

Hydrothermal and ionothermal synthesis of mineral-related arsenates in the system $\text{CdO-MO-As}_2\text{O}_5$ ($M^{2+} = \text{Mg, Co, Ni, Cu, Zn}$) and their crystal structures

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Abstract: During systematic research on the mineral-related arsenates in the system $\text{CdO-MO-As}_2\text{O}_5\text{-H}_2\text{O}$ ($M^{2+} = \text{Mg, Co, Ni, Cu, Zn}$), three new Cd-containing arsenates $\text{Cd}_{4.65}\text{Ni}_{0.35}(\text{AsO}_4)_2(\text{HAsO}_4)_2 \cdot 4\text{H}_2\text{O}$ (**1**), $\text{Cd}_{0.75}\text{Co}_{2.75}(\text{H}_{0.5}\text{AsO}_4)_2(\text{HAsO}_4)_2$ (**2**) and $\text{Cd}_{1.25}\text{Zn}_{0.75}(\text{HAsO}_4)_2 \cdot 2\text{H}_2\text{O}$ (**3**) have been synthesized under hydrothermal conditions, while the Zn-arsenate $\text{Zn}_9(\text{AsO}_4)_6 \cdot 4\text{H}_2\text{O}$ (**4**) and again **2** have been prepared under ionothermal conditions using the ionic liquid 1-ethyl-3-methylimidazolium bromide, ($\text{C}_6\text{H}_{11}\text{N}_2$)Br, as the solvent. Their crystal structures were determined using single-crystal X-ray diffraction data and refined to the reasonably low R -values: **1** – $R_1 = 0.030$; **2** – $R_1 = 0.047$; **3** – $R_1 = 0.029$; **6** – $R_1 = 0.029$. The compounds **1**, **2** and **3** are structural analogues of three different arsenate mineral phases. Compound **4** was for the first time synthesized using ionic liquid as the solvent and the hydrogen atoms were found and refined. Infrared and Raman spectra were measured and evaluated in order to obtain further information on the anion groups and especially on the short hydrogen bonds. The OH stretching frequency is in good agreement with the observed O...O distances. The different approaches in the synthesis of mineral-related arsenates, the temperature treatment as well as the role of added water in ionothermal synthesis are also discussed.

Key-words: cadmium; arsenic; arsenates; crystal structure; single-crystal X-ray diffraction; hydrothermal synthesis; ionothermal synthesis; vibrational spectroscopy; hydrogen bonding.

1. Introduction

Cadmium (Cd) and arsenic (As) are chemical elements that represent major ecological hazards. Therefore, they are often main topics of a great number of environmental studies (Mirlean & Roisenberg, 2006). Arsenic pollution can be from both natural and anthropogenic sources, while contamination with cadmium occurs mainly through anthropogenic discharge (Luo *et al.*, 2011). These two toxic elements can exist together in smelting operations, metal–arsenic bearing materials (Cd–As pesticides, *etc.*) and mine drainage (Gräfe *et al.*, 2004). However, heavy metals exist as multiple pollutants, including different metals and different forms of the same metals, in different kind of mine and industrial wastes. One of the most serious environmental problems associated with these kinds of wastes is their tendency to chemically react with water to produce contaminated water (Nordstrom, 2011). The fundamental processes that control whether potentially toxic elements are released or restored involve mineral–water interaction. In order to understand the chemical reactions involved, it is important to characterize the reactive minerals and possible mineral-related compounds present in fresh and weathered mine wastes and industrial

sites. This knowledge would help to improve both risk assessment and remediation design (Hudson-Edwards *et al.*, 2011).

Although arsenic is an abundant natural hazard, many crystal structures of oxoarsenates(V) are still unknown. This leads to misinterpreting the behaviour of arsenates in natural environments, because it requires detailed knowledge of thermodynamic properties and in particular of formation conditions of arsenate phases and their respective crystal structures (O'Day, 2006). In nature, arsenates are formed either by weathering of the primary ores or by hydrothermal processes. Therefore, mineral-related arsenates are usually synthesized hydrothermally. However, using ionic-liquid low-temperature assisted synthesis, we have succeeded in synthesising more than a dozen mineral-related arsenates and two (**2** and **4**) of them are described here.

During the structural study on the environmentally relevant, mineral-related synthetic arsenic oxosalts in the system $M1\text{O-M}2\text{O-As}_2\text{O}_3/\text{As}_2\text{O}_5\text{-H}_2\text{O}$ ($M1 = \text{Sr}^{2+}, \text{Cd}^{2+}, \text{Ba}^{2+}, \text{Bi}^{3+}, \text{Hg}^{2+}; M2 = \text{Mg}^{2+}, \text{Mn}^{2+,3+}, \text{Fe}^{2+,3+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}$), a large number of new metal arsenates and arsenites were already synthesised using hydrothermal technique and characterised structurally,

and, in part, also by spectroscopic techniques (Mihajlović & Effenberger, 2004, 2006; Mihajlović *et al.*, 2004a,b; Đorđević, 2008a,b, 2011, 2015; Đorđević *et al.*, 2008, 2015a,b, 2016a; Weil *et al.*, 2009; Đorđević & Karanović, 2008, 2010; Stojanović *et al.*, 2012; Đorđević & Kolitsch, 2013; Karanović *et al.*, 2016). Furthermore, we have also synthesised and structurally characterized two organic–inorganic hybrid compounds using ionic liquids as a solvent and template (Karanović *et al.*, 2014; Đorđević *et al.*, 2016b).

In this article, the preparation, crystal structures and spectroscopic behaviour of four arsenates are reported: $\text{Cd}_{4.65}\text{Ni}_{0.35}(\text{AsO}_4)_2(\text{HAsO}_4)_2 \cdot 4\text{H}_2\text{O}$ (**1**), $\text{Cd}_{0.75}\text{Co}_{2.75}(\text{H}_0.5\text{AsO}_4)_2(\text{HAsO}_4)$ (**2**), $\text{Cd}_{1.25}\text{Zn}_{0.75}(\text{HAsO}_4)_2 \cdot 2\text{H}_2\text{O}$ (**3**) and $\text{Zn}_9(\text{AsO}_4)_6 \cdot 4\text{H}_2\text{O}$ (**4**). The **1**, **2** and **3** compounds are structural analogues of three different arsenate mineral phases, whereas **4**, the already known compound, was for the first time synthesised using ionic liquid as the solvent and H atoms of water molecules were detected in the electron density map and included into the structural model. The effects of the temperature and the role of added water in ionothermal synthesis of arsenates are also discussed in this article.

2. Experimental procedure

2.1. Synthesis of the single crystals

The materials used were: $\text{Cd}(\text{OH})_2$ (Alfa Products, 89297), CdO (Fluka 20913, 100 g, $\geq 99\%$), $\text{Mg}(\text{OH})_2$ (Fluka 63081, 250 g, $\geq 99\%$), $5\text{ZnO} \cdot 2\text{CO}_3 \cdot 4\text{H}_2\text{O}$ (Alfa Products 308764), $\text{Co}(\text{OH})_2$ (Sigma-Aldrich, 342440, tech. 95 %), $\text{Ni}(\text{OH})_2$ (Sigma-Aldrich S58362-518-500G), As_2O_5 (Alfa Products 87687, $>99.9\%$), 1-ethyl-3-methylimidazolium bromide, dry (Fluka 03938-25G, $\geq 98.5\%$).

During an on-going research on synthetic mineral-like arsenites and arsenates in the $M1\text{--}M2\text{--As--H--(Cl)}$ system ($M1 = \text{Na}^+, \text{K}^+, \text{Sr}^{2+}, \text{Cd}^{2+}, \text{Ba}^{2+}$; $M2 = \text{Mg}^{2+}, \text{Mn}^{2+,3+}, \text{Fe}^{2+,3+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}$), with a focus on their structural and spectroscopic classification, single crystals of **1**, **2**, and **3** were obtained. They were grown under hydrothermal conditions in Teflon-lined stainless steel autoclaves. The initial homogenized mixtures were closed in the autoclaves, filled with distilled water to approximately 80 % of their inner volume. The pH values of the starting solutions were measured as 3 for all three mixtures. The crystallisation was carried out by placing the autoclaves in an oven under air atmosphere and heating the mixtures under autogenous pressure from room temperature.

For **1**, the solution of homogenized 1 g mixture of CdO , $\text{Ni}(\text{OH})_2$, As_2O_5 in molar ratio 2:2:1 in distilled water was used as the starting material. A three-step heating regime was chosen: the autoclaves were heated from 20 to 120 °C (4 h), held at 120 °C for 72 h, and finally cooled to room temperature within 99 h. The pH value of the supernatant solution was 4. The obtained products were washed with distilled water, filtered and dried in the air at room temperature. Compound **1** crystallised as very light-green

transparent needles (yield 30 %) together with crystals of CdO (~yield 60 %) and $\text{Cd}(\text{OH})_2$ (~yield 10 %). The maximal length of crystals **1** was 0.05 mm.

For **2**, the solution of 1 g mixture of $\text{Cd}(\text{OH})_2$, $\text{Co}(\text{OH})_2$, As_2O_5 in molar ratio 1:3:1 in (i) distilled water and (ii) mixture of distilled water and ionic liquid 1-ethyl-3-methylimidazolium bromide (emimBr) in volumetric ratio 1:6 were used as the starting material. A three-step heating regime was chosen for both mixtures: the autoclaves were heated from 20 to 220 °C (4 h), held at 220 °C for 72 h, and finally cooled to room temperature within 72 h. The pH value of supernatant solution was 4. The obtained products were washed with distilled water, filtered and dried in the air at room temperature. Phase **2** crystallised as transparent dark pink elongated prisms (yield 80 %) together with crystals of $\text{Cd}(\text{OH})_2$ (~yield 10 %) and one or more unidentified phases. The maximal length of crystals was about 0.75 mm in the case (i) or 1 mm in the case (ii). For crystal-structure analysis a single crystal from (i) was used.

For **3**, the 1 g homogenized mixture of $\text{Cd}(\text{OH})_2$, $5\text{ZnO} \cdot 2\text{CO}_3 \cdot 4\text{H}_2\text{O}$, As_2O_5 and distilled H_2O in molar ratio 2:1:1 was used as the starting material. A three-step heating regime was chosen: the autoclaves were heated from 20 to 220 °C (4 h), held at 220 °C for 60 h, cooled to 150 °C for 4 h, held at 150 °C for 10 h and finally cooled to room temperature within 4 h. The pH value of the supernatant solution was 3. The obtained products were washed with distilled water, filtered and dried in the air at room temperature. Phase **3** crystallised as transparent elongated prisms (yield 40 %) (Fig. 1) together with small needles of $\text{Cd}_2\text{As}_2\text{O}_7$ (yield 60 %) (Weil, 2001). The maximal length of the crystals of **3** was about 0.6 mm.

For **4**, the mixture of CdO , $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, As_2O_5 in the molar ratio 2:2:1 was mixed with firstly molten emimBr. A three-step heating regime was chosen: the autoclaves were heated from 20 to 160 °C (4 h), held at 160 °C for 72 h, and finally cooled to room temperature within 99 h. The obtained products were washed with ethanol, filtered and dried in the air at room temperature. Phase **4** crystallised as elongated, prismatic crystals (~yield 10 %) together with crystals of the monoclinic polymorph of $[\text{C}_6\text{H}_{11}\text{N}_2]_2[\text{CdBr}_4]$ (~yield 25 %) (Gou *et al.*, 2016) and synthetic adamite, $\text{Zn}_2(\text{AsO}_4)(\text{OH})$ (~yield 65 %). The crystals of **4** are no more than 0.3 mm in length.

