. Displacement ellipsoids are drawn at the 97% probability level; Hg atoms are blue, $[AsO_4]$ tetrahedra are red, octahedra around $M2^{II}$ are orange, and $O-H\cdots O$ hydrogen bonds are displayed in green. For clarity, only strong $Hg-O$ bonds < 2.4 Å are shown. (b) Representative for the crystal structures of $HgM2^{III}(O)[AsO_4]$ ($M^{III} = Mn, Fe$) compounds, the Fe-member is given in a projection along $[010]$. Displacement ellipsoids and colour codes are as in (a), except octahedra around $M2^{III}$ that are yellow. (c) The crystal structure of $HgCu(OH)[AsO_4]$ in a projection along $[010]$. Displacement ellipsoids and colour codes are as in (a), except octahedra around Cu^{II} that are turquoise.

distortion is observed that, to a much greater extent, is obvious for the Mn- and in particular for the Cu-member. In general, Mn^{III} and Cu^{II} cations have $3d^4$ and $3d^9$ electronic configurations, respectively, and exhibit a strong Jahn-Teller effect (Norrestam, 1994; Foley *et al.*, 1997) that becomes manifest in a significant distortion of the coordination sphere. In the majority of cases a [4 + 2] distribution with four short (equatorial) and two longer (axial) metal-ligand bonds results. The same kind of [4 + 2] distortion is also observed for the $[M2O_6]$ octahedra in $HgMn(O)(AsO_4)$ and $HgCu(OH)(AsO_4)$.

The $[AsO_4]$ tetrahedra in all mercury-containing descloizite structures are rather regular, indicated by the small quadratic elongation parameters Δ_{tet} (Robinson *et al.*, 1971; values multiplied by 10^3): Mg = 0.27; Mn = 0.01; Fe = 0.17; Co = 0.27; Ni = 0.20; Cu = 0.04; Zn = 0.22. The average As–O bond length in each of the structures is 1.69 Å, in very good agreement with the average value of 1.687 Å determined for numerous tetrahedral arsenate groups (Gagné & Hawthorne, 2018).

In both $HgM2^{II}(OH)[AsO_4]$ and $HgM2^{III}(O)[AsO_4]$ structures, the coordination numbers of O1 and O2 and the types of bonding partners are the same, *i.e.* four bonding partners for O1 (one As, one M2 and two Hg atoms at longer distances) and two for O2 (one As, one Hg at short distances). O4 has four coordination partners in the OH-bearing structure (one H, one Hg at short distances and two M2) and three in the other structure, due to omission of the H atom. Likewise, O3 reduces its coordination number from four in the $HgM2^{II}(OH)(AsO_4)$ structures, where it is bonded to one As, two M2 and one Hg atoms, to three in the $HgM2^{III}(O)(AsO_4)$ structures, where a significant Hg–O interaction is missing, thus reducing the overall coordination number of the Hg^{II} atom in these structures from 7 to 6 as discussed above.

According to the O4...O2 donor...acceptor distances, the hydrogen bonding interactions in the $HgM2^{II}(OH)[AsO_4]$ structures are of medium to weak strengths. In the structures of the Mg-, Co-, Ni- (and Zn)-members, the acceptor atom O2 is approximately 2.95 Å away from the donor O4 atom and shows the longest of all As–O distances with an O4–H1...O2 angle of about 160° (Table 4). In the structure of the Cu-member, acceptor atom O2 is situated much closer to the donor atom (2.64 Å) but with a more bent O4–H1...O2 angle of 140°. With respect to the arsenate tetrahedron, this atom now has the shortest As–O bond but also a considerably longer Hg–O bond (2.36 Å) in comparison with the other $HgM2^{II}(OH)[AsO_4]$ structures. In addition to acceptor atom O2, two O1 acceptor atoms are also in the vicinity of the hydroxyl group to be considered as relevant for hydrogen bonding in $HgCu(OH)(AsO_4)$ (2.84 Å; O4–H1...O2 = 112°), revealing an overall trifurcated hydrogen bond in this structure.

