An update on the mineral-like Sr-containing transition metal arsenates

Tamara Đorđević1* and Ljiljana Karanović2

1Institut für Mineralogie und Kristallographie, Universität Wien, Althanstr. 14, A-1090 Wien, Austria; and 2Laboratory of Crystallography, Faculty of Mining and Geology, Dušina 7, 11000 Belgrade, Serbia.

Abstract
We report on the crystal structures of three novel synthetic SrM-arsenates (M = Ni and Fe3+), isostructural or structurally related to the minerals from tsumcorite, carminite and brackebuschite groups. They were synthesised under mild hydrothermal conditions and further characterised using single-crystal X-ray diffraction (SXRD), scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) and Raman spectroscopy. SXRD and SEM-EDS yielded formulae: (I) SrNi2(AsO4)2·2H2O, (II) Sr1.4Fe1.6(AsO4)2(OH)1.6 and (III) SrFe3+(AsO4)2(AsO3OH). All three structures are built up of slightly distorted MO6 octahedra and AsO4 tetrahedra that are linked by Sr2+ with different coordination geometries and hydrogen bonds. I represent a basic structure type typical for tsumcorite-group minerals (space group C2/m) while II has a new intermediate structure between carminite, PbFe3+(AsO4)2(OH)2 and arsenbrackebuschite, Pb3Fe5+(AsO4)2(OH) (s.g. Pm). III is triclinic and adopts a new structure-type (s.g. P1). The structure of I is built up of infinite linear edge-sharing NiO6 octahedral chains, extending along [010] and linked by AsO4 tetrahedra, SrO8 polyhedra and hydrogen bonds. The structure of II is characterised by the carminite-like FeO4(OH)2 octahedral chains and Edshammar-polyhedral chains, which involves SrO11 coordination polyhedra similar to that of PbO11 in arsenbrackebuschite. Both chains in II are aligned parallel to the b axis of the monoclinic unit cell and connected together by the arsenate AsO4 tetrahedra, SrO8 polyhedra and the hydrogen-bonding network. The compound III has a new type of crystal structure based on the unusual corrugated octahedral–tetrahedral-quadruple chains. These are made up of a central double-sided chain linked to two single-sided chains into a quadruple chain extended along the a axis. The chains in III are built up of FeO6 octahedra and AsO4 tetrahedra further linked to each other by shared vertices. The quadruple chains are interconnected by additional AsO4 tetrahedra forming a heteropolyhedral 3D open framework. Strontium atoms are situated in the two channels. The structural connections to related minerals and inorganic compounds are discussed.

Keywords: metal arsenates, crystal structure, single-crystal X-ray diffraction, hydrothermal synthesis, Raman spectroscopy, environmentally relevant compounds, arsenic

Introduction
Even though it is well known that arsenic is one of the most naturally abundant toxic metalloids, many crystal structures of arsenic oxosalts remain either undetermined or only poorly determined. This causes misunderstandings of their behaviour in various environmental media, such as soils, sediments and waters because it requires detailed knowledge of thermodynamic properties and, in particular, of formation conditions of arsenic phases and their respective crystal structures (O’Day, 2006; Drahota and Filippi, 2009). Furthermore, the crystal chemistry of transition-metal arsenates and phosphates reveals an interesting field of research for both mineralogists and solid-state researchers. Many natural or synthetic phosphates, arsenates and vanadates are of great interest due to their structural variability. In combination with the different oxidation states of some transition metals, there is a great variety of ternary and quaternary compounds. They can foster potential applications and original physical properties such as magnetism, heterogeneous catalysis, ion exchange, optics or thermal expansion (de Pedro et al., 2011; Đorđević et al., 2018 and references therein). In this context, the preparation, crystal structures, spectroscopic behaviour and some physical properties of numerous alkali-, alkali-earth and transition-metal arsenic oxosalts have been investigated (Đorđević and Karanović, 2018 and references therein).

In the present contribution we are reporting on the preparation, description of the crystal structures, and spectroscopic investigation of the three novel strontium arsenates, I-SrNi2(AsO4)2·2H2O, II-Sr1.4Fe1.6(AsO4)2(OH)1.6 and III-SrFe3+(AsO4)2(AsO3OH). Compound I, SrNi2(AsO4)2·2H2O, is isostructural with the monoclinic members of the tsumcorite-group minerals and inorganic compounds (space group C2/m with Z = 2). Furthermore, it is the first compound synthesised and described in the SrO–NiO–As2O3–H2O system. Compound II, Sr1.4Fe1.6(AsO4)2(OH)1.6, has a new crystal structure, which is an intermediate between carminite- (PbFe3+(AsO4)2(OH)2; Kharisun et al., 1996) and arsenbrackebuschite-type (Pb3Fe5+(AsO4)2(OH); Hofmeister and Tillmanns, 1978) structures. Compound III, SrFe3+(AsO4)2(AsO3OH)
Compounds I–III were synthesised using low-temperature hydrothermal methods. The following reagents were used in stoichiometric quantities: Sr(NO$_3$)$_2$ (Sigma-Aldrich, 243426, 500 g), As$_2$O$_5$ (Alfa Products 87687, >99.9%), Ni(OH)$_2$ (Sigma-Aldrich, S58362-518, 250 g) and FeCl$_2$·4H$_2$O (Fluka 44939, 250 g).

The mixtures were transferred into polytetrafluoroethylene autoclaves and heated under autogenous pressure under the following heating and cooling conditions: the mixtures were heated from room temperature to 220°C (4 h), held at that temperature for 48 h, and cooled to room temperature (96 h). After cooling the pH values were measured as 3 for I, and 1 for II and III. The reaction products were filtered and washed several times using distilled water.

Compound I crystallised as a light green glassy-like fragment (Fig. 1) up to 0.15 mm long (yield ca. 60%) accompanied by green needles of SrNiAs$_2$O$_7$ (unpublished work) (yield ca. 40%). II crystallised as ruby red octahedra (yield ca. 20%) up to 120 μm long together with the colourless prisms of III, up to 0.2 mm long (yield ca. 80%) (Fig. 1).

Single-crystal X-ray diffraction

The intensity data for I and III were collected on a Nonius Kappa CCD single-crystal four-circle diffractometer (MoKα 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). A single-crystal of II was studied on a STOE StadiVari diffractometer with open Eulerian cradle, dual-beam source (sealed-tube and microfocus source) and Dectris PILATUS 300K pixel detector. Data collection for II was performed with X-AREA (Stoe, 2013), cell refinement was done using X-AREA (Stoe, 2013) and data reduction was performed with X-RED (Stoe, 2013). Single-crystal X-ray diffraction data were collected at ambient conditions, integrated and corrected for Lorentz and polarization factors and absorption by scaling of partial multi-scans. The structures of I, II and III were solved by direct methods using SHELXT (Sheldrick, 2015a) and WinGX (Farrugia, 2012). The coordinates and the anisotropic displacement parameters for all non-hydrogen atoms were refined by full-matrix least-squares methods based on F$^2$ values by SHELXL (Sheldrick, 2015b).

For I anisotropic displacement parameters were allowed to vary for all atoms, except the hydrogen atoms. Hydrogen atoms from water molecules were located in the difference-Fourier map and refined using a riding model where $U_{	ext{iso}}$(H) = 1.5$U_{	ext{eq}}$(O) and with DFIX distance restraints for O–H = 0.85 Å and H...H = 1.37 Å.

For II the initially determined orthorhombic unit cell typical for the carminite structure type [$a = 16.500(3)$, $b = 7.5457(15)$, $c = 12.227(2)$ Å, $V = 1522.4(5)$ Å$^3$ and $Z = 8$] gave high values for R-factors and weighting scheme parameters. The electron density observed was higher than desired at two of the O atom positions from the OH groups (O6 and O7), but lower at the Fe sites. Using the known model of carminite, the residual electron density could not explain such high values. Therefore, a new model was developed in space group P1, with the same lattice parameters. An additional symmetry check indicated that the smaller monoclinic cell [$a = 9.0719(15)$, $b = 12.227(2)$, $c = 7.5457(15)$ Å, $b = 114.575(6)$, $V = 761.2(2)$ Å$^3$ and $Z = 4$] and the Pm space group is more appropriate and the unit cell was transformed using the matrix $[\frac{1}{2} \frac{1}{2} 0 / 0 0 1 / 0 1 0]$. All atoms in the monoclinic unit cell are situated in general 2c positions excluding Sr21, Sr22, As11–As14, O21–O24, O31–O34 and mixed sites Sr61/O61–Sr64/O64, which are in special positions 1a and 1b on the mirror planes (site symmetry $m$) at $y = 0$ and $y = \frac{1}{2}$, respectively. The structure was refined as an inversion twin. The obtained Flack parameter $x = 0.570(18)$ indicate equivalence inversion twins. The transformation to monoclinic symmetry gave more than satisfactory results. The final difference-Fourier map showed no unusual features or spurious peaks around the refined positions of the atoms. The highest peak ($\Delta\rho_{\text{max}} = 0.65$ e$^{-3}$) in the map was found 0.80 Å from O11.
In order to find out how many octahedral vacancies are present, it was necessary to refine the site occupancies of four iron atoms, Fe11–Fe14, in the unit cell. The refinement of iron site occupancies showed that the Fe11 and Fe12 sites are more iron deficient than Fe13 and Fe14, which are almost fully occupied (63 and 97%, respectively). This explains the observed lower electron density at the iron position in the initially determined orthorhombic unit cell. Therefore, a simple constraint using free variables was applied: the same site occupancy was refined for Fe11 and Fe12 atoms and oxygens O61, O62 and O71 from additional partly occupied Sr sites of very low occupancy (ca. 10% of available sites), denoted as Sr81 and Sr82 and separated from Sr71 atoms was found, resulting in the appearance of two additional partly occupied Sr sites refined as identical.