2.2. Single-crystal X-ray diffraction measurements

The room-temperature intensity data for **1–4** were collected on a Nonius Kappa CCD single-crystal four-circle diffractometer (MoK α radiation, graphite monochromator), equipped with a 300-nm diameter capillary-optics collimator. The unit-cell parameters were determined with HKL SCALEPACK (Nonius, 2005–2007). A complete sphere of reciprocal space (φ and ω scans) was measured. The intensity data were processed with the Nonius program suite DENZO-SMN (Nonius, 2005–2007) and corrected for absorption by the multi-scan method (Otwinowski *et al.*, 2003). All structures were

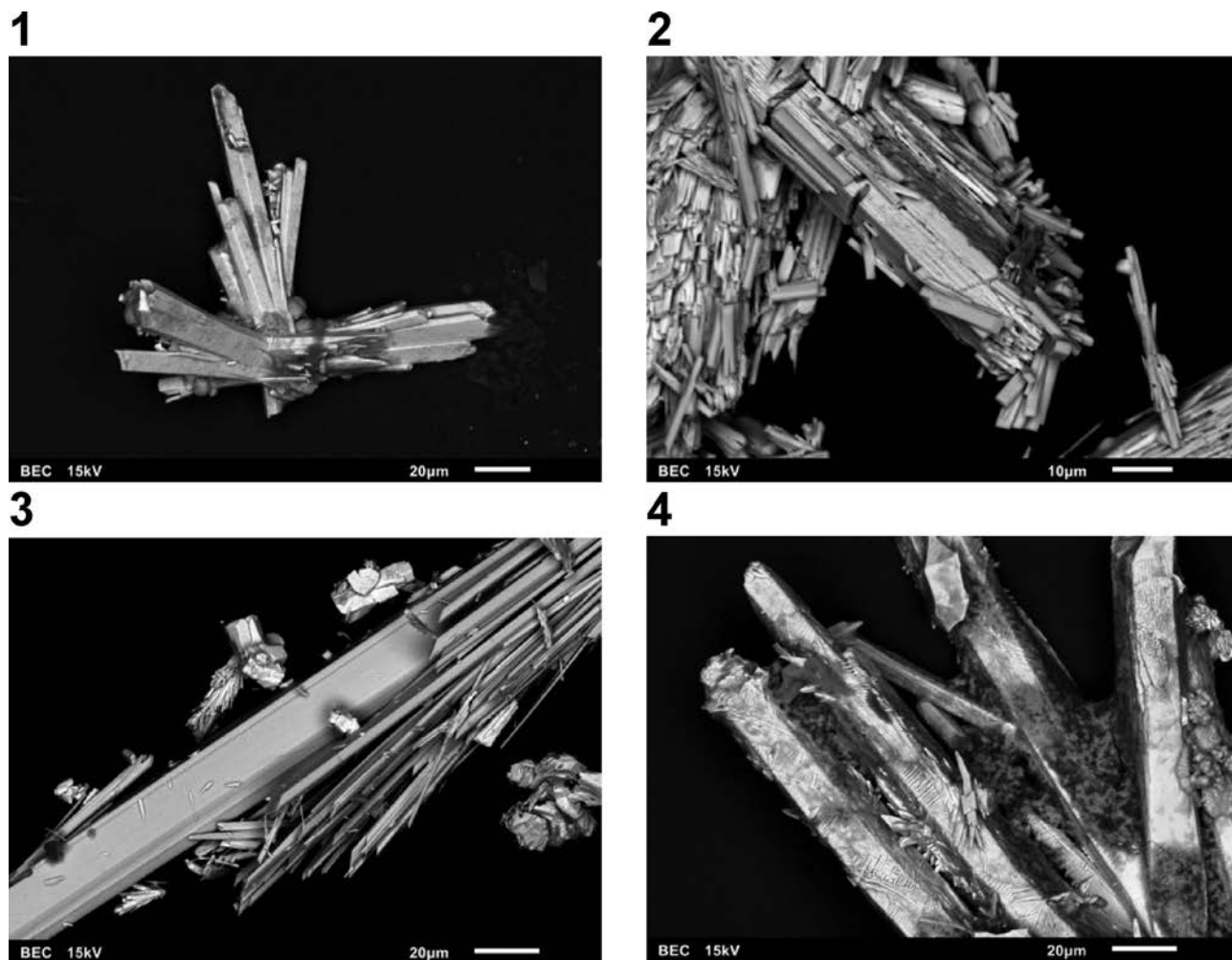


Fig. 1. Backscattered electron micrographs of compounds **1** to **4**. In the picture of **2**, darker crystals contain more Co, and brighter contain more Cd.

solved by direct methods using SIR97 (Altomare *et al.*, 1999) and refined on F^2 by full-matrix least-squares using SHELXL97 (Sheldrick, 2008) and WinGX (Farrugia, 2012). For compound **2** from cell metrics and intensity distribution a close structural relationship with the 'synthetic alluaudite-type arsenates' was expected (Đorđević *et al.*, 2015a). In the first step, the crystal structure of **2** was refined in the parental monoclinic space group $C2/c$. However, the number of 'systematic absence violations' in the output file was 49. Mostly, they are indicating that no c -glide ($h0l$ with $l=2n$) is present and that the symmetry is lower than $C2/c$. Possible subgroups of $C2/c$ without a c -glide are $C2$, $P2_1/n$, and $P2_1/n$. The presence of an n -glide ($h0l$ with $h+l=2n$) is also contradicted by many reflections, leaving the space group $C2$ as the only possible candidate for this compound. The second WGHT parameter was also too high (62.7882 and 14.8474 for $C2/c$ and $C2$, respectively) as well as the goodness of fit, which is strongly influenced by the weighting scheme (1.237 and 1.031 for $C2/c$ and $C2$, respectively). The R_1 agreement factor was slightly lower

in $C2$ (0.0544 and 0.0465 for $C2/c$ and $C2$, respectively), which is partly since the number of refined parameters is larger (90 and 164 for $C2/c$ and $C2$, respectively). The R_{int} -value for the higher symmetry Laue group is only slightly higher than for the lower symmetry Laue group (0.046 and 0.040 for $C2/c$ and $C2$, respectively), which can be the warning sign for twinning. Additionally, for the most disagreeable reflections F_o^2 was always greater than F_c^2 , the factor $K(=\langle F_o^2 \rangle / \langle F_c^2 \rangle)$ was high for the reflections with low intensity indicating twinning as well. Having all that in mind, compound **2** was refined as an inversion twin in the space group $C2$. The refinement of the mixed sites was carried out using restraints, *i.e.* mixed sites were refined with the same coordinates and atomic displacement parameters. Anisotropic displacement parameters were allowed to vary for all atoms, except the H atoms. Hydrogen atoms from hydroxyl groups and water molecules in **1**, **2**, **3** and **4** were placed in geometrically calculated positions and refined using the rigid model, with $\text{O-H}=0.82 \text{ \AA}$ and $U_{\text{iso}}(\text{H})=1.2 U_{\text{eq}}(\text{O})$ for hydroxyl groups (Shelx constraint AFIX 83 was used for **1**–**3**) and

Table 1. Crystal data, data collection and refinement details for compounds **1–4**.

Compound (no. in text)	1	2	3	4
<i>Crystal data</i>				
Chemical formula	As ₄ Cd _{4.65} H ₁₀ Ni _{0.35} O ₂₀	As ₃ Cd _{0.75} Co _{2.75} H ₂ O ₁₂	As ₂ Cd _{1.25} H ₆ O ₁₀ Zn _{0.75}	As ₆ H ₈ O ₂₈ Zn ₉
Structural formula	Cd ₄ (Cd _{0.65} Ni _{0.35})(AsO ₄) ₂ (HAsO ₄) ₂ ·4H ₂ O	Cd _{0.5} (Co _{0.75} Cd _{0.25})Co ₂ (H ₅ AsO ₄) ₂ (HAsO ₄)	Cd(Zn _{0.75} Cd _{0.25})(HAsO ₄) ₂ ·2H ₂ O	Zn ₉ (AsO ₄) ₆ ·4H ₂ O
Space group, Z	C2/c, 4	C2, 4	P $\bar{1}$, 2	P $\bar{1}$, 1
Formula weight, M_r (g/mol)	1173.10	665.13	505.42	255.09
a (Å)	18.375(4)	11.981(2)	8.275(2)	6.6983(13)
b (Å)	9.5395(19)	12.485(3)	7.513(2)	9.1885(18)
c (Å)	9.977(2)	6.7661(14)	6.870(1)	10.146(2)
α (°)			82.79 (3)	69.44(3)
β (°)		113.23(3)	97.52 (3)	77.26(3)
γ (°)			95.32 (3)	75.78(3)
V (Å ³)	1738.6(6)	930.1(4)	418.82(16)	560.6(2)
Calculated density, D_x (g/cm ³)	4.482	4.750	4.008	4.425
Absorption coefficient, μ (mm ⁻¹)	13.63	17.19	13.20	18.37
$T_{\min}/T_{\max}$	0.728/0.761	0.544/0.709	0.242/0.778	0.418/0.576
$F(000)$	2140	1229	469	700
Crystal size (mm ³)	0.02 × 0.02 × 0.10	0.02 × 0.03 × 0.12	0.02 × 0.02 × 0.15	0.03 × 0.04 × 0.22
<i>Data collection</i>				
Range of Miller indices	−25 ≤ h ≤ 26 −13 ≤ k ≤ 13 −14 ≤ l ≤ 14	−17 ≤ h ≤ 17 −18 ≤ k ≤ 18 −9 ≤ l ≤ 9	−11 ≤ h ≤ 11 −10 ≤ k ≤ 10 −9 ≤ l ≤ 9	−10 ≤ h ≤ 10 −14 ≤ k ≤ 14 −16 ≤ l ≤ 16
Reflections collected/unique	5182/2664	6128/3099	4780/2444	9603/4876
Observed reflections [$I > 2\sigma(I)$]	2033	2473	2167	3914
R_{int}	0.032	0.040	0.022	0.031
θ_{max} (°)	30.5	31.5	30.0	35.0
<i>Refinement</i>				
Extinction coefficient, k^a	—	0.0016(3)	0.0037(6)	0.0016(3)
Refined parameters	133	164	141	208
R -indices [$F^2 > 2\sigma(F^2)$] ^b	$R_1 = 0.0295$ $wR_2 = 0.0585$	$R_1 = 0.0465$ $wR_2 = 0.1184$	$R_1 = 0.0285$ $wR_2 = 0.0728$	$R_1 = 0.0287$ $wR_2 = 0.0637$
R -indices (all data) ^b	$R_1 = 0.0508$ $wR_2 = 0.0537$	$R_1 = 0.0667$ $wR_2 = 0.1281$	$R_1 = 0.0347$ $wR_2 = 0.0756$	$R_1 = 0.0431$ $wR_2 = 0.0681$
Goodness-of-fit, S	1.023	1.031	1.097	1.023
$(\Delta/\sigma)_{\text{max}}$	0.001	0.000	0.001	0.001
Twin ratio	—	0.51(4):0.49(4)	—	—

^a $F_c^* = kF_c[1 + 0.001 \times F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$.

^b $w = 1/[\sigma^2(F_o^2) + (0.0216P)^2 + 10.3000P]$ for **1**, $w = 1/[\sigma^2(F_o^2) + (0.0657P)^2 + 14.8474P]$ for **2**, $w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 1.1101P]$ for **3** and $w = 1/[\sigma^2(F_o^2) + (0.0344P)^2]$ for **4**, where $P = (F_o^2 + 2F_c^2)/3$.

O—H = 0.85 Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{O})$ for water molecules (Shelx constraint AFIX 3 was used for **1** and **3** and, for **4**, only DFIX restraint was used).

Relevant information on crystal data, data collection, and refinements are compiled in Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters for **1–4** are presented in Tables 2–5. Selected bond lengths and angles are presented in Tables 6–9. Bond-valence sum calculations were obtained using VALIST software (Wills, 2010). All drawings were plotted using ATOMS (Dowty, 2000).

2.3. Powder X-ray diffraction measurements

X-ray powder diffraction (XRPD) patterns for the bulk product of each synthesis were obtained with a PHILIPS X-Pert diffractometer (CuK α , graphite monochromator, scintillation detector, instrument radius 171.9 mm, auto-

matic slit, 293 K, $5 < 2\theta < 140^\circ$, step length 0.01° and 5 s counting time. The program POWDER CELL (Kraus & Nolze, 1996) was used for calculation of the powder patterns of the solved crystal structures for identification of phases in measured XRPD patterns.