3.3. Structural similarities between descloizite, $HgM^{II}(OH)[AsO_4]$ (M^{II} = Mg, Co, Ni, Cu) and $HgM^{III}(O)[AsO_4]$ (M^{III} = Mn, Fe) phases

For a quantitative comparison of the $HgM2^{II}(OH)[AsO_4]$ (M^{II} = Mg, Co, Ni, Cu) and $HgM2^{III}(O)[AsO_4]$ ($M2^{III}$ = Mn,

Table 4. Details of the hydrogen bonding geometry/Å, ° in the $HgM2^{II}(OH)[AsO_4]$ crystal structures.

D	H	A	D–H	H...A	D...A	D–H...A	
$HgMg(OH)[AsO_4]$							
O4	H1	O2	0.85(1)	2.20(2)	2.999(5)	157(5)	
$HgCo(OH)[AsO_4]$							
O4	H1	O2	0.85(1)	2.127(18)	2.933(4)	158(4)	
$HgNi(OH)[AsO_4]$							
O4	H1	O2	0.85(1)	2.090(17)	2.918(5)	165(6)	
$HgCu(OH)[AsO_4]$							
O4	H1	O2	0.85(1)	1.93(4)	2.639(4)	140(5)	
O4	H1	O1	0.85(1)	2.41(4)	2.841(3)	112(4)	2x

Fe) structures with that of descloizite (Hawthorne & Faggiani, 1979) and with that of the first described mercury-containing phase, $HgZn(OH)[AsO_4]$ (Weil, 2004a), the program *compstru* (de la Flor *et al.*, 2016) available at the Bilbao Crystallographic Server (Aroyo *et al.*, 2006) was used. Numerical details of the comparisons are collated in Table 5. With respect to the descloizite structure, the degree of lattice distortion (≈ 0.044), the arithmetic mean of atomic displacements (≈ 0.4 Å) and the Δ value for the measure of similarity (≈ 0.33) are the highest for the two $HgM2^{III}(O)[AsO_4]$ (M^{III} = Mn, Fe) structures. As discussed above, the missing hydrogen bonding interactions in the two structures have a significant impact on structural details but do not lead to a change of the structure type or the symmetry relative to that of descloizite. The three values are much lower for the $HgM2^{II}(OH)[AsO_4]$ (M^{II} = Mg, Co, Ni, Cu, Zn) compounds, with similar values for each of the structures (degree of lattice distortion ≈ 0.033 ; arithmetic mean of atomic displacements ≈ 0.17 Å; Δ value for the measure of similarity ≈ 0.12). On average, the highest atomic displacements are observed for atoms O2 and O4 that considerably move towards the Hg^{II} cation to which they are much shorter bonded compared to their coordination to the Pb^{II} cation in descloizite.

The comparison of the $HgM2^{II}(OH)[AsO_4]$ (M^{II} = Mg, Co, Ni, Cu) and $HgM2^{III}(O)[AsO_4]$ (M^{III} = Mn, Fe) structures with that of $HgZn(OH)[AsO_4]$ shows, as expected, a high similarity between the Mg-, Co-, Ni- and Zn-members, as indicated by the very low values for the degree of lattice distortion (≈ 0.002), the arithmetic mean of atomic displacements (≈ 0.03 Å) and the Δ value for the measure of similarity (≈ 0.015). All these values increase significantly for the Jahn-Teller affected Cu-member, in particular for the arithmetic mean of atomic displacements that raises to a value of 0.23 Å. Here the highest individual displacement is observed for atom O3 (0.42 Å) that, owing to the Jahn-Teller distortion of the $[CuO_6]$ octahedron, defines the tetragonally elongated axial Cu–O bonds. Again, the two $HgM2^{III}(O)[AsO_4]$ (M^{III} = Mn, Fe) structures show the lowest similarity relative to $HgZn(OH)[AsO_4]$, however with somewhat lower values for the degree of lattice distortion (≈ 0.018), the arithmetic mean of atomic displacements (≈ 0.30 Å) and the Δ value for the measure of similarity (≈ 0.21) in the relation with the structure of descloizite.

Table 5. Numerical details from the comparison of the crystal structures of PbZn(OH)[VO₄] (descloizite) and HgZn(OH)[AsO₄] with its HgM^{II}(OH)[AsO₄] and HgM^{III}(O)[AsO₄] analogues using the *compstru* program (de la Flor *et al.*, 2016).