In the latter cycles of refinement the presence of disordered Sr71 atoms was found, resulting in the appearance of two additional partly occupied Sr sites of very low occupancy (ca. 10% of available sites), denoted as Sr81 and Sr82 and separated from Sr71 by a distance of only 0.728(6) and 0.697(5) Å, respectively. Similarly, the Sr72 position is also partly occupied and disordered, showing Sr atoms greater than expected for oxygen atoms and explains the higher electron density at positions O6 and O7 in the initially determined orthorhombic unit cell. The atomic coordinates and atomic displacement parameters of the Sr and corresponding O atoms in mixed Sr/O sites were refined as identical.

### Table 1. Crystal data, data collection and refinement details for I–III.

|     | I       | II       | III      |
|-----|---------|----------|----------|
| **Crystal data** |         |          |          |
| Chemical formula | \( \text{As}_2\text{H}_4\text{Ni}_2\text{O}_{12}\text{Sr} \) | \( \text{As}_2\text{H}_4\text{Fe}_{11,0}\text{O}_{10,0}\text{Sr}_{1,4} \) | \( \text{As}_2\text{HFe}_4\text{O}_{12} \) |
| \( M_r \) | 518.91  | 517.08   | 422.32   |
| Crystal system, space group | Monoclinic, \( \text{C}2/\text{m} \) | Monoclinic, \( \text{P}2 \) | Triclinic, \( \text{P}1 \) |
| Temperature (K) | 298     | 295      | 298      |
| \( a, b, c \) (Å) | 9.173(3), 6.2025(12), 7.562(3) | 9.0719(15), 12.2272(15), 7.5457(15) | 6.6379(13), 9.6849(19), 12.666(3) |
| \( \alpha, \beta, \gamma \) (°) | 90, 114.41(2), 90 | 90, 114.57(6), 90 | 90, 114.57(6), 90 |
| \( V \) (Å\(^3\)) | 391.8(2) | 761.2(2) | 741.8(3) |
| \( Z \) | 2       | 2        | 4        |
| Radiation type | \( \text{MoK} \lambda = 0.71073 \text{Å} \) | \( \text{MoK} \lambda = 0.71073 \text{Å} \) | \( \text{MoK} \lambda = 0.71073 \text{Å} \) |
| \( \mu \) (mm\(^{-1}\)) | 19.97   | 21.45    | 18.01    |
| Crystal size (mm) | 0.03 × 0.02 × 0.01 | 0.03 × 0.02 × 0.01 | 0.02 × 0.02 × 0.03 |
| **Data collection** |         |          |          |
| Diffractometer | Nonius Kappa CCD | STOE StadiVari diffractometer | Nonius Kappa CCD |
| Absorption correction | Multi-scan | Multi-scan | Multi-scan |
| No. of measured, independent and observed \( | \( | \) > 2σ(| \( | \) |) \) | 1116, 606, 536 | 18131, 4785, 4001 | 5166, 2590, 2042 |
| **Refinement on \( F^2 \)** |         |          |          |
| No. of reflections | 5186, 4785, 2590 | 5186, 4785, 2590 | 5186, 4785, 2590 |
| No. of refined parameters | 48 | 18 | 1 |
| Hydrogen site location | Difference-Fourier map | Inferred from neighbouring sites | Inferred from neighbouring sites |
| H-atom treatment | H atoms refined using DFIX distance restraints with \( O-H = 0.85 \text{Å} \) and \( U_{eq}(O) = 1.5U_{eq}(\text{Sr}) \) | H atoms placed in geometrically calculated positions and refined using DFIX distance restraints with \( O-H = 0.85 \text{Å} \) and \( U_{eq}(O) = 1.5U_{eq}(\text{Sr}) \) | H atoms placed in geometrically calculated positions and refined using the riding model \( (\text{AFIX} 83) \) with \( O-H = 0.82 \text{Å} \) and \( U_{eq}(H) = 1.5U_{eq}(O) \) |
| Weighting | \( w = 1/[\sigma(F^2)^2 + (0.0186F^2)^2] + 3.637\text{P} \) | \( w = 1/[\sigma(F^2)^2 + (0.0178F^2)^2 + 1.8268\text{P}] \) | \( w = 1/[\sigma(F^2)^2 + (0.0388F^2)^2 + 25.0224\text{P}] \) |
| \( \Delta \rho_{\text{max}}, \Delta \rho_{\text{min}} \) (e Å\(^{-3}\)) | 1.05, -0.88 | 0.65, -1.01 | 1.52, -1.24 |
| Absolute structure | Referred as an inversion twin | – | – |
| Absolute structure parameter, \( x \) | – | – | – |
| Extinction coefficient, \( k \) | 0.0017(5) \(^5\) | \( k = \frac{\sigma(F^2)}{[\sigma(F^2)^2 + (0.001 \times F^2)^2 \times \sin(20)]} \) |

\(^5\)
Table 2. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²) for I.

|   | x          | y          | z          | U(eq)  |
|---|------------|------------|------------|--------|
| Sr1 | 0          | ½          | 0          | 0.0205(2) |
| As1 | −0.41918(7) | ½          | −0.22558(9) | 0.01074(18) |
| Ni1 | ¼          | ¼          | ½          | 0.0131(2) |
| O1  | 0.3267(5)  | 1          | 0.3814(8)  | 0.0230(11) |
| O2  | 0.3056(5)  | ½          | 0.3556(6)  | 0.0163(9) |
| O3  | −0.3310(3) | 0.7745(5)  | −0.2685(4) | 0.0176(6) |
| O4  | −0.2833(6) | ½          | 0.0045(7)  | 0.0304(12) |
| H1  | 0.413(2)   |            | 0.365(3)   | 0.034*  |
| H2  | 0.253(3)   | 1          | 0.265(4)   | 0.034*  |

For III all non-hydrogen atoms excluding Sr2, which displays an extremely high degree of positional disorder, were initially refined anisotropically. The refinement in the lowest symmetry space group P1 did not provide an ordered structure. However, in space group P1 two disordered Sr2 atoms in the unit cell appear distributed among 12 positions. Two pairs of sites were related by the pseudo-inversion centre, but the remaining eight were not. This means that Sr2 is distributed among at least 10 positions in P1, i.e. on 10 crystallographically independent sites Sr21–Sr30 with a multiplicity of two. Because Sr21–Sr30 atoms are spatially close they were refined with equal atomic displacement parameters. Their occupancies were refined using the free variables and SUMP instruction. The refined positions showed site occupancy factors from 0.225(6) to 0.041(4). Owing to the disorder of the Sr2 site, R parameters are large (R(F²) > 2F(F²)) = 0.14). However, it can be assumed that the structure determined is correct, except possibly for details.

Hydrogen atoms from OH groups were placed in geometrically calculated positions and refined using the riding model with O–H = 0.82 Å and isotropic displacement parameters U(eq)(H) fixed to 1.5 times the U(eq)(O) value of the atoms they are linked to.

The O34–H34–H44–O44 contacts are short to host unit-occupancy H atoms. As a consequence, O34 and O44 atoms serve as both the hydrogen bond donor and acceptor, to each other, alternatively. The donor–acceptor O34···O44 distance is 2.832(17) Å and the H34···H44 distance is 1.4827(5) Å. Therefore the H34 and H44 atom position occupancy is a maximum of 50%, which is consistent with the charge balance.

Relevant information on crystal data, data collection and refinements are compiled in Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters for I–III are presented in Tables 2–4 and anisotropic displacement parameters for I–III are presented in Supplementary Tables S1–S3. Selected bond lengths for non-H atoms are listed in Table 5 and Tables S4–S6. Bond valence analysis obtained using VALIST software (Wills, 2010) are presented in Tables S7–S9.