The measured XRPD patterns are obtained from powders remaining after separation of single crystals and calculated XRPD patterns from the solved crystal structures. The powders of all samples are not single phase. The XRPD pattern of **1** shows the presence of cubic CdO as a main crystalline phase and the solved crystal structure phase Cd_{4.65}Ni_{0.35}(AsO₄)₂(HAsO₄)₂·4H₂O, which is present in smaller quantities. The major identified crystalline peaks in sample **2** correspond to the solved crystal structure phase Cd_{0.75}Co_{2.75}(H_{0.5}AsO₄)₂(HAsO₄) and a small amount of Cd(OH)₂. The main crystalline phases in **3** were identified as predominant Cd₂As₂O₇ and smaller amount of the solved crystal structure phase

Table 2. Fractional atomic coordinates and displacement parameters for **1**. U_{eq} according to Fischer & Tillmanns (1988). For the H atoms U_{iso} is shown.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U_{iso}^*
Cd1	0.5000	0.39375(6)	0.7500	0.01629(12)
Cd2/Ni2	0.68169(2)	0.91448(4)	0.81576(4)	0.01609(13)
Cd3	0.67511(2)	0.52953(4)	0.86647(3)	0.01613(9)
As1	0.58357(3)	0.68394(5)	0.58861(5)	0.01376(11)
As2	0.65986(3)	0.23655(5)	0.62600(5)	0.01287(11)
O1	0.5765(2)	0.5685(4)	0.7122(3)	0.0211(8)
O2	0.66051(18)	0.7753(4)	0.6316(3)	0.0209(8)
O3	0.41595(19)	0.3916(4)	0.5627(3)	0.0218(8)
O4	0.66314(19)	0.7409(4)	0.9582(3)	0.0185(7)
O5	0.79456(18)	0.5891(4)	0.8257(3)	0.0174(7)
O6	0.70160(19)	0.3729(4)	0.7071(3)	0.0209(8)
O7	0.57097(17)	0.2243(4)	0.6567(3)	0.0176(7)
O8	0.5106(2)	0.7982(4)	0.5790(4)	0.0241(8)
H8	0.4876	0.7929	0.5040	0.029*
O9	0.5768(2)	1.0157(4)	0.8456(4)	0.0331(10)
H9A	0.5461	0.9523	0.8600	0.040*
H9B	0.5645	1.0567	0.7711	0.040*
O10	0.76019(19)	0.4180(4)	1.0323(3)	0.0212(8)
H10A	0.7912	0.3871	0.9828	0.025*
H10B	0.7458	0.3513	1.0790	0.025*

Table 3. Fractional atomic coordinates and displacement parameters for **2**. U_{eq} according to Fischer & Tillmanns (1988). For the H atoms U_{iso} is shown.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U_{iso}^*
Cd1	0.5000	0.4949(5)	0.5000	0.0463(9)
Cd2	0.5000	0.4827(17)	0.0000	0.0463(9)
Cd4/Co4	0.0000	0.2830(3)	0.5000	0.0154(11)
Cd3/Co3	0.0000	0.7152(3)	0.0000	0.0204(11)
Co5	0.2010(2)	0.15874(19)	0.3607(4)	0.0120(6)
Co6	0.2058(2)	0.8382(2)	−0.1326(4)	0.0158(6)
As1	0.0000	0.3094(2)	0.0000	0.0177(7)
As2	0.0000	0.68660(18)	0.5000	0.0106(6)
As3	0.28257(17)	0.38407(14)	0.6359(3)	0.0135(5)
As4	0.28417(17)	0.61410(16)	0.1403(3)	0.0155(5)
O1	0.0331(12)	0.2372(11)	0.2265(16)	0.016(3)
O2	−0.0360(11)	0.7618(11)	0.2788(18)	0.017(3)
O3	0.1156(12)	0.3915(10)	0.0214(19)	0.014(3)
H3	0.0919	0.4538	0.0063	0.021*
O4	0.1168(14)	0.6021(13)	0.517(2)	0.023(3)
H4	0.0896	0.5420	0.4770	0.034*
O5	0.3444(11)	0.3207(9)	0.8748(17)	0.0170(15)
O6	0.3496(10)	0.6748(11)	0.3788(16)	0.018(2)
O7	0.1308(13)	0.4054(12)	0.584(2)	0.018(3)
H7	0.1152	0.4694	0.5626	0.027*
O8	0.1353(14)	0.5850(11)	0.086(2)	0.023(3)
H8	0.1266	0.5199	0.0864	0.034*
O9	0.2879(11)	0.3101(9)	0.4353(18)	0.0170(15)
O10	0.2897(10)	0.6850(11)	−0.0636(17)	0.017(2)
O11	0.3546(10)	0.5022(9)	0.6457(16)	0.0170(15)
O12	0.3563(10)	0.4965(13)	0.1670(18)	0.027(3)

Table 4. Fractional atomic coordinates and displacement parameters for **3**. U_{eq} according to Fischer & Tillmanns (1988). For the H atoms U_{iso} is shown.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U_{iso}^*
Cd1	0.16988(3)	0.09896(4)	0.87243(4)	0.01681(10)
Cd2/Zn2	0.42160(5)	−0.15377(6)	0.65950(6)	0.01613(16)
As1	0.18196(5)	0.13699(5)	1.36366(6)	0.01345(11)
As2	0.57079(5)	0.22649(5)	0.84118(6)	0.01276(11)
O1	0.0541(4)	0.2949(4)	1.4040(5)	0.0266(7)
H1	−0.0347	0.2444	1.4270	0.032*
O2	0.0920(4)	0.0279(4)	1.1759(4)	0.0199(6)
O3	0.2022(3)	−0.0018(4)	0.5768(4)	0.0150(5)
O4	0.3502(3)	0.2657(4)	1.3113(4)	0.0196(6)
O5	0.3892(3)	0.3017(4)	0.8487(4)	0.0187(6)
O6	0.3496(4)	−0.1280(4)	0.9392(4)	0.0186(6)
O7	0.5691(3)	0.0942(4)	0.6622(4)	0.0161(5)
O8	0.7093(4)	0.4047(4)	0.7787(5)	0.0242(6)
H8	0.6679	0.4998	0.7785	0.029*
O9	0.0498(4)	0.3627(5)	0.8626(6)	0.0351(8)
H9A	0.087(8)	0.448(6)	0.783(8)	0.042*
H9B	−0.050(2)	0.382(9)	0.856(9)	0.042*
O10	0.2894(4)	−0.4014(5)	0.6363(5)	0.0253(7)
H10A	0.269(7)	−0.449(7)	0.529(5)	0.030*
H10B	0.302(7)	−0.503(4)	0.703(7)	0.030*

Table 5. Fractional atomic coordinates and displacement parameters for **4**. U_{eq} according to Fischer & Tillmanns (1988). For the H atoms U_{iso} is shown.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U_{iso}^*
Zn1	0.0000	1.0000	0.5000	0.01189(9)
Zn2	0.56648(5)	0.83563(4)	−0.28120(3)	0.01121(7)
Zn3	0.03487(5)	0.74835(4)	0.33276(3)	0.01262(7)
Zn4	0.79614(5)	0.61741(4)	0.02418(3)	0.01098(7)
Zn5	0.47974(5)	0.50656(4)	0.30231(3)	0.01042(7)
As1	0.26611(4)	0.71834(3)	0.02669(3)	0.00818(6)
As2	−0.01832(4)	0.60900(3)	0.68564(3)	0.00767(6)
As3	0.49781(4)	0.79540(3)	−0.57659(3)	0.00838(6)
O1	0.0071(3)	0.7622(2)	0.53227(19)	0.0120(4)
O2	0.4844(3)	0.6004(2)	0.0918(2)	0.0115(4)
O3	0.3342(3)	0.8418(2)	−0.1370(2)	0.0140(4)
O4	0.5158(3)	0.7214(2)	−0.3999(2)	0.0117(4)
O5	0.3837(3)	0.6753(3)	0.3856(2)	0.0176(4)
O6	0.1423(3)	0.8335(2)	0.1272(2)	0.0155(4)
O7	0.1139(3)	0.6047(2)	0.0125(2)	0.0126(4)
O8	0.6651(3)	1.0272(2)	−0.4061(2)	0.0121(4)
O9	0.8184(3)	0.7032(2)	−0.2005(2)	0.0111(4)
O10	0.7966(3)	0.4860(2)	0.2493(2)	0.0123(4)
O11	−0.2757(3)	0.8205(3)	0.3202(2)	0.0149(4)
O12	0.1343(3)	0.5193(2)	0.3402(2)	0.0127(4)
O13	−0.0277(3)	1.0369(3)	0.2912(2)	0.0148(4)
H13A	−0.141(3)	1.063(4)	0.256(3)	0.018*
H13B	0.049(4)	1.097(3)	0.227(3)	0.018*
O14	0.7220(4)	0.8542(3)	0.0304(3)	0.0225(5)
H14A	0.766(5)	0.941(2)	−0.014(3)	0.027*
H14B	0.735(5)	0.858(3)	0.1108	0.027*

$\text{Cd}_{1.25}\text{Zn}_{0.75}(\text{HAsO}_4)_2 \cdot 2\text{H}_2\text{O}$. It seemed possible that in sample **3** one alluaudite-like compound is also present but, because of very small quantities and low crystallinity, its unambiguous identification based on XRPD measure-

ments was not possible. The XRPD pattern of **4** shows the presence of synthetic adamite, $\text{Zn}_2(\text{AsO}_4)(\text{OH})$, monoclinic $(\text{C}_6\text{H}_{11}\text{N}_2)_2[\text{CdBr}_4]$ and small amount of the solved crystal structure phase $\text{Zn}_9(\text{AsO}_4)_6 \cdot 4\text{H}_2\text{O}$.

Table 6. Selected bond distances (Å) for **1**.

Cd1—O1	2.239(4)	Cd3—O4	2.235(3)	As2—O6	1.673(3)
Cd1—O1 ⁱ	2.239(4)	Cd3—O6	2.273(3)	As2—O5 ^v	1.681(3)
Cd1—O3 ⁱ	2.292(3)	Cd3—O1	2.278(4)	As2—O4 ^{vi}	1.695(3)
Cd1—O3	2.292(3)	Cd3—O3 ⁱ	2.299(4)	As2—O7	1.698(3)
Cd1—O7 ⁱ	2.333(3)	Cd3—O5	2.345(3)	⟨As2—O⟩	1.687
Cd1—O7	2.333(3)	Cd3—O10	2.399(4)		
⟨Cd1—O⟩	2.288	⟨Cd3—O⟩	2.305		
M2—O9	2.205(4)	As1—O1	1.669(3)		
M2—O6 ⁱⁱ	2.217(3)	As1—O3 ^{iv}	1.673(3)		
M2—O4	2.232(3)	As1—O2	1.677(3)		
M2—O5 ⁱⁱ	2.256(3)	As1—O8	1.723(3)		
M2—O2	2.266(4)	⟨As1—O⟩	1.685		
M2—O10 ⁱⁱⁱ	2.375(4)				
⟨Cd2—O⟩	2.258				
M2=Cd2 _{0.83} Ni2 _{0.17}					

Symmetry codes: (i) $-x + 1, y, -z + 3/2$; (ii) $-x + 3/2, y + 1/2, -z + 3/2$; (iii) $-x + 3/2, -y + 3/2, -z + 2$; (iv) $-x + 1, -y + 1, -z + 1$; (v) $-x + 3/2, y - 1/2, -z + 3/2$; (vi) $x, -y + 1, z - 1/2$.

Hydrogen bonds

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> —H... <i>A</i>	<i>D</i> ... <i>A</i>
O8—H8...O7 ⁱⁱ	0.82	1.84	175	2.657(5)
O9—H9B...O7 ^{viii}	0.85	1.98	149	2.735(5)
O9—H9A...O8 ⁱ	0.85	1.94	169	2.776(5)
O10—H10B...O2 ⁱⁱⁱ	0.85	2.09	149	2.851(5)
O10—H10A...O2 ^x	0.85	1.86	163	2.677(5)

Symmetry codes: (i) $-x + 1, y, -z + 3/2$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $x, -y + 1, z + 1/2$; (viii) $x, y + 1, z$; (x) $-x + 3/2, y - 1/2, -z + 3/2$.

2.4. Scanning electron microscopy/Energy-dispersive spectroscopy (SEM/EDS)

Elemental analysis was performed using a JEOL JSM-6610 LV scanning electron microscope (SEM) with thermic wolfram cathode, equipped with secondary- and backscattered-electron-detectors and EDS, EBSD and cathodoluminescence under high vacuum.

The investigated single-crystals were mounted on carbon tape attached to Al-sample holder and analysed using a 15 kV accelerating voltage and an accumulation time of 20 s. As a qualitative measure, EDS confirmed the presence of Cd, Ni, As and O in **1**, Cd, Co, As and O in **2**, Cd, Zn, As and O in **3**, and Zn, As and O in **4** (Table 10).

The measured concentrations of Ni in **1** are somewhat higher than the value observed by XRD, implying various chemical compositions of different single crystals. In spite of the differences of the local chemical composition, the ratio of (Cd + Ni) : As has been preserved close to 1.25 (ranged from 1.12 to 1.25). The same holds for the single crystals of **2** which show variable chemical composition from crystal to crystal. However, the ratio of (Cd + Co): as has been preserved close to 1.16 (ranged from 1.05 to 1.18). Since no SEM-EDS analysis was done on the structurally determined single-crystal, the chemical formula of **2** resulting from the structural analysis must not be directly compared to the results of the SEM-EDS investigations.