M2	Mg	Mn	Fe	Co	Ni	Cu	Zn
PbZn(OH)[VO ₄] (descloizite) versus HgM ^{II} (OH)[AsO ₄] or HgM ^{III} (O)[AsO ₄]							
Atom, atomic displacement u /Å							
Zn/M1	0	0	0	0	0	0	0
Pb/Hg1	0.1832	0.4397	0.4620	0.1665	0.1615	0.0361	0.1547
V/As1	0.1632	0.3750	0.4215	0.1326	0.1347	0.2342	0.1172
O1	0.1215	0.3767	0.4136	0.1075	0.0946	0.2197	0.0940
O2	0.4410	0.5056	0.5129	0.4265	0.4117	0.4018	0.4302
O3	0.2287	0.5357	0.5225	0.1964	0.2223	0.2431	0.1693
O4	0.2323	0.4788	0.4963	0.2338	0.2038	0.4018	0.2217
Degree of lattice distortion (S)	0.0335	0.0462	0.0426	0.0339	0.0331	0.0370	0.0318
Arithmetic mean (<i>d</i> _{av})	0.1864	0.3860	0.4053	0.1714	0.1654	0.1877	0.1601
Measure of similarity (Δ)	0.132	0.346	0.310	0.109	0.114	0.156	0.109
HgZn(OH)[AsO ₄] versus HgM ^{II} (OH)[AsO ₄] or HgM ^{III} (O)[AsO ₄]							
Atom, atomic displacement u /Å							
Zn/M1	0	0	0	0	0	0	0
Hg1	0.0285	0.2857	0.3070	0.0135	0.0096	0.1753	
As1	0.0625	0.3135	0.3510	0.0315	0.0426	0.3268	
O1	0.0553	0.3392	0.3723	0.0290	0.0454	0.2521	
O2	0.0625	0.3567	0.4015	0.0253	0.0362	0.3133	
O3	0.0590	0.3685	0.3492	0.0270	0.0527	0.4118	
O4	0.0172	0.3359	0.3200	0.0127	0.0188	0.1344	
Degree of lattice distortion (S)	0.0023	0.0209	0.0168	0.0022	0.0048	0.0063	
Arithmetic mean (<i>d</i> _{av})	0.0425	0.2923	0.3092	0.0210	0.0313	0.2332	
Measure of similarity (Δ)	0.024	0.230	0.196	0.005	0.010	0.082	

As detailed above, atoms in the two HgM^{III}(O)[AsO₄] structures show comparatively large displacements relative to the structures of HgM^{II}(OH)[AsO₄] which indicates a high strain in the OH-free structures. This strain possibly is responsible for the observed poor crystal quality. In this regard the atom with the most oblate displacement ellipsoid is O3 in the structure of HgMn(O)[AsO₄]. O3 is also the atom with the largest displacement relative to the structures of descloizite and of HgZn(OH)[AsO₄] (Table 5).

It should be stressed out that the observed isotypism between the structures of HgM^{II}(OH)[AsO₄] (*M*^{II} = Mg, Co, Ni, Cu, Zn) and HgM^{III}(O)[AsO₄] (*M*^{III} = Mn, Fe) is a rare case where the replacement of an OH[−] group by an oxidic O^{2−} ion (and the concomitant oxidation of transition metals from +II to +III) does not result in another unit cell volume or another symmetry. For example, the replacement OH[−] → O^{2−} in hydroxy-apatite Ca₁₀(PO₄)₆(OH)₂ leads to a lowering of space group symmetry from *P*6₃/*m* (Sudarsanan & Young, 1969) to *P*6 for the oxy-apatite Ca₁₀(PO₄)₆O (Henning *et al.*, 1999), demonstrating that O–H...O hydrogen bonding interactions are an obvious structure-directing feature in the apatite structure. In comparison, the role of hydrogen bonding interactions in descloizite-type HgM^{II}(OH)[AsO₄] phases in fact shows some variations as discussed for the Mg-, Co-, Ni- and Zn-members compared with the Cu-member, but apparently is not very distinct and hence allows an OH[−] → O^{2−} substitution without changing the structure type for the resulting HgM^{III}(O)[AsO₄] phases. In this context the existence of other HgM^{III}(O)[AsO₄] phases appears possible where M^{III} is a cation with a radius comparable to that of Mn^{III} or Fe^{III}. A possible candidate is

Cr^{III}, and first formation studies of ‘‘HgCr(O)[AsO₄]’’ with chromium(III) nitrate as the transition metal source are currently in progress.