Elemental Analysis

Elemental analysis was performed on the hydrothermally synthesised crystals with a JEOL JSM-6610 LV scanning electron microscope (SEM) connected to an Oxford INCA Energy 350 EDX analysis unit. The single crystals were mounted with conducting carbon onto Al sample holders. The sample holder was then coated with a thin layer of carbon. An accelerating voltage of 20 kV and accumulation time of 20 s were used for the chemical analysis. As a qualitative measure, energy dispersive spectroscopy confirmed the presence of each reported element in the title compounds. Semi-quantitative chemical analyses gave the presence of strontium in the range of 17.0–17.4 at.%, arsenic in the range 28.8–29.3 at% and nickel in the range 17.8–18.9 at% for I, strontium in the range of 26.8–27.4 at.%, arsenic in the range 28.3–28.4 at.%, and iron in the range 12.9–15.2 at% for II and
strontium of 15.4 at.%, arsenic of 34.5 at.% and iron of 10.3 at.% for III. The atomic proportions of constituent elements calculated from atomic % are Sr:Ni:As = 1.2:1:3.2:0 for I, Sr:Fe:As = 1:1:9.2 for II and Sr:Fe:As = 0.9:1:1.2 for III and correspond quite well with the ratios obtained from the structural analyses.

### Raman spectroscopy

To obtain further information on the anion groups, Raman spectra were acquired. Non-oriented single-crystal Raman spectra of I–III on the randomly oriented single-crystals were collected using a Horiba LabRam HR Evolution system equipped with a Si-based, Peltier-cooled CCD detector in the spectral range from 4000 to 60 cm⁻¹. The 633 nm excitation line of a He–Ne laser was focused with a 50× objective on the randomly oriented single crystals of I–III. The samples spectra were acquired with a nominal exposure time of 10 s (confocal mode, Olympus 1800 lines/mm, 1.5 µm lateral resolutions and ~3 µm depth resolution).

### Results and discussion

#### Description of the crystal structures

**Crystal structure of SrNi₂(AsO₄)₂·2H₂O (I)**

The basic building units in the structure of I are infinite linear chains of edge-sharing NiO₆(OH₂)₂ octahedra, extending along [010] (Fig. 2a). The coordination environment of NiI generates a tetragonal slightly elongated octahedron NiI₀₆(OH₂)₂ having two pairs of symmetry equivalent O atoms (two O₁ at a distance of 2.055(3) Å and two O₃ at a distance of 2.054(3) Å, Table S4) and two apical O₂ at a distance of 2.078(3) Å. The NiO₆(OH₂)₂ octahedra are almost perfect with an average <Ni–O> distance of 2.062 Å, which is in agreement with the value of 2.09 Å calculated from the sum (0.69 + 1.4 = 2.09 Å) of effective ionic radii (Shannon, 1976).

Adjacent octahedral chains are linked to each other by sharing corners with AsO₄ tetrahedra (Fig. 2a, b). The individual As−O bond lengths vary from 1.669(5) to 1.702(4) Å, the average <As−O> distance is 1.685 Å which is close to the sum of the effective ionic radii of As⁵⁺ in tetrahedral coordination and O²⁻ (0.335 + 1.4 = 1.735 Å; Shannon, 1976). The linear octahedral chains and AsO₄ tetrahedra are arranged in layers parallel to (001) (Fig. 2a, b). The topology of the layer is identical to that in natrochalite, NaCu₂(SO₄)₂(H₃O₂) (Krickl et al., 2007; Hawthorne et al., 2000; Hawthorne, 2014).

Between these layers are situated 8-coordinated (6+2) Sr²⁺ cations. The mutually isolated SrO₂ coordination polyhedra can be described as a somewhat distorted orthorhombic prism or dipyramidal slightly elongated octahedron, where the four symmetry equivalent O₃ oxygen atoms are located in the equatorial plane and two O₄ are at the vertices. In addition, two opposite triangular faces are capped by two O₂ atoms at longer distances. The Sr–O distances are in the range 2.573(3)–2.976(5) Å and the average value is 2.684 Å (Table S4), which is in agreement with the value of 2.66 Å calculated from the sum (1.26+1.4 = 2.66 Å) of effective ionic radii for Sr²⁺ with coordination number (CN) = 8 (Shannon, 1976).

The other way of describing the crystals structure of I are two kind of slabs positioned alternately along the [001] direction (Fig. 2b). The SrO₂ polyhedra share two edges and four vertices with six adjacent AsO₄ tetrahedra forming the first slab situated between z at approximately 0.33 and 0.33. The thickness of this slab is approximately double the thickness of the second slab which hosts NiI₀₆(OH₂)₂ octahedra chains combined with intralayer hydrogen bonds. Its boundaries lie between z at approximately 0.33 and 0.67.

**Bond-valence calculations** (Brown and Altermatt, 1985; Brese and O’Keeffe, 1991) show that the Sr–O, Ni–O and As–O bond lengths are consistent with the presence of Sr²⁺, Ni²⁺, As⁵⁺ and...
O1–H1···O3W̄ ‚ (0.85(2)) 2.36(2) 2.935(10) 125(1) 0.85(2)
O1–H1···O3W  ‚ (0.85(2)) 2.29(1) 2.909(5) 130(1) 0.85(2)
O1–H1···O3W  ‚ (0.85(2)) 2.29(1) 2.909(5) 130(1) 0.86(2)
O1–H2···O4W  ‚ (0.86(2)) 1.86(4) 2.601(7) 144(4) 0.86(2)

Symmetry codes: (xiii) x + ½, y + ½, z [ox] –x+1, –y+2, –z+1; (ox) –x+½, –y+3/2, –z; [oxii] –x+½, y+½, –z.

Table 7. Hydrogen-bond geometry (Å, °) for II.

| D–H···A | D–H | H···A | D–A | D–H···A |
|---------|-----|------|-----|---------|
| O61–H61···O32 | 0.85(2) | 1.95(2) | 2.745(8) | 155(5) |
| O62–H62···O31 | 0.86(2) | 1.95(2) | 2.748(8) | 154(5) |
| O63–H63···O34 | 0.85(2) | 1.95(2) | 2.728(10) | 153(5) |
| O64–H64···O33 | 0.85(2) | 1.95(2) | 2.721(10) | 151(4) |
| O71–H71···O72w | 0.84(2) | 1.95(2) | 2.695(5) | 147(3) |
| O72–H72···O72w | 0.85(2) | 1.95(2) | 2.695(5) | 145(3) |

Symmetry code: [vii] x, y, z–2; [vi] x, y, z+1.

O2+ (ΣVij = 1.886(6) valence units (v.u) for Sr1 with CN = 8, ΣVij = 2.106(6) v.u for Ni1 with CN = 6, ΣVij = 4.991(1) v.u for As1 with CN = 4). If four symmetry equivalent O4 atoms at very long distances of 3.675(3) Å are included, the bond valence sum (Σνij = 4.991(1) v.u) is very close to the nominal valence of 2+ for Sr1 with CN = 8, ΣVij = 2.106(6) v.u for Ni1 with CN = 6, ΣVij = 4.991(1) v.u for As1 with CN = 4). If four symmetry equivalent O4 atoms at very long distances of 3.675(3) Å are included, the bond valence sum (Σνij = 4.991(1) v.u) is very close to the nominal valence of 2+ for Sr1 with CN = 8, ΣVij = 2.106(6) v.u for Ni1 with CN = 6, ΣVij = 4.991(1) v.u for As1 with CN = 4).

Table 8. Hydrogen-bond geometry (Å, °) for III.

| D–H···A | D–H | H···A | D–A | D–H···A |
|---------|-----|------|-----|---------|
| O24–H24···O44wi | 0.82 | 2.36 | 3.114(16) | 153 |
| O34–H34···O43wi | 0.82 | 1.97 | 2.631(16) | 137 |
| O34–H34···O44 | 0.82 | 2.26 | 2.833(15) | 128 |
| O44–H44···O34 | 0.82 | 2.08 | 2.833(15) | 152 |
| O44–H44···O43wi | 0.82 | 2.58 | 3.123(14) | 125 |

Symmetry codes: (ii) –x+1, –y+1, –z+1; [xi] x, y, z.

Crystal structure of Sr1.4Fe1.6(AsO4)2(OH)1.6 (II) Compounds II is only partly (ca. 80%) isostuctural with carminite, Pb2Fe3+(AsO4)2(OH)2, which means that there are regions where the carminite-type structure is maintained in the form of octahedral Fe(O,OH)6 chains (Fig. 3a). In contrast to carminite, the structure of II contains four partially vacant Fe and six mixed Sr/O sites in which 11-coordinated Sr and oxygen atoms from OH groups statistically share the same position. Therefore, in addition to edge-sharing octahedral Fe2(O,OH)6 dimers that build infinite octahedral chains running along [010], such as in carminite, a new type of chain is formed. These new chains (Figs 3b, c) are similar to the PbO11-chains in arseenackebschite and can be described as trapezoidal face-sharing Sr centered Edshummar polyhedra connected along [010].