2.5. Vibrational spectroscopy

Fourier-transform infrared (FTIR) absorption single-crystal infrared spectra of **2** and **3** were recorded on a Bruker Tensor 27 FTIR spectrophotometer with a mid-IR glowbar light source and KBr beam splitter, attached to a Hyperion 2000 FTIR microscope with liquid nitrogen-cooled mid-IR broad band MCT detector. A total of 128 scans were accumulated between 4000 and 550 cm⁻¹ with a 100 µm diameter circular sample aperture and ATR 15× objective.

The Raman spectrum of a randomly oriented single crystal of **3** was measured with a Renishaw RM1000 notch filter-based micro-Raman system in the spectroscopic range from 4000 to 60 cm⁻¹. The 632.8 nm excitation line of a He–Ne ion laser was used. The crystal was focused with a 50×/0.75 objective on the crystal faces of the single crystals. Raman intensities were collected with a thermo-electrically cooled CCD array detector. The spectra were acquired with a nominal exposure time of 30 s (resolution: 4–5 cm⁻¹; mode: continuous grating scan mode, 1200 lines/mm grating).

The single-crystal Raman spectra of **1**, **2** and **4** were collected using a Horiba LabRAM HR Evolution system equipped with a Si-based, Peltier-cooled CCD detector in the spectral range 4000–60 cm⁻¹. The 633 nm excitation line of a He–Ne ion laser was focused with a 50×/0.9 objective on the crystal faces of the randomly oriented single crystals. The sample spectra were acquired with a

Table 7. Selected bond distances (Å) for **2**.

Cd1—O12 ⁱ	2.231(11)	M4—O7 ^{vi}	2.101(14)	As1—O3	1.684(14)
Cd1—O12	2.231(11)	M4—O7	2.101(15)	As1—O3 ^{xi}	1.684(13)
Cd1—O11	2.318(11)	M4—O1	2.119(12)	As1—O1	1.685(12)
Cd1—O11 ⁱ	2.318(11)	M4—O1 ^{vi}	2.119(12)	As1—O1 ^{xi}	1.685(12)
Cd1—O6 ⁱ	2.793(15)	M4—O6 ^{vii}	2.140(12)	⟨As1—O⟩	1.685
Cd1—O6	2.793(15)	M4—O6 ^{viii}	2.140(12)		
⟨Cd1—O⟩	2.447	⟨M4—O⟩	2.120	As2—O2 ^{vi}	1.673(12)
				As2—O2	1.673(12)
Cd2—O11 ⁱ	2.355(11)	Co5—O11 ^{viii}	2.060(12)	As2—O4 ^{vi}	1.720(17)
Cd2—O11 ⁱⁱⁱ	2.355(11)	Co5—O10 ^{xiii}	2.082(11)	As2—O4	1.720(17)
Cd2—O12	2.409(11)	Co5—O6 ^{viii}	2.087(11)	⟨As2—O⟩	1.697
Cd2—O12 ^{iv}	2.409(11)	Co5—O1	2.095(14)		
Cd2—O5 ⁱⁱⁱ	2.65(2)	Co5—O9	2.120(11)	As3—O9	1.664(11)
Cd2—O5	2.65(2)	Co5—O4 ^{viii}	2.127(16)	As3—O5	1.686(11)
⟨Cd2—O⟩	2.471	⟨Co5—O⟩	2.095	As3—O11	1.696(11)
				As3—O7	1.732(15)
M3—O5 ^{ix}	2.164(12)	Co6—O5 ^{ix}	2.069(11)	⟨As3—O⟩	1.695
M3—O5 ^x	2.164(12)	Co6—O3 ^{xiv}	2.077(14)		
M3—O2	2.174(12)	Co6—O12 ^{xiv}	2.092(16)	As4—O10	1.663(11)
M3—O2 ^{xi}	2.174(12)	Co6—O2 ^{xi}	2.107(12)	As4—O6	1.671(11)
M3—O8 ^{xi}	2.206(16)	Co6—O9 ^{xiv}	2.108(11)	As4—O12	1.677(16)
M3—O8	2.206(16)	Co6—O10	2.126(14)	As4—O8	1.711(16)
⟨M3—O⟩	2.181	⟨Co6—O⟩	2.097	⟨As4—O⟩	1.681

M3=Cd₃_{0.35}Co₃_{0.65}M4=Cd₄_{0.17}Co₄_{0.83}

Symmetry codes: (i) $-x+1, y, -z+1$; (ii) $x, y, z+1$; (iii) $x, y, z-1$; (iv) $-x+1, y, -z$; (v) $x+1/2, y-1/2, z$; (vi) $-x, y, -z+1$; (vii) $x-1/2, y-1/2, z$; (viii) $-x+1/2, y-1/2, -z+1$; (ix) $-x+1/2, y+1/2, -z+1$; (x) $x-1/2, y+1/2, z-1$; (xi) $-x, y, -z$; (xii) $x-1/2, y+1/2, z$; (xiii) $-x+1/2, y-1/2, -z$; (xiv) $-x+1/2, y+1/2, -z$.

Hydrogen bonds

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> —H... <i>A</i>	<i>D</i> ... <i>A</i>
O4—H4...O7	0.82	1.84	135	2.49(2)
O7—H7...O4	0.82	1.69	166	2.49(2)
O8—H8...O3	0.82	1.65	163	2.449(17)
O3—H3...O8	0.82	1.74	144	2.449(17)

nominal exposure time of 2×5 s (confocal mode, Olympus grating 1800 lines/mm, 1.5 μ m lateral resolution, approximately 3 μ m depth resolution).

3. Results and discussion

3.1. Influence of the synthesis conditions on the phase formation

In nature, oxosalts of arsenic are formed either by weathering of the primary ores or by hydrothermal processes. Therefore, the synthesis of mineral-related arsenates is mostly performed under hydrothermal conditions. The current research has shown that the moderate pH values (pH=3–6) with additional arsenic acid provides the ideal mixture to grow suitable good-quality single crystals of most mineral-related arsenates or new arsenate structures in the CdO—MO—As₂O₅—H₂O (M =Mg²⁺, Mn^{2+,3+}, Fe^{2+,3+}, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺) system. The molar ratios of the Cd and M reagents did not have a major influence on the outcome of the syntheses, nor did the synthesis time. The greatest influence in this respect can be attributed to arsenic acid and water; the

arsenic acid reagent has the greatest influence as it controls the pH of the mixture, which in turn influences the solubility of the other reagents. H₂O as the major transporting agent during hydrothermal synthesis also plays an important part and indeed, the best crystals were obtained when large amounts of water were used (filling volume >80 %).

In exploratory ionothermal syntheses in the M1O—M2O—As₂O₅—(H₂O) ($M1$ =Cd²⁺, Ba²⁺; $M2$ =Mg²⁺, Mn^{2+,3+}, Fe^{2+,3+}, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺) system, the ionic liquid emimBr (1-ethyl-3-methylimidazolium bromide) was tested as the solvent and template for arsenate synthesis. The ionic liquid emimBr possesses several properties that make it worthy of further study. Like many ionic liquids, it has a wide liquid range (despite being a solid at room temperature, with a melting point of 83 °C), low vapour pressure (meaning that there is no pressure build up during heating, which alleviates some of the safety concerns of hydrothermal synthesis) and it has been used extensively for ionothermal synthesis, because it is a relatively polar solvent that dissolves framework precursors. The ionic liquid emimBr is rather hygroscopic, meaning that there is always a small amount of water

Table 8. Selected bond distances (Å) for **3**.

Cd1—O2	2.248(3)	Cd2—O10	2.082(4)	As1—O2	1.671(3)
Cd1—O5	2.268(3)	Cd2—O4 ⁱⁱⁱ	2.114(3)	As1—O4	1.672(3)
Cd1—O2 ⁱ	2.286(3)	Cd2—O6	2.121(3)	As1—O3 ^{vi}	1.687(3)
Cd1—O9	2.288(4)	Cd2—O7	2.131(3)	As1—O1	1.731(3)
Cd1—O3	2.310(3)	Cd2—O3	2.207(3)	⟨As1—O⟩	1.690
Cd1—O6	2.330(3)	Cd2—O7 ^v	2.209(3)	As2—O5	1.663(3)
⟨Cd1—O⟩	2.288	⟨M2—O⟩	2.144	As2—O7	1.673(3)
				As2—O6 ⁱⁱⁱ	1.675(3)
				As2—O8	1.729(3)
				⟨As2—O⟩	1.685

Symmetry codes: (i) $-x, -y, -z + 2$; (ii) $x, y, z - 1$; (iii) $-x + 1, -y, -z + 2$; (iv) $x, y + 1, z$; (v) $-x + 1, -y, -z + 1$; (vi) $x, y, z + 1$; (vii) $-x + 1, -y + 1, -z + 2$; (viii) $-x, -y, -z + 3$; (ix) $x, y + 1, z + 1$; (x) $-x, -y + 1, -z + 2$; (xi) $x + 1, y, z$; (xii) $x - 1, y, z$; (xiii) $x, y - 1, z$; (xiv) $x, y - 1, z - 1$.

Hydrogen bonds. For comparison, less probable hydrogen bonds are given in italics

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D—H...A</i>	<i>D...A</i>
O1—H1...O3 ⁱ	0.82	2.186	148.28	2.915(4)
<i>O1—H1...O10ⁱ</i>	<i>0.82</i>	<i>2.473</i>	<i>122.32</i>	<i>2.993(4)</i>
O8—H8...O4 ⁱⁱ	0.82	1.805	150.81	2.552(4)
O9—H9A...O10 ^{viii}	0.85	2.216	151.62	2.992(4)
<i>O9—H9A...O1ⁱ</i>	<i>0.85</i>	<i>2.478</i>	<i>129.20</i>	<i>3.086(5)</i>
O9—H9B...O8 ^{iv}	0.85	2.007	166.64	2.840(5)
O10—H10A...O8 ^{vi}	0.85	2.128	143.37	2.856(5)
<i>O10—H10A...O^{viii}</i>	<i>0.85</i>	<i>2.642</i>	<i>134.03</i>	<i>3.290(5)</i>
O10—H10B...O5 ^v	0.85	1.819	163.48	2.645(5)
<i>O10—H10B...O9^v</i>	<i>0.85</i>	<i>2.547</i>	<i>113.80</i>	<i>2.992(5)</i>

Symmetry codes: (i) $-x, -y + 1, -z + 2$; (ii) $-x + 1, -y + 1, -z + 2$; (iv) $x - 1, y, z$; (v) $x, y - 1, z$; (vi) $-x + 1, -y, -z + 1$; (vii) $x, y + 1, z$; (viii) $x, y - 1, z - 1$.

present in the system, even when the ionic liquid is heated to drive off the water added with the arsenic acid starting material. However, it is not as thermally stable as some other ionic liquids. It has been shown to decompose under vacuum at temperatures in excess 220–260 °C.

The ionothermal syntheses in the system CdO–M2O–As₂O₅ were performed at temperatures ranging between 120 and 220 °C. When using CdO, M2-hydroxide and As₂O₅ as the starting reagents at 120, 140, 160 and 180 °C, in each synthesis run a monoclinic polymorph of the organic–inorganic hybrid compound (C₆H₁₁N₂)₂[CdBr₄] was obtained besides already known arsenates (*i.e.* Zn₂(AsO₄)(OH), Zn₃(AsO₄)₂, Cd_{1.16}Zn_{2.34}(AsO₄)_{1.5}–(HAsO₄)(H₂AsO₄)_{0.5}, Mn-arsenates and Cd–Mn arsenates) as one of the synthesis products. At temperatures above 200 °C, in only one synthesis run at 220 °C, the tetragonal polymorph of (C₆H₁₁N₂)₂[CdBr₄] (Đorđević *et al.*, 2016b) crystallized. Above 220 °C emimBr is not stable anymore and the ionothermal synthesis is not possible.

Single crystals of **2** could be synthesized using water, as well as emimBr as the solvent. However, the best results in terms of larger crystal size (approximately 30 % longer than in hydrothermal synthesis) and shorter synthesis time were obtained when adding just small amounts of water in the ionothermal system (emimBr to water ratio ~6:1). At low water concentration, the strong hydrogen bonding of the water molecules in ionic liquids leads to water being less reactive than similar amounts in other solvents, which

would cause the different chemistry of ionothermal condition in contrast to the routine hydro/solvothermal conditions (Morris, 2009). Furthermore, the pressure developed in the reaction increases in a linear manner with the amount of added water. However, addition of even a very small amount of water sometimes resulted in very high pressure. This effect was also encountered in ionothermal synthesis using microwave radiation, when adding of just small amounts of water (few drops) causes the breakdown of the ionic liquid and the explosion of the Teflon liners, even at temperatures lower than 160 °C. Microwave heating is known to promote the breakdown of ionic liquids, which is most likely related to sudden local overheating (hotspots), when the ionic liquid is breaking down to pyridine (Wragg *et al.*, 2009).