3.4. Comparison with other structure families

As pointed out by Đorđević *et al.* (2016) there is no obvious correlation between the space-group symmetry, the type of cations at the M1 and M2 position or the type of tetrahedral XO₄ groups for M^{I,II}M^{II,III}(OH,O)[X^{V,VI}(O₄,O₃OH)] members of the descloizite-adelite family. However, it is notable that for M1 = Hg and X = As, all known phases (this work; Weil, 2004a) adopt the descloizite-type of structure. The same is true for all phases with M1 = Cd and X = As (Đorđević *et al.*, 2016) but not for phases with M1 = Ca and X = As and varying M2 that all adopt the adelite-type of structure despite very similar ionic radii for Hg²⁺ (1.02 Å), Cd²⁺ (0.95 Å) and Ca²⁺ (1.00 Å) for coordination number 6 (Shannon, 1976).

Apart from the obvious relation between the descloizite- and adelite-type of structures with a ratio of 1:1:1 between M1, M2 and X, some structural features of the HgM^{II/III}(OH,O)[AsO₄] phases are also realized for the structures of the brackebuschite- and tsumcorite-family that show different M1:M2:X ratios. The brackebuschite family has monoclinic symmetry (space-group type *P*2₁/*m*) and can be described by the general formula M₁₂M₂(H₂O,OH)[XO₄]₂ with M1 = Ca^{II}, Sr^{II}, Ba^{II}, Pb^{II}; M2 = Al^{III}, Mn^{II}, Mn^{III}, Fe^{II}, Fe^{III}, Zn^{II}; X = P^V, S^{VI}, V^V, As^V, *i.e.* the M1:M2:X ratio is 2:1:1. Members of the tsumcorite family have either monoclinic symmetry (space-group type *C*2/*m*) or triclinic

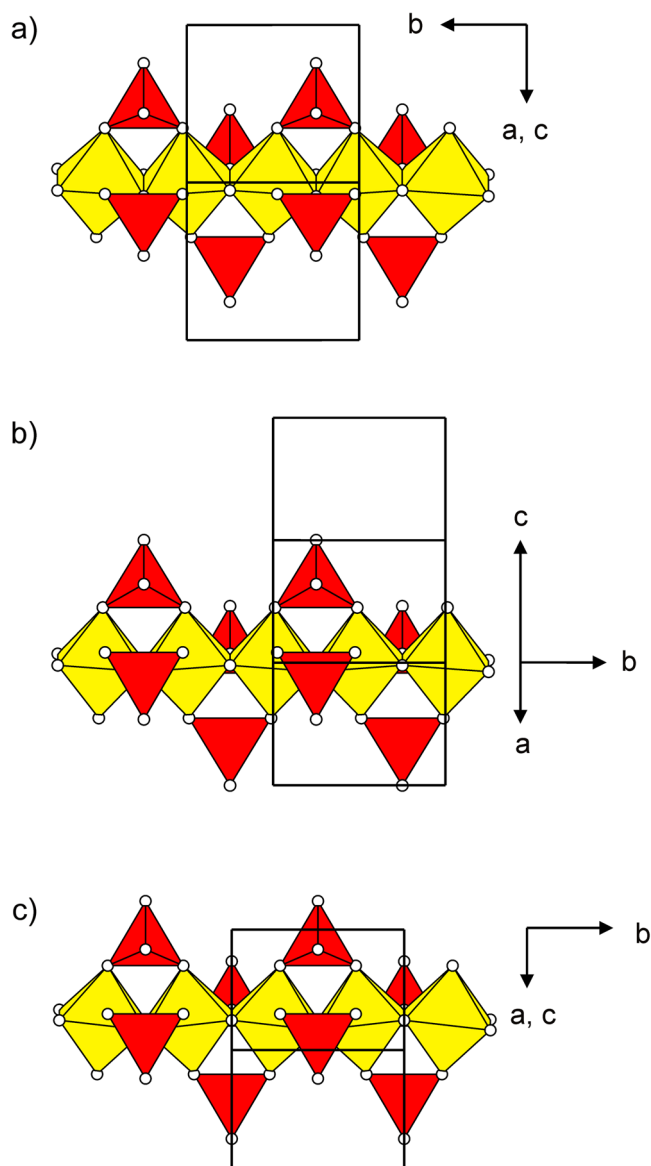


Fig. 2. ${}^1_{\infty}[M2O_{2/1}O_{4/2}]_1$ chains of edge-sharing octahedra (yellow) decorated by $[XO_4]$ tetrahedra (red) in the crystal structures of (a) $HgCo(OH)[AsO_4]$, (b) brackebuschite and (c) tsumcorite in projections along $[10\bar{1}]$, $[201]$ and $[\bar{1}01]$, respectively. Structure data for $HgCo(OH)[AsO_4]$ were taken from this work, for brackebuschite from Lafuente & Downs (2016), and for tsumcorite from Tillmanns & Gebert (1973). For clarity, H atoms were omitted.