The parallel octahedral Fe(O,OH)6-chains and Edshummar polyhedral SrO11-chains are distributed statistically over two parallel rows in the unit cell. The octahedral Fe(O,OH)6-chain in the first row consists of edge-sharing Fe112(O,OH)10 and Fe122(O,OH)10 octahedral dimers which are linked in chains sharing corners. In the second row, the chain is formed by similar edge-sharing Fe132(O,OH)10 and Fe142(O,OH)10 octahedral dimers which are linked in chains sharing corners. In the second row, the chain is formed by similar edge-sharing Fe132(O,OH)10 and Fe142(O,OH)10 octahedral dimers which are linked in chains sharing corners.

Four iron cations Fe11–Fe14, situated at general positions on the pseudo-inversion centre, are coordinated by the four oxygen anions belonging to the AsO4 tetrahedra and two oxygen anions belonging to the hydroxyl groups. The Fe(O,OH)6 dimeric octahedra are distorted showing one shorter, four typical and one longer Fe–O bonds close to the calculated value from effective ionic radii of 6-coordinated Fe3+ cations (0.65 + 1.4 = 2.05 Å; Shannon, 1976). Oxygen from the common edge of the dimer and the oxygen from the hydroxyl group bridging two adjacent dimers in the octahedral chain form the longest and the shortest Fe–O interatomic distances, respectively. The average Fe3+–O bond distances are similar and very close to the calculated value: 2.021, 2.015, 2.019 and 2.022 Å for Fe11(O,OH)6, Fe12(O,OH)6, Fe13(O,OH)6, and Fe14(O,OH)6 octahedra, respectively (Table 5).

All arsenic atoms are coordinated by four nearest oxygens, adopting a typical tetrahedral coordination. In the carminite
part of structure four arsenic atoms As11–As14 share only three oxygens with the Fe(O,OH)₆ octahedra, while the forth oxygen is bonded, besides As, only to 8-coordinated Sr. The other two arsenic atoms As21 and As22 are linked through all four vertices to As, Sr and to the adjacent octahedral chains. In the less pronounced arsenbrackebuschite part of structure only two oxygens from AsO₄ tetrahedra are shared with Fe(O,OH)₆ octahedra. The other two As–O bonds in tetrahedra, which vary from 1.657(9) to 1.692(8) Å, only As13–O24 and As14–O23 bond distances are slightly elongated (1.741(9) and 1.736(8) Å), indicating a disorder and the possible involvement in hydrogen bonding.

The average <As–O> bond distances (1.680, 1.682, 1.688, 1.692, 1.681 and 1.671 Å for <As11–O>, <As14–O>, <As21–O> and <As22–O>, respectively) are in accordance, or slightly shorter, than the sum of the effective ionic radii of As⁵⁺ in tetrahedral coordination and O²⁻ (0.335 + 1.4 = 1.735 Å; Shannon, 1976).

Another type of chain in the structure of II involves SrO₁₁ coordination polyhedra, which are known as Edshammar polyhedra because this polyhedron was first described by Edshammar (1969). Each 11-vertex Edshammar polyhedron SrO₁₁ consists of a trigonal bipyramid SrO₅ (two O atoms at apices, usually at the longest, and three O atoms in the equatorial plane, typically at the shortest Sr–O distances) combined with the trigonal, rather
deformed, prism SrO$_6$ (Fig. 3b). Therefore, the strontium coordination of polyhedron SrO$_{11}$ can be described as a combination of a trigonal bipyramid and trigonal prism centred by the same Sr atom surrounded by 11 oxygen atoms at distances ranging from 2.567(11) to 3.102(8) Å in Sr61O$_{11}$, from 2.574(10) to 3.048(8) Å in Sr62O$_{11}$, from 2.650(8) to 3.091(4) Å in Sr71O$_{11}$, from 2.568(11) to 3.017(11) Å in Sr63O$_{11}$, from 2.561(12) to 3.035(11) Å in Sr64O$_{11}$ and from 2.695(5) to 3.087(7) Å in Sr72O$_{11}$. Observed values of 2.865, 2.858, 2.844, 2.851, 2.864 and 2.861 Å for the average <Sr–O> bond distances are very similar and close to the calculated value from effective ionic radii of Sr$^{2+}$ cations with CN = 11 (1.4 + 1.4 = 2.8 Å). The value of 1.4 Å for Sr$^{2+}$ with CN = 11 was estimated from 1.36 and 1.44 Å given by Shannon (1976) for Sr$^{2+}$ with CN = 10 and CN = 12, respectively. In addition, this is consistent with recent work (Gagné and Hawthorne, 2016). By sharing common trapezoidal faces, each Edshummar polyhedron is linked to two similar neighbouring polyhedra. Each Edshummar polyhedron SrO$_{11}$ shares four oxygen atoms (two from a trigonal bipyramid and two from a trigonal prism) with the neighbouring SrO$_{11}$-polyhedron from one side, and additional four vertices from another side, in order to form trapezoidal face-sharing SrO$_{11}$-chains (Fig. 3c).

The partial occupancy of mixed sites Sr71/O71 and Sr72/O72 by Sr are accompanied by the appearance of extra atoms (Fig. 3e) at distances less than 1 Å from Sr71 (Sr81 and Sr82) and Sr72 (Sr83 and Sr84). The four additional 11-coordinated Sr81–Sr84 atoms are of very low occupancy (ca. 10% of available sites) and are surrounded by oxygen atoms in a similar way, like Sr71 and Sr72 atoms (Table S5). Some displacement ellipsoids of these oxygen atoms have a small problematic form indicating a disorder in this part of structure.

Similar to I the 8-coordinated Sr$^{2+}$ cations are situated in holes between the layers of octahedral chains linked by AsO$_4$ tetrahedra (Fig. 3a). For 8-coordinated Sr$^{2+}$ cations the bond lengths Sr11–O, Sr21–O and Sr22–O vary in the intervals 2.507(7)–2.789(8), 2.512(11)–3.081(10) and 2.496(7)–3.090(9) Å, respectively. The average <Sr$^{2+}$–O> bond distances are similar: 2.663, 2.656 and 2.651 Å for <Sr11–O>, <Sr21–O> and <Sr22–O>, respectively, which is very close to the calculated value from effective ionic radii of 8-coordinated Sr$^{2+}$ cations (1.26 + 1.4 = 2.66 Å; Shannon, 1976) and mean bond length of 2.656 Å given by Gagné and Hawthorne (2016). The Sr11O$_8$ polyhedron, having four shorter and four longer Sr–O distances, can be described as an intermediate between the considerably distorted orthorhombic prism and the tetragonal elongated double split octahedron with the four axial bonds longer (<2.795 Å) than the four equatorial bonds (<2.531 Å). Another two strontium atoms display a bicappedoctahedral geometry with six shorter (<2.543 Å) and two longer bonds (<2.993 Å) in Sr21O$_8$ and Sr22O$_8$, respectively. The four next-nearest oxygen atoms are more than 3.5 Å away from the central Sr11, Sr21 and Sr22 atoms.

The difference-Fourier map did not reveal the positions of the H atoms. This was expected considering their amount, as well as the substitutional and positional disorder of Sr. Therefore the hydrogen-bonding system is complex. However, bond-valence calculations (Brown and Altermatt, 1985, Brese and O’Keefe, 1991) show that the Sr–O, Fe–O and As–O bond lengths are consistent with the presence of 8-coordinated and 11-coordinated Sr$^{2+}$, 6-coordinated Fe$^{3+}$, 4-coordinated As$^{5+}$ and O$^{2–}$ ($\Sigma v_j = 1.988(1)$, $2.100(7)$ and $2.126(9)$ vu for Sr11, Sr21 and Sr22, $\Sigma v_j = 3.072(3)$, 3.106(3), 3.007(0) and 2.994(1) vu for Fe11–Fe14, $\Sigma v_j = 5.043(3)$, 5.086(2), 4.987(2), 4.890(2), 5.050(2) and 5.083(1) vu for As11–As14, As21 and As22). The bond valence sums $\Sigma v_j$ for O61–O64, O71 and O72 without the contributions of H are close to 1, while that of O31–O34 are near 1.6 vu indicating that they are involved in hydrogen bonding (Table S8). Except O23 and O24, the calculated bond valence sums for the other oxygen atoms were $\approx$ 2 indicating that they hardly participate in hydrogen-bonding interactions. The small undersaturation of O23 and O24 can be the result of a positional and substitutional disorder, i.e. the displacements of O23 and O24 oxygen atoms due to the substitutions of differently sized and charged ions (Sr72 and O72) and their amounts in the coordination sphere as well as the positional disorder of Sr72.