Besides monoclinic [C₆H₁₁N₂]₂[CdBr₄], synthesis in the system CdO/ZnO/As₂O₅ using emimBr as the solvent at 140 °C yielded synthetic adamite, Zn₂(AsO₄)(OH) and phase **4**. This is the first report on the synthesis of Zn-arsenates using ionothermal synthesis.

3.2. Description of the crystal structures

3.2.1. Cd_{0.65}Ni_{0.35}(AsO₄)₂(HAsO₄)₂·4H₂O (**1**) and sainfeldite–miguelromeroite mineral group

The compound **1** is isostructural with minerals of the sainfeldite–miguelromeroite series, Ca₅(AsO₄)₂(HAsO₄)₂·4H₂O–Mn₅(AsO₄)₂(HAsO₄)₂ (Ferraris & Abbona, 1972; Stock *et al.*, 2002; Kampf, 2009). These minerals adopt

Table 9. Selected bond distances (Å) for **4**.

As1—O6	1.674(2)	Zn1—O13	2.068(2)	Zn4—O2	2.0754(19)
As1—O7	1.6859(19)	Zn1—O13 ^{vii}	2.068(2)	Zn4—O7 ^{ix}	2.0820(19)
As1—O3	1.688(2)	Zn1—O1	2.083(2)	Zn4—O9	2.118(2)
As1—O2	1.7013(19)	Zn1—O1 ^{vii}	2.083(2)	Zn4—O7 ^x	2.121(2)
⟨As1—O⟩	1.687	Zn1—O8 ⁱⁱⁱ	2.225(2)	Zn4—O14	2.130(2)
		Zn1—O8 ^{viii}	2.225(2)	Zn4—O10	2.177(2)
As2—O10 ⁱ	1.672(2)	⟨Zn1—O⟩	2.125	⟨Zn4—O⟩	2.116
As2—O12 ⁱⁱ	1.6790(19)				
As2—O1	1.701(2)	Zn2—O3	1.891(2)	Zn5—O5	1.930(2)
As2—O9 ⁱⁱⁱ	1.7211(19)	Zn2—O8	1.943(2)	Zn5—O4 ^x	1.973(2)
⟨As2—O⟩	1.695	Zn2—O9	1.975(2)	Zn5—O2	1.999(2)
		Zn2—O4	1.9773(19)	Zn5—O10	2.0494(19)
As3—O11 ^{iv}	1.6590(19)	⟨Zn2—O⟩	1.948	Zn5—O12	2.2409(19)
As3—O5 ^v	1.670(2)			⟨Zn5—O⟩	2.038
As3—O8 ^{vi}	1.699(2)	Zn3—O6	1.987(2)		
As3—O4	1.7003(19)	Zn3—O12	2.025(2)		
⟨As3—O⟩	1.682	Zn3—O1	2.0377(19)		
		Zn3—O11	2.041(2)		
		Zn3—O5	2.393(2)		
		Zn3—O13	2.476(2)		
		⟨Zn3—O⟩	2.160		

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y+1, -z+1$; (iii) $x-1, y, z+1$; (iv) $x+1, y, z-1$; (v) $x, y, z-1$; (vi) $-x+1, -y+2, -z-1$; (vii) $-x, -y+2, -z+1$; (viii) $-x+1, -y+2, -z$; (ix) $x+1, y, z$; (x) $-x+1, -y+1, -z$.

Hydrogen bonds

$D-H\cdots A$	$D-H$	$H\cdots A$	$D-H\cdots A$	$D\cdots A$
O13—H13A $\cdots$ O3 ^{xiv}	0.86(1)	1.81(1)	162(3)	2.641(3)
O13—H13B $\cdots$ O9 ^{viii}	0.86(1)	2.14(2)	138(3)	2.837(3)
O14—H14A $\cdots$ O6 ^{viii}	0.86(1)	2.15(1)	177(3)	3.006(3)
O14—H14B $\cdots$ O11 ^{ix}	0.86(1)	2.02(1)	165(1)	2.850(3)

Symmetry codes: (viii) $-x+1, -y+2, -z$; (ix) $x+1, y, z$; (xiv) $-x, -y+2, -z$.

Table 10. Results of EDS analysis for compounds **1–4**, in at%.

1 — $\text{Cd}_{4.75}\text{Ni}_{0.25}(\text{AsO}_4)_2(\text{HAsO}_4)_2 \cdot 4\text{H}_2\text{O}$				
Point	O	As	Cd	Ni
1	74.30	12.27	10.30	3.14
2	76.05	10.35	10.79	2.80
2 — $\text{Cd}_{0.75}\text{Co}_{2.75}(\text{H}_2\text{O}_{0.5}\text{AsO}_4)_2(\text{HAsO}_4)_2$				
Point	O	As	Co	Cd
1	63.23	17.26	11.51	8.00
2	61.34	19.63	13.25	5.78
3	61.08	18.40	17.26	2.87
4	65.74	16.31	12.56	5.39
3 — $\text{Cd}_{1.25}\text{Zn}_{0.75}(\text{HAsO}_4)_2 \cdot 2\text{H}_2\text{O}$				
Point	O	As	Cd	Zn
1	66.11	17.46	10.13	6.30
2	66.64	17.91	10.64	5.81
4 — $\text{Zn}_9(\text{AsO}_4)_6 \cdot 4\text{H}_2\text{O}$				
Point	O	As	Zn	
1	66.32	13.17	20.5	
2	64.58	13.83	21.59	

hureaulite structure type, named after the mineral hureaulite, $\text{Mn}_5(\text{PO}_4)_2(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}$, the phosphate analogue of miguelromeroite (Menchetti & Sabelli, 1973; Gatta *et al.*, 2016). The structure of **1** is equivalent with the structure of

previously reported undoped pentacadmiumdihydrogentetrakis(arsenate) tetrahydrate, $\text{Cd}_5(\text{AsO}_4)_2(\text{HAsO}_4)_2 \cdot 4\text{H}_2\text{O}$ (Johnson *et al.*, 2003). The hureaulite structure type is characterized by clusters of five edge-sharing $M^{\text{II}}\text{O}_6$ (M^{II} = divalent cation) octahedra, *i.e.* pentamers. In **1**, these pentamers are linked into a framework by sharing corners with octahedra in adjacent pentamers, as well as with AsO_4 and HAsO_4 tetrahedra (Fig. 2). As expected, lattice parameters of **1** are similar to that of previously reported arsenates adopting hureaulite structure type (Table 11). As a rule, the increase of unit-cell volumes directly follows the increase of the ionic radii of divalent cations M^{II} .

Three crystallographically distinct, octahedrally coordinated divalent cations ($M1$, $M2$, $M3$) are present in the structure. $M1$ is placed at the half-occupied special position on the two-fold axis and the other two are in general positions ($M2$ and $M3$). The $M1$ and $M3$ sites are fully occupied by Cd, while $M2$ is occupied by 83 % Cd and 17 % Ni. The average $\langle\text{Cd—O}\rangle$ distances are 2.288, 2.258 and 2.305 Å for Cd1O_6 , $(\text{Cd}_{2.83}\text{Ni}_{0.17})\text{O}_4(\text{OH}_2)_2$ and Cd3O_6 octahedra, respectively. The Cd1—O distances range from 2.239(4) to 2.332(3) Å, Cd3—O distances vary from 2.235(4) to 2.399(4) Å, while the $\text{Cd}_{2.83}\text{Ni}_{0.17}\text{—O}$ distances are slightly shorter due to substitution of Cd2 by smaller Ni2 and range from 2.205(4) to 2.375(4) Å (Table 6).

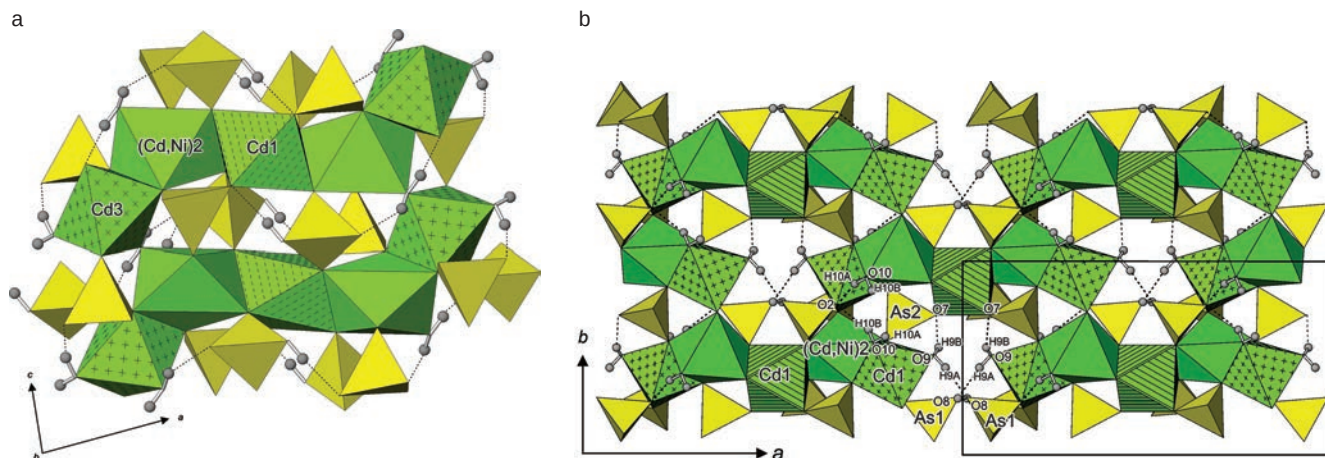


Fig. 2. The linkage of octahedral pentamers in the projection along the [010] (a); Projection of the structure of **1** along the [001]. The pentamers connected by AsO_4 and HAsO_4 tetrahedra together with hydrogen bonds (b).

Table 11. Comparison of unit-cell parameters for arsenates with hureaulite-type structures.

Chemical composition	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	<i>V</i> (Å ³)	References
$(\text{Mn}_{4.57}\text{Zn}_{0.32}\text{Ca}_{0.08})(\text{AsO}_4)_2(\text{HAsO}_4)_2 \cdot 4\text{H}_2\text{O}$	18.015(5)	9.261(2)	9.770(3)	96.238(7)	1620.35	Kampf (2009)
$\text{Mn}_5(\text{AsO}_4)_2(\text{HAsO}_4)_2 \cdot 4\text{H}_2\text{O}$	18.030(1)	9.2715(5)	9.7756(5)	96.266(2)	1624.38	Kampf (2009)
$\text{Mn}_5(\text{AsO}_4)_2(\text{HAsO}_4)_2 \cdot 4\text{H}_2\text{O}$	18.1090(40)	9.3323(19)	9.8092(19)	96.172(4)	1648.13	Stock <i>et al.</i> (2002)
$(\text{Cd}_{0.65}\text{Ni}_{0.35})_5(\text{AsO}_4)_2(\text{HAsO}_4)_2 \cdot 4\text{H}_2\text{O}$	18.375(4)	9.5395(19)	9.977(2)	96.19(3)	1738.63	This work
$\text{Cd}_5(\text{AsO}_4)_2(\text{HAsO}_4)_2 \cdot 4\text{H}_2\text{O}$	18.382(2)	9.7192(13)	9.9791(13)	96.369(3)	1771.85	Johnson <i>et al.</i> , (2003)
$\text{Ca}_5(\text{AsO}_4)_2(\text{HAsO}_4)_2 \cdot 4\text{H}_2\text{O}$	18.7810(70)	9.820(4)	10.191(4)	97.02(5)	1865.43	Ferraris & Abbona (1972)

The pentamer, as primary building unit, is formed by five octahedra sharing edges according to the sequence $(\text{Cd}_{2.83}\text{Ni}_{2.17})\text{O}_4(\text{OH}_2)_2\text{—Cd}_3\text{O}_6\text{—Cd}_1\text{O}_6\text{—Cd}_3\text{O}_6\text{—}(\text{Cd}_{2.83}\text{Ni}_{2.17})\text{O}_4(\text{OH}_2)_2$. This indicates that Ni has a preference for the peripheral $\text{Cd}_{2.83}\text{Ni}_{2.17}$ site at the margin of the pentamer (Fig. 2). The central Cd_1O_6 octahedron in pentamer shares all six of its oxygen atoms with adjacent AsO_4 tetrahedra and two Cd_3O_6 octahedra through two edges.