symmetry and have a general formula $M1M2_2(H_2O,OH)_2[XO_4]_2$ with $M1 = Na^I, K^I, Rb^I, Ag^I, NH_4^I, Ca^{II}, Pb^{II}, Bi^{III}, Tl^{III}; M2 = Al^{III}, Mn^{III}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}; X = P^V, As^V, V^V, S^{VI}, Se^{VI}, Mo^{VI}$, i.e. the $M1:M2:X$ ratio is 1:2:2. In all three structure families the same type of ${}^1_{\infty}[M2O_{2/1}O_{4/2}]$ chains made up from edge-sharing octahedra decorated by $[XO_4]$ tetrahedra is present (Fig. 2). In descloizite-type structures adjacent chains are connected through vertex-sharing $[XO_4]$ tetrahedra into a three-dimensional network, in brackebuschite-type structures the chains are isolated, and in tsumcorite-type structures they

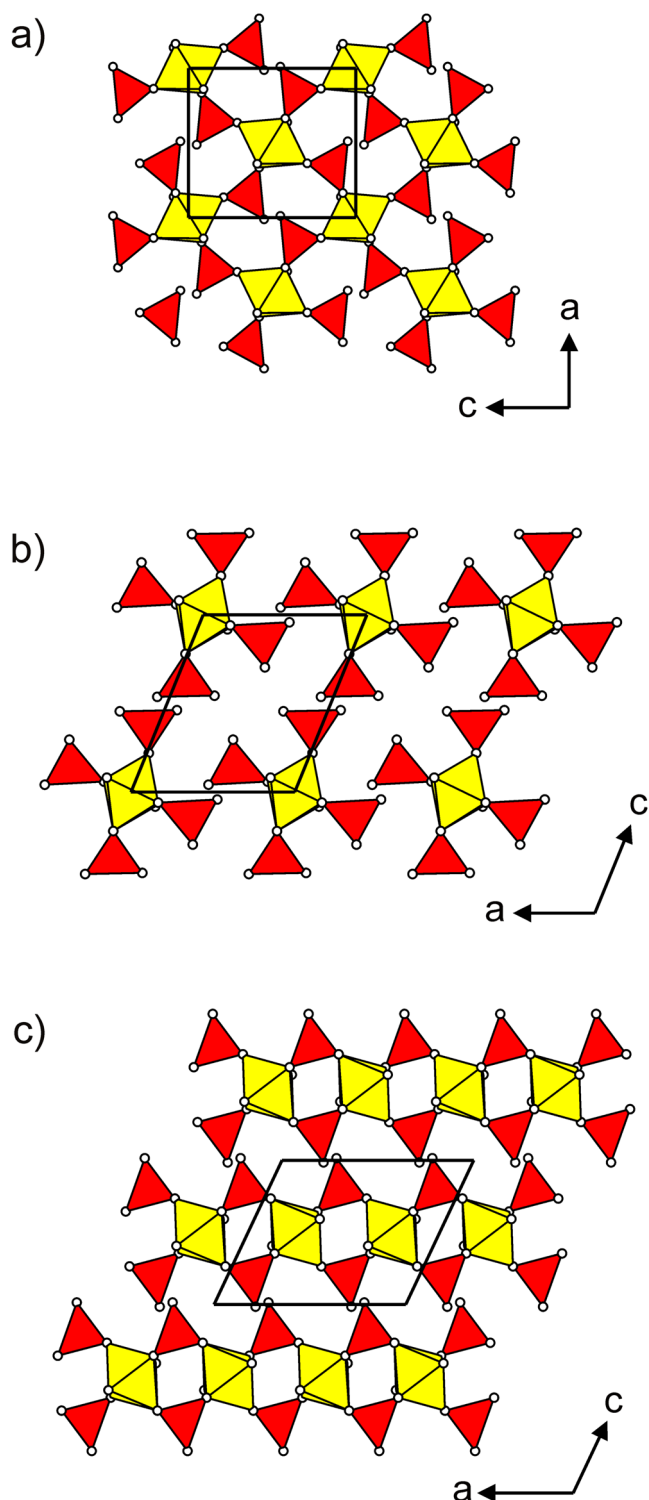


Fig. 3. Arrangement of ${}^1_{\infty}[M2O_{2/1}O_{4/2}]$ chains and $[XO_4]$ tetrahedra in the structures of (a) $HgCo(OH)[AsO_4]$, (b) brackebuschite and (c) tsumcorite in projections along the chain direction $[010]$. Colour codes and structure data are as in Fig. 2.

are connected into layers (Fig. 3). In the three structure families the $M1$ cations are located in the remaining space of the crystal structures and, dependent on their sizes, can vary in coordination numbers from 7 to 10.

4. Conclusion

Descloizite is a typical secondary mineral occurring in oxidized portions of lead-bearing veins, in particular of lead–zinc–copper deposits. Analogous to descloizite, natural members of the series $\text{HgM}^{\text{II/III}}(\text{OH},\text{O})[\text{AsO}_4]$ that are currently known only for synthetic phases may exist as secondary minerals in oxidized portions of mercury-bearing veins with a high arsenic concentration. Such deposits are, for example, Khaidarkan (Fergana Valley, Alai Range, Osh Oblast, Kyrgyzstan) and Gomi (Oni District, Racha-Lochkhumi-Kvemo Svaneti Region, Georgia).