The four OH groups (O61H61–O64H64) act as hydrogen-bond donors to the oxygen atoms O31–O34 (D–A distances are in the range 2.721(10)–2.748(8) Å and D–H···A angles are from 151(4)–155(5)°). Another two OH groups (O71H71 and O72H72) are alternately single hydrogen bond donors and acceptors to one another (D–A distance is 2.695(5) Å and D–H···A angles are 147(3) and 143(3)°, respectively). All these hydrogen bonds are of average strength (Table 7).

It should be kept in mind that O72 has 97% occupancy, O71 has 63% and that they can be single hydrogen-bond donors and acceptors to one another in a maximum 50% of unit cells. If O71 and O72 are always protonated, which oxygen atoms can act as hydrogen-bond acceptors? The nearest neighbours of O72 and O71 are O11–O14 (interatomic distances O72–O12, O72–O11, O71–O13 and O71–O14 are 2.969(11), 2.979(11), 3.042(9) and 3.032(9) Å; symmetry codes: (vii) x, y, z; (viii) x, y, z+1) indicating possible weak hydrogen bonds. The bond valence sums for O11–O14 are 2.102, 2.111, 2.087 and 2.052 vu. The slight oversaturation at the O11–O14 sites, coupled with the very small contributions of hydrogen bonds, could be interpreted as due to disorder and limitations of bond-valence analysis (Figs 3d, e).

Crystal structure of SrFe(AsO$_4$)/(AsO$_4$OH) (III).

In contrast to I and II, in the structure of III the FeO$_6$ octahedra are completely isolated from one another by the surrounding arsenate tetrahedra. This arrangement produces unique metal arsenate octahedral–tetrahedral-quadruple chains, which are composed of one central double and two peripheral single chains extended along the a axis (Fig. 4a). The central double chain is built up of alternating corner-sharing Fe1O$_6$ octahedra and As1O$_4$ tetrahedra. The two sides of the double chain are ‘out of phase’ meaning that Fe1O$_6$ octahedra in one side are arranged in a line with, and are linked to, As1O$_4$ tetrahedra on the other side. The peripheral single chains are made up of alternating corner-sharing Fe2O$_6$ octahedra and As2O$_4$ tetrahedra, which are also ‘out of phase’ with regard to the central double chain. These octahedral–tetrahedral-quadruple chains are centred around the inversion centre at (0,0,0) with one single and one half of a double chain on each side (Fig. 4b). The chains are further linked by As3O$_4$ tetrahedra to form a slab parallel to the (010) plane. A slab is placed between the relative heights, $y$, from approximately −0.35 to 0.35 (Fig. 4b). The three-dimensional structure is formed by interconnected slabs through bridging As4O$_4$ tetrahedra and hydrogen bonds. The adjacent slabs are linked additionally to each other via bonds to Sr$^{2+}$ cations, which are accommodated inside the channels of the hetero-polyhedral three-dimensional open framework.

The slightly distorted Fe1O$_6$ and Fe2O$_6$ octahedra share all six corners with adjacent arsenate tetrahedra. The individual Fe1–O bond lengths vary from 1.926(9) to 2.107(10) Å, while Fe2–O bond lengths vary from 1.948(9) to 2.126(9) Å (Table 5).
average $<\text{Fe}^{3+}-\text{O}>$ bond distances are similar: 2.016 and 2.002 Å for $<\text{Fe}^1-\text{O}>$ and $<\text{Fe}^2-\text{O}>$, respectively. These average values are close to the calculated from effective ionic radii of 6-coordinated Fe$^{3+}$ ions (0.65 + 1.4 = 2.05 Å; Shannon, 1976).

Although the mean $<\text{As}-\text{O}>$ bond lengths are almost the same for all arsenate tetrahedra ($<\text{As}^1-\text{O}> = 1.679$, $<\text{As}^2-\text{O}> = 1.683$, $<\text{As}^3-\text{O}> = 1.682$ and $<\text{As}^4-\text{O}> = 1.686$ Å), the individual bond lengths vary from 1.657(10) to 1.698(10), from 1.657(9) to 1.714(10), from 1.653(9) to 1.722(10) and from 1.655(9) to 1.720(10) Å for $\text{As}^1-\text{O}$, $\text{As}^2-\text{O}$, $\text{As}^3-\text{O}$ and $\text{As}^4-\text{O}$, respectively. These average distances are close to the sum of the effective ionic radii of As$^{5+}$ in tetrahedral coordination and O$^{2-}$ (0.335 + 1.4 = 1.735 Å; Shannon, 1976).

Sr-ions are also linked by sharing O and OH groups. The Sr1 atoms are located inside the small channels extending nearly along [010]. The channels are centred on the inversion centre at 0.5, 0.5, 0.5 and are bounded by octahedral–tetrahedral chains with AsO$_4$ and AsO$_4$ tetrahedra. By sharing a common two symmetry-equivalent oxygen atom O23, two 9-coordinated Sr1 form a Sr$_1$O$_{16}$ dimer. The nine Sr–O distances range from 2.473(10) to 3.120(9) Å.

The Sr2 atoms inside the large channels along [100] are highly mobile in the crystal lattice. They appear distributed among ten positions in the channels. These Sr2–Sr30 positions are too close to be occupied simultaneously and therefore Sr2 atoms are actually distributed randomly over ten pairs of symmetry-equivalent sites. The site occupancy factors of the four most occupied positions are refined to 0.210(6), 0.225(6), 0.140(6) and 0.113(6). The other Sr2 positions in the channels are statistically position. These Sr$_2$O$_{18}$ dimers are green (c is horizontal); H atoms are presented as small spheres of arbitrary radii; (b) the linkages of quadruple chains into slabs projected along [100] direction (d is horizontal); (c) projection of III along the a-axis showing the channels where Sr2 (small blue ellipsoids) is statistically positioned in 20 sites. The Sr1$\bar{2}$O$_{18}$ dimers are green (c is horizontal); H atoms are presented as small spheres and H bonds are shown as broken lines.

Average $<\text{As}^3-\text{O}>$ and $<\text{Fe}^3-\text{O}>$ bond lengths are almost the same (1.683 Å). However, $<\text{Fe}^1-\text{O}>$ and $<\text{Fe}^2-\text{O}>$ are found at 1.679 and 1.683 Å, respectively. These differences are due to the presence of Fe$^{3+}$ in these compounds.

Raman spectroscopy
In all Sm$^3+$-arsenate hydrates ($M = \text{Ni}^{2+}$ and Fe$^{3+}$) presented in this study, Raman bands in the 1000–700 cm$^{-1}$ region are assigned to the symmetric and antisymmetric stretching modes of the (AsO$_4$)$^{3-}$ and/or (AsO$_4$OH)$^{2-}$ groups, whereas internal bending vibrations of these tetrahedra are observed below 550 cm$^{-1}$, whereas they are partially overlaid by various external and lattice modes.

Raman spectra of I are shown on Fig. 5 together with Raman spectra of SrCo$_2$(AsO$_4$)(As$_2$O$_7$OH)(H$_2$O) (Mihailović and Effenberger, 2004) and Raman spectra of the mineral tsunctorite, PbZn$_2$(AsO$_4$)$_2$·2H$_2$O (RUFF database: R100185, https://rruff.info/). SrCo$_2$(AsO$_4$)(As$_2$O$_7$OH)(H$_2$O) was synthesised in the scope of previous work of the first author of this paper, but its Raman spectra are presented here for the first time (vs = very strong, s = strong, m = medium, w = weak, sh = shoulder). In the 1000–700 cm$^{-1}$ range, I shows the As–O stretching modes of the (AsO$_4$)$^{3-}$ groups at: 870 (sh, s), 828 (vs), 776 (m) and 741 (w) cm$^{-1}$, which compare very well with the spectra of isostructural mineral tsunctorite, having its characteristic Raman bands at 870 (vs), 827 (s) and 734 (s) cm$^{-1}$. The Raman spectra
of the SrCo-arsenate are more complex due to the lowering of the space-group symmetry to $P\overline{2}1/a$ and the introduction of the protonated (AsO$_3$OH)$_2^-$ group. In the As–O stretching region the SrCo-arsenate shows characteristic Raman bands at 862 (vs), 832 (vs), 890 (sh, m), 790 (sh, m) and 717 (s) cm$^{-1}$.

Raman spectra of II are characterised with the As–O symmetric and antisymmetric stretching modes of the (AsO$_4$)$_3^-$ groups at 916 (sh, w), 864 (vs), 851 (vs) and 814 (s) cm$^{-1}$. The band at 740 (m) cm$^{-1}$ may be attributed to the hydroxyl deformation mode (Fig. 6). They are compared to the Raman spectra of structurally related carminite, PbFe$_3^+$ (AsO$_4$)$_2$(OH)$_2$ (RRUFF data base: R061061; https://rruff.info/) and arsenbrackebuschite, Pb$_2$(Fe$^{3+}$, Zn)(AsO$_4$)$_2$(OH,H$_2$O) (RRUFF database: R100184; https://rruff.info/). In the region 1000–600 cm$^{-1}$, the new compound II is more similar to carminite, then brackebuschite, which was also confirmed by the structural analysis.