The Cd_3O_6 octahedron shares five of its oxygen atoms with adjacent AsO_4 tetrahedra and CdO_6 octahedra through two edges and one corner. The sixth vertex is occupied by oxygen O10 from the water molecule bridging Cd3 and $\text{Cd}_{2.83}\text{Ni}_{2.17}$. The peripheral $(\text{Cd}_{2.83}\text{Ni}_{2.17})\text{O}_4(\text{OH}_2)_2$ octahedron shares four of its oxygen atoms with adjacent AsO_4 tetrahedra. Two of them also belong to adjacent Cd_3O_6 octahedra through one edge and one corner.

The two water molecules are both coordinated to $(\text{Cd}_{2.83}\text{Ni}_{2.17})$, with oxygen O9 of one water molecule exclusively coordinated to $(\text{Cd}_{2.83}\text{Ni}_{2.17})$ and oxygen O10 of the other water molecule bridging $(\text{Cd}_{2.83}\text{Ni}_{2.17})$ and Cd3 from the adjacent pentamer (Fig. 3). Each pentamer is joined by two corners (O4, O10) to the neighbouring pentamers. Additionally, the cations are bridged by arsenate groups.

The As cations are situated in two distinct tetrahedral sites, forming HAsO_4 and As_2O_4 tetrahedra. Each tetrahedron shares vertices with adjacent octahedra, while

the OH group is involved in hydrogen bonding and links two tetrahedra. The As1—OH bond is as expected considerably longer [1.723(4) Å] than other As—O distances, which range from 1.669(4) to 1.677(3) and from 1.673(4) to 1.698(3) in HAsO_4 and As_2O_4 , respectively. The average $\langle\text{As—O}\rangle$ distances are 1.686 and 1.687 Å for HAsO_4 and As_2O_4 , respectively.

The oxygen O8 from OH group acts as a hydrogen-bond donor to O7 and as a hydrogen-bond acceptor from the water molecule. The hydrogen bond $\text{O8—H8}\cdots\text{O7}$ is quite short [$\text{O8—O7}=2.657(5)$ Å], almost linear ($\text{O8—H8}\cdots\text{O7}=175^\circ$) and the strongest hydrogen bond in **1**. Two oxygen atoms, O9 and O10, from two water molecules act as double bond donors toward O7 and O8, as well as two symmetry equivalents of O2, respectively. The donor–acceptor distances are in the range 2.677(5)–2.851(5) Å, which indicate the presence of strong to middle strong hydrogen bonds.

Bond-valence calculations show that the Cd—O and As—O bond lengths are consistent with the presence of Cd^{2+} , As^{5+} and O^{2-} . Taking into account the contribution of non-hydrogen atoms only, the oxygens that are involved in hydrogen bonding are undersaturated: 1.63(2) for double acceptor O2, 1.52(2) for double acceptor O7, 1.13(4) for single donor and acceptor O8, 0.41(8) for double donor O9 and 0.54(7) v.u. for double donor O10. The other values are very close to the nominal valence of 2+.

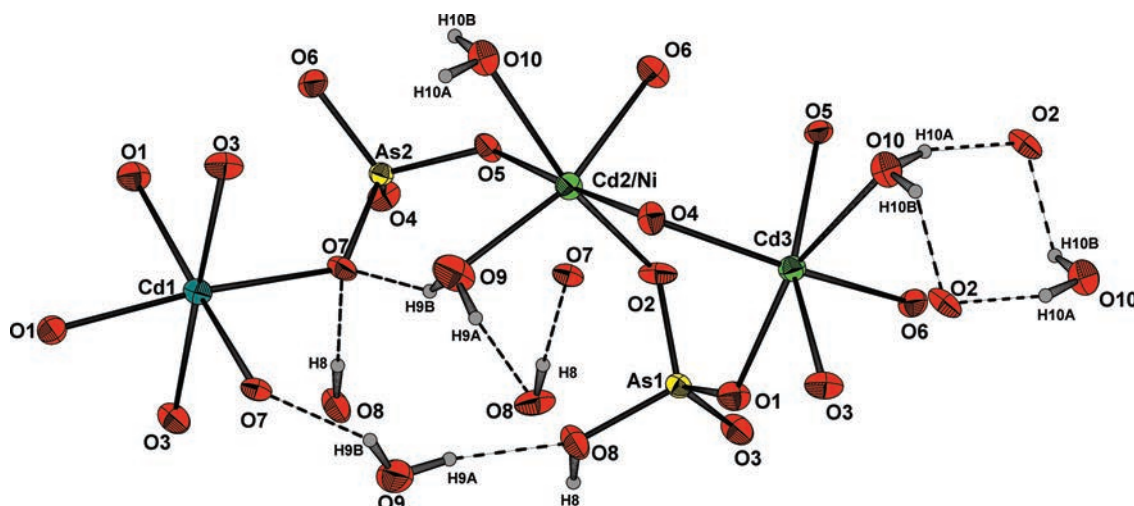


Fig. 3. Perspective view of **1** with ellipsoids of ADP (50% probability), hydrogen bonds and atomic labelling scheme.

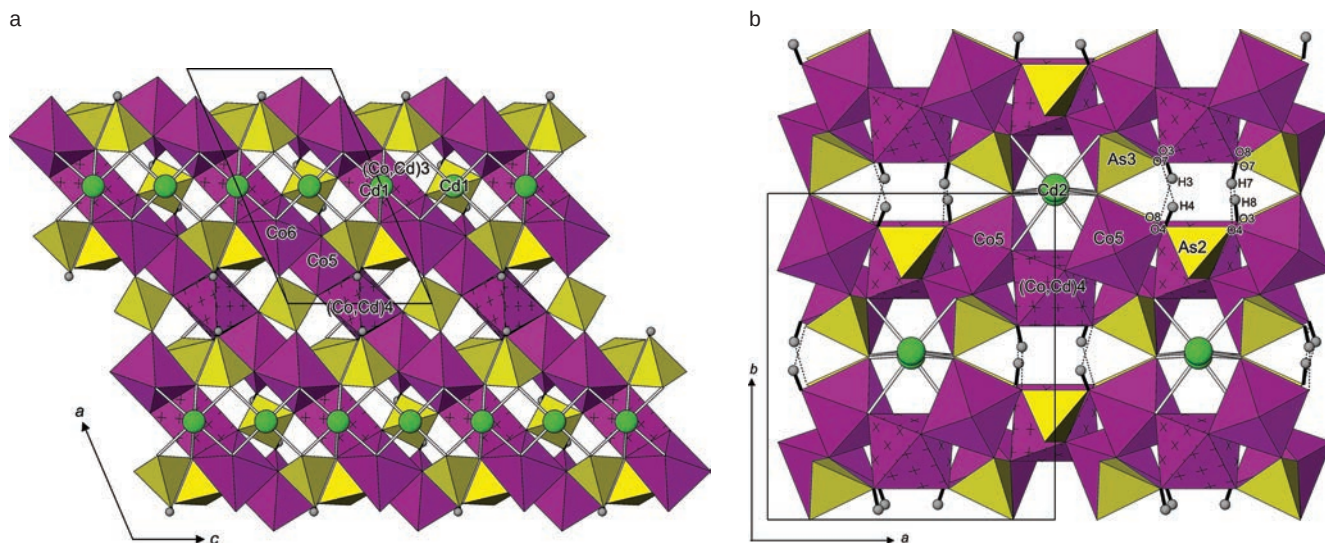


Fig. 4. The layer in the structure **2** parallel to the (010) plane. The octahedral chains [magenta are for $\text{Co}_2\text{O}_{10}(\text{H}_{0.5})_2$ octahedral pairs and magenta hachured for the mixed site coordination octahedra $\text{M3O}_4(\text{H}_{0.5})_2$ and $\text{M4O}_4(\text{H}_{0.5})_2$, [$\text{M3} = \text{Cd}_{3.0.35}\text{Co}_{3.0.65}$, $\text{M4} = \text{Cd}_{4.0.17}\text{Co}_{4.0.83}$] running parallel to (101) planes with arsenate groups and Cd and H atoms (a) and three adjacent layers of the structure **2** approximately along [001] and in between them Cd and H atoms in channels 2 and 1, respectively (b). The half of hydrogen atoms is arbitrary omitted in order to illustrate their half-occupied positions.

3.2.2. $\text{Cd}_{0.75}\text{Co}_{2.75}(\text{H}_{0.5}\text{AsO}_4)_2(\text{HAsO}_4)$ (**2**) and the alluaudite mineral group

Compound **2** is a member of the alluaudite-like arsenates that crystallize in the monoclinic space group *C2* (Stojanović *et al.*, 2012). The core of the alluaudite-like structure **2** is kinked octahedral chains of variously distorted edge-sharing octahedra running in the [101] direction (Fig. 4a). The chains contain edge-sharing $\text{Co}_2\text{O}_{10}(\text{H}_{0.5})_2$ octahedral pairs, which further share opposite edges with adjacent $\text{M3O}_4(\text{H}_{0.5})_2$ and $\text{M4O}_4(\text{H}_{0.5})_2$ mixed-cation octahedra ($\text{M3} = \text{Cd}_{3.0.35}\text{Co}_{3.0.65}$, $\text{M4} = \text{Cd}_{4.0.17}\text{Co}_{4.0.83}$). The octahedra sequence in the chain is $\text{Co}_5\text{O}_6\text{H}_{0.5}-\text{Co}_6\text{O}_6\text{H}_{0.5}-(\text{Cd}_{3.0.35}\text{Co}_{3.0.65})\text{O}_4(\text{OH}_{0.5})_2-\text{Co}_6\text{O}_6\text{H}_{0.5}-\text{Co}_5\text{O}_6\text{H}_{0.5}-\text{Cd}_{4.0.17}\text{Co}_{4.0.83}\text{O}_4(\text{OH}_{0.5})_2-\text{Co}_5\text{O}_6\text{H}_{0.5}$. These octahedra are

linked by four $(\text{H}_{0.5})_2\text{As1O}_4$, $(\text{H}_{0.5})_2\text{As2O}_4$, $\text{H}_{0.5}\text{As3O}_4$ and $\text{H}_{0.5}\text{As4O}_4$ tetrahedra into layers, which are normal to the *b*-axis. The adjacent layers are connected by sharing corners to form a heteropolyhedral 3D framework, which generates two crystallographically distinct types of parallel channels along [001] (Fig. 4b). All hydrogens are involved in the strong hydrogen-bonding in channel 1, while the Cd1 and Cd2 atoms are situated in channel 2.

Both Cd1 and Cd2 atoms are positioned on neighbouring two-fold axes in partially occupied special positions. These $\text{Cd}_{1.0.76}\square_{0.24}$ and $\text{Cd}_{2.0.24}\square_{0.76}$ cation sites are characterized by incomplete occupation and positional disorder. Both Cd1 and Cd2 atoms have six O ligands at shorter (Cd1–O distances ranging from 2.231(11) to 2.793(15) Å and Cd2–O vary from 2.355(11) to 2.65(2) Å) and

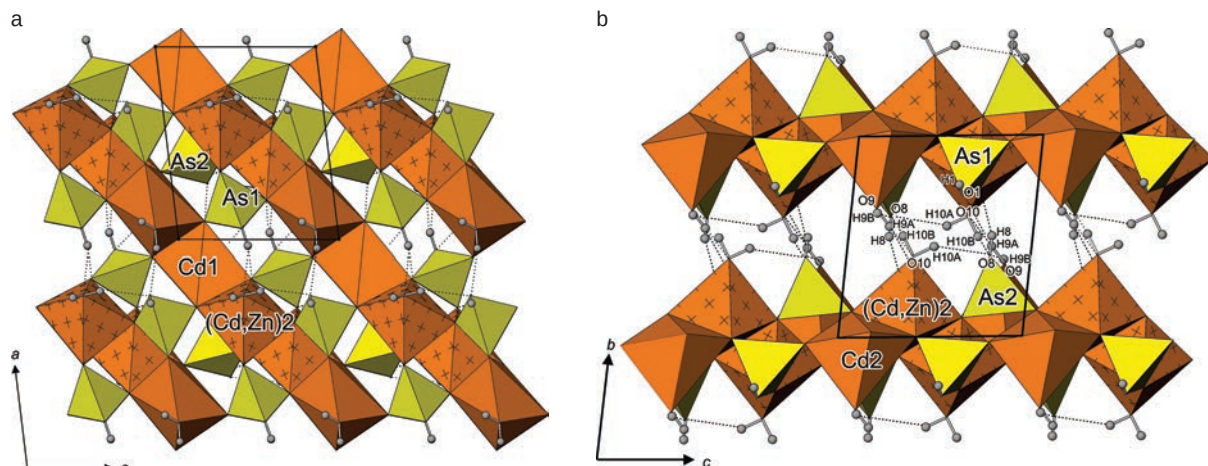


Fig. 5. The polyhedral view of the structure **3** along (a) [010] and (b) [100]. The octahedral chains are connected by HAsO_4 tetrahedra together with H-bonds involving both water molecules and OH groups.

four and six, respectively, at very long distances. The contribution from each very long bond to bond valence sum is less than 3% each.