Phase formation studies under hydrothermal conditions revealed the existence of six new mercury-containing phases with formula types $\text{HgM}^{\text{II}}(\text{OH})[\text{AsO}_4]$ ($M^{\text{II}} = \text{Mg}, \text{Co}, \text{Ni}, \text{Cu}$) and $\text{HgM}^{\text{III}}(\text{O})[\text{AsO}_4]$ ($M^{\text{III}} = \text{Mn}, \text{Fe}$). The first family has the same formula type as representatives of the adelite and descloizite family whereas the missing hydroxyl group in $\text{HgM}^{\text{III}}(\text{O})[\text{AsO}_4]$ phases is compensated by an oxidation of the transition metal from +II to +III. Nevertheless, all $\text{HgM}^{\text{II}}(\text{OH})[\text{AsO}_4]$ and $\text{HgM}^{\text{III}}(\text{O})[\text{AsO}_4]$ compounds adopt the descloizite structure type. In agreement with a previous review of natural and synthetic compounds with adelite- (space-group type $P2_12_12_1$) and descloizite-type (space-group type $Pnma$) structures (Đorđević *et al.*, 2016), a correlation between the space-group symmetry, the type of cations at the $M1$ and $M2$ position or the type of tetrahedral $[\text{XO}_4]$ groups is not obvious. For the descloizite-type $\text{HgM}^{\text{II}}(\text{OH})[\text{AsO}_4]$ and $\text{HgM}^{\text{III}}(\text{O})[\text{AsO}_4]$ phases a high degree of structural flexibility is apparent because neither the presence of a Jahn-Teller active ion ($\text{Cu}^{\text{II}}, \text{Mn}^{\text{III}}$) nor the missing hydrogen bonding interactions in the $\text{HgM}^{\text{III}}(\text{O})[\text{AsO}_4]$ structures lead to a change of the structure type. Therefore the $\text{HgM}^{\text{II}}(\text{OH})[\text{AsO}_4]$ and $\text{HgM}^{\text{III}}(\text{O})[\text{AsO}_4]$ structures are rare examples for an $\text{OH} \rightarrow \text{O}^{2-}$ substitution under retention of the space group type. The present investigations suggest that the existence of (additional) natural and/or synthetic descloizite-types phases containing mercury is possible, including “ $\text{HgCr}^{\text{III}}(\text{O})[\text{AsO}_4]$ ” or related $\text{HgM}^{\text{III}}(\text{O})[\text{XO}_4]$ and $\text{HgM}^{\text{II}}(\text{OH})[\text{XO}_4]$ phases where the arsenate anion $[\text{AsO}_4^{3-}]$ is replaced by a vanadate anion $[\text{VO}_4^{3-}]$.

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