Raman spectra of III reflect the complexity of the crystal structure. The considerably large number of bands, which cannot be certainly specified, are caused by the four crystallographically different AsO$_4$ tetrahedra (of which three are protonated AsO$_3$OH groups). Spectral data on orthoarsenates that have been published previously are, so far, somewhat incomplete and not in good agreement with each other. Therefore, attempts to compare with them failed. However, the distinct frequency ranges may be assigned as follows:

Based on the $d$–$v$ correlation for hydrogen bonds (Libowitzky, 1999), the 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 2.63(2) and 3.12(1) Å (corresponding Raman bands obtained between 2500 and 3700 cm$^{-1}$) (Fig. 7).

The 1000–700 cm$^{-1}$ range shows the As–O stretching modes of the (AsO$_3$OH)$_2^-$ and (AsO$_4$)$_3^-$ groups at: 934 (sh, m), 915 (vs), 901 (sh, m), 881 (m), 40 (sh, s), 824 (s), 790 (sh, m), 775 (m) and 733 (w) cm$^{-1}$. The most intense Raman bands at ~915, 840 and 824 cm$^{-1}$ correspond to the stretching vibrations of (AsO$_3$OH)$_2^-$ and (AsO$_4$)$_3^-$ groups.

Structural relations to the associated minerals and inorganic compounds
SrNi$_2$(AsO$_4$)$_2$·2H$_2$O (I) is isostructural with minerals of the tsumcorite group, which adopt the monoclinic symmetry, space group $C2/m$ ($Z = 2$). The general formula of the tsumcorite group is $A$(M$^{2+,3+}$)$_2$(XO$_4$)$_2$(H$_2$O,H$_2$O)$_2$ (A is a large cation, M$^{2+,3+}$ is usually an octahedrally coordinated transition metal cation and X is a tetrahedrally coordinated small cation). The
minerals of this group have been described with Pb, Ca, Bi and Na on the A site, Zn, Fe	extsuperscript{3+}, Cu	extsuperscript{2+}, Mn	extsuperscript{3+} and Co on the M site, and As	extsuperscript{5+}, P	extsuperscript{5+}, V	extsuperscript{5+} and S	extsuperscript{6+} on the X site (Tillmanns and Gebert, 1973; Pring et al., 1989; Kharisun et al., 1997; Krause et al., 1998, 2001a, 2001b, 2002; Effenberger et al., 2000; Brugger et al., 2000, 2001, 2002; Yang et al., 2012; Elliott and Pring, 2015; Pekov et al., 2016). They display either monoclinic or triclinic symmetry, depending on the chemical composition as well as ordering of the hydrogen bonds and cations on the M sites. The basic tsumcorite-type structure mentioned previously is monoclinic (space group \(C2/m\), \(Z=2\)) and represents the parental structure of the group referred to as tsumcorite-type structure. It was determined by Tillmanns and Gebert (1973). The majority of the tsumcorite-group minerals (Table 9) crystallise in space group \(C2/m\), but some members display lower symmetry. The next modification is also monoclinic referred to as the Sr-Co-type structure. It is characterised by protonated anion tetrahedra (Mihajlović and Effenberger, 2004) and a doubled cell volume (\(Z=4\)). In addition, the space-group symmetry is lowered to the \(P2_1/a\). The triclinic members of the tsumcorite group (Table 9) crystallise in space group \(P\bar{1}\) (\(Z=1\)) and can be divided into the helmutwinklerite and rappoldite subgroup (Effenberger et al., 2000). In the helmutwinklerite subgroup, referred to as a helmutwinklerite-type structure, the symmetry reduction is due to the ordering of the hydrogen bonds. The characteristic of this subgroup is two H	extsubscript{2}O per formula unit and the hydrogen atoms are rearranged in order to avoid the symmetry-restricted hydrogen bonds. These changes in hydrogen bonding induce structural transformations that cause the transition from the monoclinic tsumcorite-type structure to the triclinic helmutwinklerite-type structure (Krause et al., 1998, 2001b; Effenberger et al., 2000; Elliott and Pring, 2015). In the second triclinic subgroup, referred to as the gartrellite type, symmetry reduction is due to the cation ordering on the two M positions in the triclinic unit cell.

The compound \(\text{II, Sr}_{1.4}\text{Fe}_{1.6}(\text{AsO}_4)_2(\text{OH})_{1.6}\) adopts a novel intermediate crystal structure between carminite and arsenbrackebusche, nominally PbFe	extsuperscript{2+}\text{Fe}_3\textsuperscript{3+} (\text{AsO}_4)_2(\text{OH})_2 and Pb\text{Fe}_3\textsuperscript{3+} (\text{AsO}_4)_2(\text{OH})_2, respectively (Donaldson et al. 1955; Finney, 1963; Hofmeister and Tillmanns, 1978; Olmi and Sabelli, 1995; Kharisun et al., 1996; Foley et al., 1997; Gonzalez del Tanago et al., 2003; Sanjeeewa et al., 2015; Lafuente and Downs, 2016; Table 10). Carminite is also related structurally to the phosphate analogue crimsonite, Pb\text{Fe}_2\textsuperscript{3+}\text{Fe}_3\textsuperscript{3+} (\text{PO}_4)_2(\text{OH})_2 and the Ca analogue sewardite, Ca\text{Fe}_3\textsuperscript{3+}\text{Fe}_3\textsuperscript{3+} (\text{AsO}_4)_2(\text{OH})_2 (Kampf et al., 2016; Roberts et al., 2002). Mawbyite, nominally Pb\text{Fe}_3\textsuperscript{3+}\text{Fe}_3\textsuperscript{3+} (\text{AsO}_4)_2(\text{OH})_2, is a dimorph of carminite (the same formula, but different structure) and Fe analogue of tsumcorite (Kharisun et al., 1997, Pring et al., 1989, Table 10). One of the main differences between these three structures is the \(A:M^{3+}\) ratio, which is 1:2 for carminite, 1:0:1:14 for \(\text{II}\) and 1:0:5 for arsenbrackebusche. These structures are also related to previously mentioned tsumcorite, nominally PbFe\textsuperscript{2+}\text{Fe}_2\textsuperscript{3+} (\text{AsO}_4)_2\cdot2\text{H}_2\text{O}, both in chemical composition and in structure properties. Carminite and tsumcorite have the same general formula \(A(M^{2+3+})_2(XO)_2(\text{H}_2\text{O})_2\). The changing of the cation valence and size in the octahedral sites from basically \(M^{3+}\) in carminite to \(M^{2+}\) in tsumcorite causes changes in the octahedral chains, which are the main building units. The presence of

---

**Fig. 7.** Raman spectrum of III.
Table 9. Comparison of the unit-cell parameters of the compounds adopting the tsucmorcorite-type of structure, $A(M^{2+},M^{3+})_2(VO_4)_2(H_2O,OH)_2$ (s.g. $C2/m$, $Z = 2$ for 1–18, s.g. $P2_1/a$, $Z = 4$ for 19 and s.g. $P\bar{1}$, $Z = 1$ for 20–25).