Different cation distributions were found in mixed sites: $M3$ is occupied by Cd3/Co3 with proportions 0.35/0.65 and $M4$ with proportions 0.17/0.83. The obtained $\text{Cd}_{0.35}\text{Co}_{0.65}\text{—O}$ and $\text{Cd}_{0.17}\text{Co}_{0.83}\text{—O}$ distances are shorter due to the considerable substitution of Cd by smaller Co and range from 2.164(12) to 2.206(16), ($\langle M3\text{—O} \rangle = 2.181$) and from 2.101(15) to 2.140(12), ($\langle M4\text{—O} \rangle = 2.120$) Å, respectively. In $\text{Co}_2\text{O}_{10}(\text{H}_{0.5})_2$ octahedral pairs, the Co5—O distances range from 2.060(12) to 2.127(16) ($\langle \text{Co5—O} \rangle = 2.095$), while Co6—O distances vary from 2.069(11) to 2.126(14) ($\langle \text{Co6—O} \rangle = 2.097$) Å (Table 7).

Each As, situated in a slightly deformed tetrahedron, shares common O atoms and OH groups from octahedral chains and link them. Two As cations are situated on the two-fold axis in special positions and two in general sites forming $(\text{H}_{0.5})_2\text{As1O}_4$, $(\text{H}_{0.5})_2\text{As2O}_4$, $\text{H}_{0.5}\text{As3O}_4$ and $\text{H}_{0.5}\text{As4O}_4$ tetrahedra. The As—OH bonds are expectedly longer than As—O distances, except As1—OH3 [1.684(13) Å], probably because of structure disorder.

Two pairs of hydroxyl groups, OH3 and OH8 as well as OH4 and OH7, act as hydrogen-bond donors and acceptors to each other. Each OH group acts as a hydrogen-bond donor toward the oxygen O from neighbouring layer.

The structural formula is in agreement with bond-valence. Bond valence sum for Cd1^{2+} , Cd2^{2+} , $(\text{Cd}_{0.35}\text{Co}_{0.65})^{2+}$, $(\text{Cd}_{0.17}\text{Co}_{0.83})^{2+}$, Co^{5+} , Co^{6+} , As1^{5+} , As2^{5+} , As3^{5+} and As4^{5+} ions are as expected. The Cd1^{2+} and Cd2^{2+} are undersaturated indicating not fully occupied positions and significant disorder in the channel **2** [1.76 for Cd1 and 1.38 v.u. for Cd2]. Taking into account the contribution of non-hydrogen atoms only, the oxygens that are involved in hydrogen bonding are undersaturated: [1.60 for O3, 1.45 for O4, 1.47 for O7 and 1.48 v.u. for O8]. The other values are very close to the nominal valence of 2+.

3.2.3. $\text{Cd}_{1.25}\text{Zn}_{0.75}(\text{HAsO}_4)_2 \cdot 2\text{H}_2\text{O}$ (**3**) and the mineral fluckite

Compound **3** is isostructural with the mineral fluckite, $\text{CaMn}(\text{HAsO}_4)_2 \cdot 2\text{H}_2\text{O}$ (Catti *et al.*, 1980). Fluckite is the intermediate member between haidingerite, $\text{Ca}(\text{HAsO}_4) \cdot \text{H}_2\text{O}$, and krautite, $\text{Mn}(\text{HAsO}_4) \cdot \text{H}_2\text{O}$. The octahedral–tetrahedral structure is built up of octahedral chains extending parallel to $(10\bar{1})$ planes similar to the octahedral chains in **2** (Fig. 5a).

Between these edge-linked octahedral chains lie HAsO_4 tetrahedra, which bond adjacent chains into layers sharing common vertices. These layers are positioned parallel to the (010) plane and are connected to each other only by interlayer hydrogen bonds (Fig. 5b).

There are two distinct octahedrally coordinated cationic sites: one is fully occupied by Cd1 and the other shows mixed occupancy by Cd2/Zn2 in the proportion 0.25/0.75. Thus the compound contains two types of octahedra, $\text{Cd1O}_5(\text{OH}_2)$ and $(\text{Cd}_{0.25}\text{Zn}_{0.75})\text{O}_5(\text{OH}_2)$. Sharing common edges they form octahedral pairs $\text{Cd1}_2\text{O}_8(\text{OH}_2)_2$ and $(\text{Cd}_{0.25}\text{Zn}_{0.75})_2\text{O}_8(\text{OH}_2)_2$. These octahedral pairs are further linked by edges, forming chains in $\text{Cd1}_2\text{O}_8(\text{OH}_2)_2\text{—}(\text{Cd}_{0.25}\text{Zn}_{0.75})_2\text{O}_8(\text{OH}_2)_2\text{—Cd1}_2\text{O}_8(\text{OH}_2)_2$ sequence. The Cd1—O distances range from 2.248(3) to 2.330(3) Å ($\langle \text{Cd1—O} \rangle = 2.288$ Å), while the Cd2/Zn2—O distances are shorter due to substitution of Cd2 by smaller Zn2, they range from 2.082(4) to 2.209(3) Å ($\langle \text{Cd2/Zn2—O} \rangle = 2.144$ Å, Table 8). Four of the oxygen atoms, O2, O3, O6 and O7, are trigonally coordinated between cations of two metals and one As, while O4 and O5 are bicoordinated between one metal and one As.

The As cations are situated in two distinct tetrahedral sites, forming HAsO_4 tetrahedra. These HAsO_4 tetrahedra are linked to octahedral chains sharing common vertices and, together with intralayer $\text{O—H}\cdots\text{O}$ hydrogen bonds, define the connectivity within the layers. Each HAsO_4 tetrahedron shares three oxygens with adjacent octahedra, while OH groups are involved in hydrogen

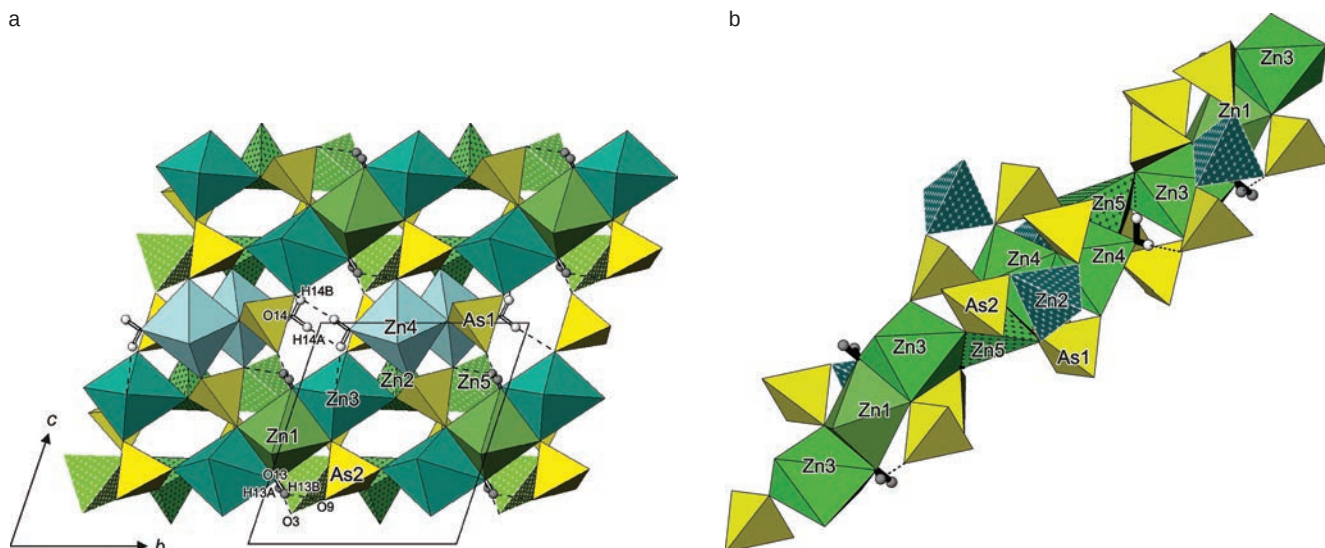


Fig. 6. Crystal structure of **4** viewed along [100] (a) and zigzag chain of edge-sharing Zn-polyhedra along [111] (b).

bonding. The As—OH bonds (1.729(3) and 1.730(3) Å in As1O₃OH and As2O₃OH, respectively) are as expected considerably longer than As—O distances, which range from 1.663(3) to 1.676(3) Å and from 1.671(3) to 1.686(3) Å in HAs1O₄ and HAs2O₄, respectively. Both hydroxyl groups (OH1, OH8) and water molecules (H₂O9, H₂O10) form O—H...O hydrogen bonds. The OH1 group acts as a hydrogen-bond donor to O3. The hydrogen bond O1—H1...O3 is weak intralayer hydrogen bond. The other OH8 group acts as a hydrogen-bond donor toward O4 located in the adjacent layer, forming strong interlayer hydrogen bond (*D*...*A* distance is 2.552 (4) and *D*—H...*A* angle is 151°). Two oxygens from water molecules, O9 and O10, are double bond donors toward O10 and O8, as well as O8 and O5, respectively. Each of them forms one intralayer (O9—H9B...O8 and O10—H10A...O8) and one interlayer (O9—H9A...O10 and O10—H10B...O5) hydrogen bonds. All are somewhat bent (*D*—H...*A* angles are 143–167°). There are additionally four considerably bent (*D*—H...*A* angles are 122, 129, 134 and 114°) and slightly elongated hydrogen bonds (O1—H1...O10, O9—H9A...O1, O10—H10A...O1 and O10—H10B...O9), which indicates the possible existence of bifurcated hydrogen bonds.

Neglecting the contribution from the hydrogen bonds, the bond-valence sum for oxygens O1 and O8 from hydroxyl group as well as O9 and O10 from water molecules are considerably undersaturated (Σv_{ij} is 1.10 (5), 1.11(5), 0.35(8) and 0.52(5) v.u., respectively), while O4 and O5 oxygen atoms, which are coordinated to only one metal site and one As and act as hydrogen-bond acceptors, are somewhat undersaturated (Σv_{ij} is 1.77(1) and 1.72(1) v.u., respectively).

3.2.4. $\text{Zn}_9(\text{AsO}_4)_6 \cdot 4\text{H}_2\text{O}$ (**4**)

The phase **4** presented in this study is the example of a synthetic zinc orthoarsenate hydrate that is not known as a mineral. For the first time **4** was synthesized ionother-

mally, as reported here. This zinc arsenate hydrate presents a previously known structure (Feng *et al.*, 1997; Jansen *et al.*, 1998) but, until now, the H positions of water molecules have not been determined. Here, H atoms of water molecules were detected in the electron density map and included into the structural model. It is interesting to notice that the compound $\text{Zn}_4\text{Fe}^{\text{II}}_5(\text{PO}_4)_6 \cdot 4\text{H}_2\text{O}$ adopts the same type of structure (Schmidt & Kniep, 1992) as **4**.

Besides three unique arsenic tetrahedra, AsO₄, the crystal structure of **4** contains three Zn atoms in octahedral [$\text{Zn1O}_4(\text{OH}_2)_2$, Zn3O_6 and $\text{Zn4O}_5(\text{OH}_2)$], one in trigonal bipyramidal (Zn5O_5) and one in tetrahedral (Zn2O_4) coordination (Fig. 6). Only Zn1 is placed on the special position (0, 0, 1/2). The oxygen atoms O3, O6 and O11 are bicoordinated between one Zn and one As, while the remaining O atoms are trigonally coordinated between two Zn and one As cations. Sharing common edges, polyhedra around Zn form zigzag chains in $\text{Zn1O}_4(\text{OH}_2)_2$ – Zn3O_6 – Zn5O_5 – $\text{Zn4O}_5(\text{OH}_2)$ – $\text{Zn4O}_5(\text{OH}_2)$ – Zn5O_5 – Zn3O_6 – $\text{Zn1O}_4(\text{OH}_2)_2$ sequence (Fig. 6b). The chains are running approximately along the [111] direction and are interconnected *via* clusters of AO_4 (*A* = As, Zn2) tetrahedra and hydrogen bonds. The As—O distances range from 1.659(2) to 1.721(2) Å. The Zn—O distances in $\text{Zn1O}_4(\text{OH}_2)_2$, Zn3O_6 and $\text{Zn4O}_5(\text{OH}_2)$ octahedra vary from 2.068(2) to 2.225(2), from 1.987(2) to 2.476(2) and from 2.075(2) to 2.177(2) Å, respectively. In trigonal bipyramidal and in tetrahedral geometry they range from 1.930(2) to 2.241(2) and from 1.891(2) to 1.977(2) Å in Zn5O_5 and Zn2O_4 , respectively (Table 9).