| Formula, mineral name | $a$ (Å) | $b$ (Å) | $c$ (Å) | $\alpha$//$\beta$//$\gamma$ (°) | Volume ($Å^3$) | Reference |
|-----------------------|---------|---------|---------|-----------------------------|----------------|-----------|
| 1 Pb(Fe$_{0.39}$Co$_{0.37}$Ni$_{0.20}$Zn$_{0.02}$Al$_{0.02}$)$_2$AsO$_4$(OH)$_2$(H$_2$O)$_2$ | 9.124(3) | 6.329(2) | 7.577(2) | 115.28(3) | 395.5(4) | Tillmanns and Gebert (1973) |
| 2 Pb(As$_{0.40}$) | 9.097(2) | 6.313(2) | 7.555(3) | 115.08(2) | 393.0(1) | Krause et al. (2001a) |
| 3 Pb(As$_{0.40}$) | 9.124(8) | 6.339(3) | 7.567(7) | 115.19(6) | 396.0(7) | Pekov (2016) |
| 4 Pb(As$_{0.40}$) | 9.052(5) | 6.277(4) | 7.580(3) | 114.57(3) | 391.6(4) | Pring et al. (1989) |
| 5 Pb(As$_{0.40}$) | 9.066(4) | 6.286(3) | 7.564(3) | 114.857(5) | 391.1(3) | Kharisun et al. (1997) |
| 6 Ca(Zn$_{2.02}$Fe$_{0.98}$Mn$_{0.08}$)AsO$_4$(OH)$_2$(H$_2$O)$_2$ | 9.0727(6) | 6.2530(4) | 7.4150(5) | 116.739(4) | 375.68(4) | Yang et al. (2012) |
| 7 Ca(Zn$_{2.02}$Fe$_{0.98}$Mn$_{0.08}$)AsO$_4$(OH)$_2$(H$_2$O)$_2$ | 9.101(3) | 6.246(2) | 7.391(2) | 115.52(3) | 375.36 | Krause et al. (1998) |
| 8 Ca(Mg$_{0.50}$Fe$_{0.50}$)AsO$_4$(OH)$_2$(H$_2$O)$_2$ | 9.043(1) | 6.231(4) | 7.388(9) | 116.302(2) | 372.97(9) | Brugger et al. (2002) |
| 9 Ca(Mg$_{0.50}$Fe$_{0.50}$)AsO$_4$(OH)$_2$(H$_2$O)$_2$ | 9.050(1) | 6.205(1) | 7.411(1) | 115.31(1) | 374.41(1) | Krause et al. (2001a) |
| 10 Ca(Mg$_{0.50}$Fe$_{0.50}$)AsO$_4$(OH)$_2$(H$_2$O)$_2$ | 9.825(2) | 6.143(1) | 7.352(1) | 115.25(3) | 364.61(1) | Brugger et al. (2000) |
| 11 Ca(Mg$_{0.50}$Fe$_{0.50}$)AsO$_4$(OH)$_2$(H$_2$O)$_2$ | 9.8284(5) | 6.1314(5) | 7.3439(6) | 115.494(7) | 362.91(1) | Brugger et al. (2000) |
| 12 Ca(Mg$_{0.50}$Fe$_{0.50}$)AsO$_4$(OH)$_2$(H$_2$O)$_2$ | 9.005(1) | 6.211(1) | 7.440(1) | 115.19(1) | 376.51(1) | Krause et al. (2002) |
| 13 Ca(Mg$_{0.50}$Fe$_{0.50}$)AsO$_4$(OH)$_2$(H$_2$O)$_2$ | 8.995(1) | 6.2071(2) | 7.462(1) | 115.00(1) | 377.61(1) | Krause et al. (2002) |
| 14 PbCu$_2$Fe$_2$AsO$_4$(OH)$_2$(H$_2$O)$_2$ | 9.077(8) | 6.300(8) | 7.661(8) | 116.99(8) | 390.38 | Krause et al. (1998) |
| 15 PbCu$_2$Fe$_2$AsO$_4$(OH)$_2$(H$_2$O)$_2$ | 9.294(8) | 6.166(7) | 7.713(8) | 115.57(6) | 398.72 | Krause et al. (1998) |
| 16 PbCu$_2$Fe$_2$AsO$_4$(OH)$_2$(H$_2$O)$_2$ | 9.275(7) | 6.284(3) | 7.682(2) | 117.97(4) | 395.43(3) | Brugger et al. (2001) |
| 17 PbCu$_2$Fe$_2$AsO$_4$(OH)$_2$(H$_2$O)$_2$ | 8.8877(3) | 6.209(3) | 7.776(3) | 114.173(2) | 361.66(3) | Assani et al. (2010) |
| 18 PbCu$_2$Fe$_2$AsO$_4$(OH)$_2$(H$_2$O)$_2$ | 9.173(3) | 6.2052(12) | 7.562(3) | 114.41(2) | 391.82 | This work (f) |
| 19 SrO$_3$As$_2$O$_7$H$_2$O, synthetic compound | 9.139(2) | 12.829(3) | 7.522(2) | 114.33(3) | 803.63 | Mihajlović and Effenberger (2004) |
| 20 PbZn$_2$AsO$_4$(OH)$_2$ | 5.606(2) | 5.610(2) | 7.617(1) | 70.19(2) / 69.91(2) / 69.18(2) | 203.77 | Krause et al. (1998) |
| 21 Pb(Zn$_{2.02}$) | 5.595(1) | 5.572(1) | 7.593(1) | 70.19(1) / 70.41(1) / 69.23(1) | 201.91 | Effenberger et al. (2000) |
| 22 Pb(Zn$_{2.02}$) | 5.454(1) | 5.653(1) | 7.579(1) | 67.52(1) / 69.27(1) | 196.15 | Krause et al. (1998) |
| 23 Pb(Zn$_{2.02}$) | 5.500(1) | 5.620(1) | 7.621(1) | 68.59(1) / 69.17(1) / 69.51(1) | 200.10 | Effenberger et al. (2000) |
| 24 PbCuAl$_2$AsO$_4$(OH)$_2$(H$_2$O)$_2$ | 5.444(2) | 5.640(2) | 7.518(2) | 67.89(2) / 69.48(2) / 70.18(2) | 194.51(7) | Elliott and Pring (2015) |
| 25 CaCuFe$_3$ AsO$_4$(OH)$_2$(H$_2$O)$_2$ | 5.457(3) | 5.539(4) | 7.399(6) | 68.43(5) / 69.48(5) | 187.81 | Krause et al. (2001b) |
OH or H₂O depends on the amount of M³⁺ and M²⁺ cations and the valence and quantity of the large cation A.

The novel-type crystal structure of III is characterised by the unique octahedral–tetrahedral-quadruple, [Fe₃(AsO₄)₃]ₙ, infinite chains, which are formed of one central double and two peripheral single chains extended along the a axis. Similar vertices-sharing double-sided chains of octahedra and tetrahedra has been found in galliskuite, Ca₅Al₂(PO₄)₂Fe₃S₃H₂O (Kampf et al., 2010) and some phosphates (Mills et al., 2010a, 2010b and references therein). Dissimilar quadruple chains are found in the synthetic ferric sulfate trihydrate, Fe₂(SO₄)₃·3H₂O (Xu and Parise, 2011). Besides the exceptional occurrence of quadruple chains of FeO₆ and AsO₄ polyhedra, the characteristics of this structure are the novel chemical composition and the extremely high positional disorder of Sr₂ atoms.

### Conclusion

The results of phase formation studies in the system Sr–M³⁺–As–O–H increase the knowledge on SrM-oxoarsenates(V) and their crystal structures. All three structures have different chains as the primary building units. Compound I is a new strontium nickel analogue of tsumcorite PbZn₄(AsO₄)₂·2H₂O·2H₂O (monochlinic, s.g. C2/m) having a structure which is built up of infinite linear edge-sharing NiO₆(AsO₄)₂ octahedral chains with AsO₄ tetrahedra and SrO₆ polyhedra linking them by sharing corners. Compound II exists as an unusual intermediate form between carminite, Pb₅(AsO₄)₂(AsO₄)₃(OH)₆ and arsenbrackebuschite, Pb₅Fe₂(AsO₄)₆(OH)₂ type structures. The characteristic feature of compound II is that it hosts two type of chains: (i) octahedral vertex- and edge-sharing FeO₆(OH)₂ chains like in carminite and (ii) chains similar to arsenbrackebuschite which involves SrO₁₁ coordination polyhedra, known as Edshammar polyhedra, that can be described as a combination of a trigonal bipyramidal and trigonal prism centred by the same Sr atom surrounded by 11 oxygen atoms.

The MΦ₆ octahedra (Φ = O, OH or OH₂) in I like in tsumcorite and arsenbrackebuschite is all edge sharing, in contrast to the alternating edge and vertices sharing in carminite and II. In carminite and II structures two MΦ₆ octahedra share edges to form a M₇Φ₁₀ dimer and the M₅Φ₁₂ dimers share corners to form an M₇Φ₂ chain that is decorated by XO₄ tetrahedra. These parallel chains are linked to form a framework by sharing octahedron and tetrahedron vertices. Contrary to this, the arsenbrackebuschite and tsumcorite MΦ₆ octahedra share one set of trans edges with adjacent octahedra to form a MΦ₂ chain. Adjacent octahedra are bridged by XO₄ tetrahedra to form a decorated chain. The parallel chains in tsumcorite are further linked in the M₇(XO₄)₃Φ₂ sheets similar to those in natrochalcite (nominally NaCu₂(SO₄)₂(OH)-2H₂O). No such linkage occurs in arsenbrackebuschite where the MΦ₆ octahedra occupy only half of the octahedral sites, because every second octahedral chain is omitted and replaced by chains of 11-coordinated Pb. Similar substitutions were found in II i.e. nearly 20% of the octahedral chains are replaced by SrO₁₁ polyhedra chains. The 8- and 11-coordinated Sr atoms in II adopt an almost identical polyhedral environment, such as in the synthetic compound Sr₂V₂(VO₄)₂(OH)₆ with a brackebuschite-type structure (Sanjeewa et al., 2015).