Two water molecules (H₂O13, H₂O14) are situated in channels along [101] direction and form O—H...O hydrogen bonds (Fig. 6a). One water oxygen atom, O13, bridges the two metals, Zn1 and Zn3, while O14 is coordinated to only one metal atom, Zn4. Both oxygens from water molecules, O13 and O14, are double bond donors toward O3 and O9, as well as O6 and O11,

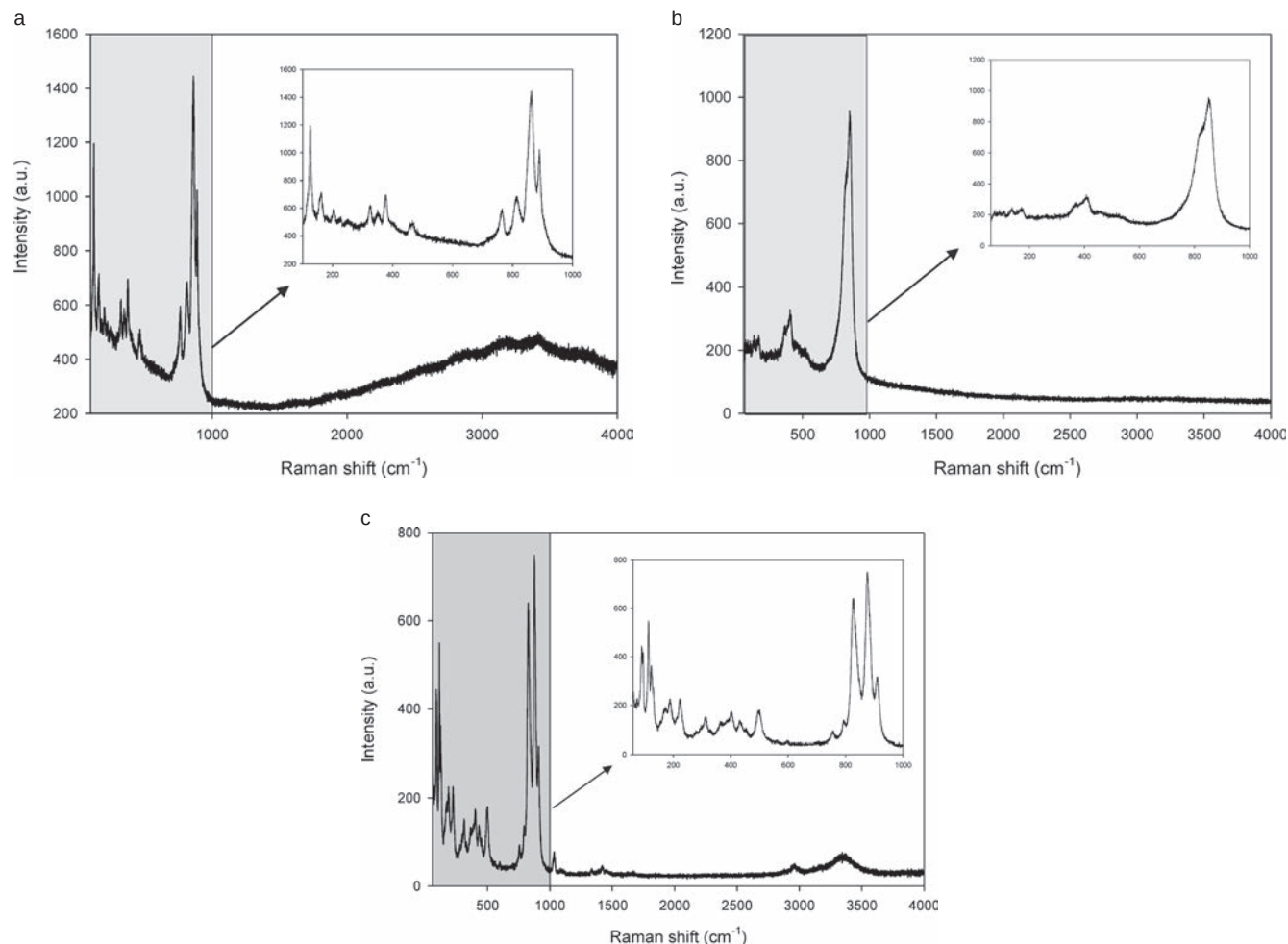


Fig. 7. Raman spectra of **1** (a), **2** (b) and **4** (c).

respectively. Hydrogen bonds (O13—H13A...O3, O13—H13B...O9, O14—H14A...O6, O14—H14B...O1) are rather bent [$D-H\cdots A$ angles are 138(3)–177(4)°].

Neglecting the contribution from the hydrogen bonds, the bond-valence sum for two oxygens from water molecules, O13 and O14, are considerably undersaturated as expected, (Σv_{ij} are 0.50(8) and 0.32(8) v.u., respectively), while O3, O9, O6 and O11 oxygen atoms, which act as a hydrogen-bond acceptors, are slightly undersaturated (Σv_{ij} are 1.841(8), 1.940(3), 1.75(1) and 1.74(1) v.u., respectively). The donor–acceptor distances are 2.641(3)–3.008(3) Å, which indicate the presence of middle to weak hydrogen bonds.

3.3. Raman and infrared spectra

Raman spectra are shown in Fig. 7. They reflect the complexity of the crystal structures. Bands in the high-energy range (2800–3800 cm^{-1}) are assigned to stretching of O—H bonds of hydroxyl groups. Bands in the 100–1200 cm^{-1} range are caused by either internal vibration of AsO_4 tetrahedra, or due to external vibrational modes.

Based on the d – ν correlation for hydrogen bonds (Libowitzky, 1999), our Raman-shift values observed in the O—H stretching region are in very good agreement with the refined O—H...O bond lengths ranging between 2.675(5) and 2.851(5) Å for **1** (corresponding Raman bands obtained between 2100 and 3750 cm^{-1}). For **2**, the infrared spectral region between 3500 and 1000 cm^{-1} shows a peculiar increase in “background absorption” (Fig. 8), which is a typical feature of compounds with very short, *i.e.* very strong hydrogen bonds [*e.g.* $\text{Cd}_{1.16}\text{Zn}_{2.34}(\text{AsO}_4)_{1.5}(\text{HAsO}_4)(\text{H}_2\text{AsO}_4)_{0.5}$ and $\text{Cd}_{0.74}\text{Mg}_{2.76}(\text{AsO}_4)_{1.5}(\text{HAsO}_4)(\text{H}_2\text{AsO}_4)_{0.5}$ (Stojanović *et al.*, 2012)]. The hydrogen bonds in **2** range from 2.449(2) to 2.491(2) Å and the infrared spectrum shows the presence of broad O—H stretching and bending vibrations centred around 3215, 2388/1395 cm^{-1} . In compound **3**, ten hydrogen bonds of various lengths (from strong to weak) are present and this is reflected by the band positions in the Raman and infrared spectra. In the Raman spectra of **3**, the O—H stretching modes vary between 2000 and 3800 cm^{-1} and in the infrared spectra of **3**, the numerous O—H stretching modes are present between 2000 and 3900 cm^{-1} . In the OH stretching region of **4**, two bands

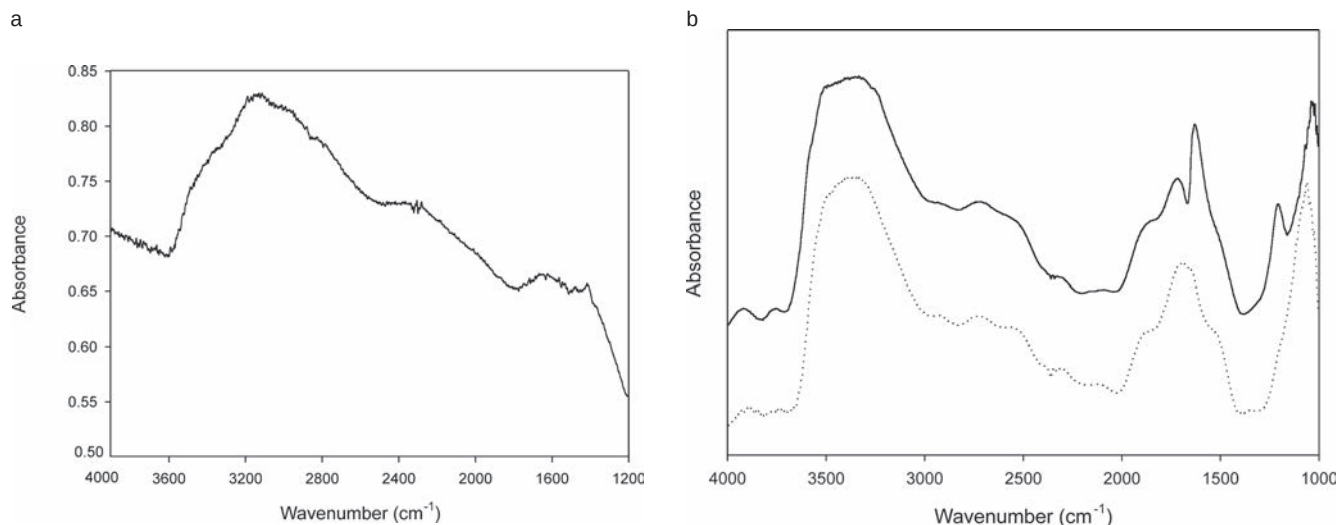


Fig. 8. Single-crystal infrared spectra of **2** (a) and **3** parallel (bold line) and perpendicular (broken line) to the elongation of the needle-like crystal (b).

centred around 2963 and 3347 cm^{-1} reflect the presence of the middle strong to weak hydrogen bonds ($\text{O}\cdots\text{O} = 2.641(3)\text{--}3.008(3)\text{ \AA}$) in **4**.

In all arsenates presented in this study, bands in the 700–1000 cm^{-1} range are assigned to symmetric and antisymmetric stretching modes of the $(\text{AsO}_4)^{3-}$ groups, whereas internal bending vibrations of these tetrahedra are observed below 550 cm^{-1} , there partially overlapped by various external modes. For all substances studied, the AsO_4 stretching bands have comparable Raman shifts. The most intense Raman bands were observed at around 889, 861, 814 and 763 cm^{-1} for **1**, 849 and 818 cm^{-1} for **2**, 871, 838, 804 and 764 cm^{-1} for **3**, 910, 878, 830 and 794 cm^{-1} for **4**. These Raman-shift values are in excellent agreement with the published data for the synthetic cadmium-arsenate members of the descloizite-group minerals, $\text{CdCo}(\text{AsO}_4\text{OH})$ and $\text{CdCu}(\text{AsO}_4)(\text{OH})$ (Đorđević *et al.*, 2016a).

4. Conclusion

This research has confirmed that synthesis of mineral-related arsenates with cadmium and/or transition metals by low-temperature hydrothermal or ionothermal method can yield structures with interesting crystal chemical properties, such as short hydrogen bond lengths, where oxygen atoms are alternately hydrogen bonding donors and acceptors to each other. We also first present the use of the ionic liquids as the solvent in the arsenate synthesis. The successful preparation of the mineral-related arsenates in ionic liquids used as the solvent (not also a template) demonstrates not only that many more mineral-related and other arsenates could be obtained but also that the ionothermal method is a promising method to synthesize new kinds of environmentally relevant materials. It was also shown that metal-arsenates are not fully structurally defined. The additional investigation of metal

arsenates with cadmium would lead to full knowledge of which topologies are likely to form under which conditions. Knowing the crystal-structural features of Cd and Zn containing arsenates, one can predict their stabilization in contaminated soils, sediments, or drainage ponds. The synthesis of these phases brought us one step further to the understanding of how the ions behave in each other's presence under differing laboratory conditions (*e.g.* pH, type of solvent, concentration, temperature), which could be directly or indirectly transposed to the environmental conditions.

Furthermore, permanent research of arsenic containing compounds should be carried out because of potentially appealing features of these compounds and since arsenic is recognized to be one of the most lethal chemical elements for our environment.

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