### Compounds

1. **Table 10. Comparison of the unit-cell parameters of the compounds adopting carminite [A(M³⁺M²⁺)₆(AsO₄)₃(H₂O,OH)]ₙ, (s.g. Ccmm, Z = 8 for 1–7) and arsenbrackebuschite [A(M³⁺M²⁺)₆(AsO₄)₃(H₂O,OH)]ₙ, (s.g. P2₁/m, Z = 2 for 8–15) structure type.**

| Formula, mineral name | a (Å) | b (Å) | c (Å) | α / β / γ (°) | Volume (Å³) | Reference |
|-----------------------|-------|-------|-------|---------------|-------------|-----------|
| 1 PbFe₃⁺(AsO₄)₂(OH)₆ carminite | 16.595(5) | 7.580(5) | 12.295(5) | 90 | 1546.59 | Finney (1963) |
| 2 PbFe₃⁺(AsO₄)₂(OH)₆ carminite | 16.604(2) | 7.586(1) | 12.274(2) | 90 | 1546.01 | Olmi and Sabelli (1995) |
| 3 PbFe₃⁺(AsO₄)₂(OH)₆ carminite | 16.617(4) | 7.585(2) | 12.272(2) | 90 | 1546.76 | Olmi and Sabelli (1995) |
| 4 PbFe₃⁺(AsO₄)₂(OH)₆ carminite | 16.602(3) | 7.586(1) | 12.268(3) | 90 | 1545.07 | Olmi and Sabelli (1995) |
| 5 PbFe₃⁺(AsO₄)₂(OH)₆ carminite | 16.591(2) | 7.580(1) | 12.285(3) | 90 | 1544.96 | Kharisum et al. (1995) |
| 6 CaFe₃⁺(AsO₄)₂(OH)₆ eddrasite | 16.461(2) | 7.434(1) | 12.131(2) | 90 | 1484.48 | Roberts et al. (2002) |
| 7 Pb₂(2H₂O (monoclinic, s.g. Ccmm | 16.253(15) | 7.4724(4) | 12.1533(9) | 90 | 1476.04(17) | Kampf et al. (2016) |
| 8 Sr₂Fe₃⁺(AsO₄)₂(OH)₁₂ synthetic compound | 9.072(2) | 12.227(2) | 7.546(2) | 114.575(6) | 761.2(2) | This work (II) |
| 9 Pb₂(2H₂O (monoclinic, s.g. Ccmm | 7.763(1) | 6.046(1) | 9.022(1) | 112.5(1) | 391.2(1) | Hofmeister and Tillmanns (1978) |
| 10 Ba₄Fe₆⁺(AsO₄)₂(OH) canosioite | 7.864(2) | 6.1083(3) | 9.1670(5) | 112.874(6) | 405.73(4) | Cámara et al. (2017) |
| 11 Pb₂(2H₂O (monoclinic, s.g. Ccmm | 7.68(1) | 6.15(5) | 16.52(2) | 93.75 | 779.525 | Donaldson et al. (1955) |
| 12 Pb₂Mn³⁺(VO₄)₂(OH) brackebuschite | 7.650(1) | 6.135(1) | 8.863(3) | 111.76(4) | 386.325 | Foley et al. (1997) |
| 13 Pb₂Mn³⁺(VO₄)₂(OH) brackebuschite | 7.649(2) | 6.126(2) | 8.924(2) | 112.195(1) | 387.20(12) | Lafuente and Downs (2016) |
| 14 Pb₂Fe(VO₄)₂(OH) calderonite | 7.649(1) | 6.10(1) | 8.904(1) | 112.23(1) | 384.6 | Gonzalez del Tanago et al. (2003) |
| 15 SrV₂(VO₄)₂(OH) synthetic compound | 7.6249(15) | 6.0903(12) | 8.8153(18) | 112.15(3) | 379.15(15) | Sanjeewa et al. (2015) |
| 16 SrFe₃⁺(AsO₄)₂(OH) synthetic compound | 6.6379(13) | 9.6849(19) | 12.666(3) | 108.86(3) / 90.97(3) / 104.49(3) | 741.8(3) | This work (III) |
We have shown that the compounds from the $M_1–M_2–As–O–H$ system ($M_1 = Ca^{2+}, Sr^{2+}$ and $Ba^{2+}$; $M_2 = Mn^{2+,3+}, Fe^{2+,3+}, Co^{2+}, Ni^{2+}, Cu^{2+}$ and $Zn$) are not fully structurally and chemically defined. However, they could play an important role as the arsenic scavengers in arsenic-extreme environments, such as sulfidic mining wastes and tailings. Two of three investigated phases crystallises in a novel structure type and thus add details to the crystal chemistry of oxoarsenate(V) compounds.

**Supplementary material.** To view supplementary material for this article, please visit https://doi.org/10.1180/mgm.2021.41

**Acknowledgements.** This work was supported financially by the Austrian Science Foundation (FWF) (Grant V203-N19) and by the Ministry of Education, Science and Technological Development of the Republic of Serbia (grant No. III4507). The article was improved by constructive reviews by Peter Leverett and one anonymous reviewer.

**References**

Assani A., Saadi M., Zriouil M. and El Ammari L. (2010) $Ni_2Sr(PO_4)_2·2H_2O$. *Acta Crystallographica*, E66, 886–887.

Breze N.E. and O'Keefe M. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, B47, 192–197.

Brown I.D. and Altermatt D. (1985) Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database. *Acta Crystallographica*, B41, 244–247.

Brugger J., Meisser N., Schenk K., Berlesch P., Bonin M., Armbruster T., Nyfeler D. and Schmidt S. (2000) Description and crystal structure of cabalzarite $Ca(Mg,Al)Fe_2(AsO_4)_2(H_2O,OH)_2$, a new mineral of the tsumcorite group. *American Mineralogist*, 85, 1307–1314.

Brugger J., Armbruster T., Criddle A.J., Berlesch P., Graeser S. and Reeves S. (2001) Description, crystal structure, and paragenesis of krettnichite, $PbMn_2(VO_4)(OH)\cdot 2H_2O$, the $Mn^{3+}$ analogue of mounanaite. *European Journal of Mineralogy*, 13, 145–158.

Brugger J., Krivovichev S.V., Kolitsch U., Meisser N., Andrut M., Ansermet S. and Burns P.C. (2002) Description and crystal structure of manganlothar- meyrite, $Ca(Mn,\text{Mg})_2[AsO_4](OH)_2\cdot (OH,\text{H}_2\text{O})_2$, from the Starlager Mn-deposit, Swiss Alps, and a redefinition of lotharhemeity Locality: Starlager Mn-deposit, Swiss Alps. *The Canadian Mineralogist*, 40, 1597–1608.

Cámara F., Bittarello E., Ciriotti M.E., Nestola F., Radica F., Massimi F., Balestra S. and Kharisun, Taylor M.R., Bevan D.J.M. and Pring A. (1996) The crystal structure of wavyleite, $PbFe_2(AsO_4)(OH)\cdot 2H_2O$, a new mineral from the Gigante granitic opencut, Broken Hill, New South Wales. *Mineralogical Magazine*, 60, 805–811.

Cámara F., Krivovichev S.V. and Burns P.C. (2000) The crystal chemistry of sulfate minerals. Pp. 1–101 in: *Sulfate Minerals – Crystallography, Geochemistry and Environmental Significance* (C.N. Alpers, J.L. Jambor and D.K. Nordstrom, editors). Reviews in Mineralogy and Geochemistry, 40. Mineralogical Society of America and the Geochemical Society, Chantilly, Virginia, USA.

Hofmeister W.E. and Tillmanns E. (1978) Strukturelle Untersuchungen an Arsenbrackebuscht. *Thermiens mineralogische und petrographische Mitteilungen*, 25, 153–163.

Kampf A.R., Adams P.M., Mills S.J. and Nash B.P. (2016) Crimsonite, $Pb_2Fe_3^2+(PO_4)(OH)_2\cdot \text{H}_2\text{O}$, the phosphate analogue of carminite from the Silver Coin mine, Valny, Nevada, USA. *Mineralogical Magazine*, 80, 925–935.

Kharisun, Taylor M.R., Bevan D.J.M. and Pring A. (1996) The crystal structure of carminite: refinement and bond valence calculations. *Mineralogical Magazine*, 60, 585–598.

Krause W., Belendorff K., Bernhardt H.-J., McCammon C., Effenberger H. and Mikenda W. (1998) Crystal chemistry of the tsumcorite-group minerals. New data on ferrilotharhemeity, tsumcorite, thometzkite, monounite, helmuvinkenite, and a redefinition of gartrellite. *European Journal of Mineralogy*, 10, 179–206.

Krause W., Bernhardt H.-J., Effenberger H. and Martin M. (2001a) Cobalttsumcorite and nickellotharhemeity, two new minerals from Schneeberg, Germany: description and crystal structure. *Neues Jahrbuch für Mineralogie, Monatshefte*, 2001, 558–576.

Krause W., Blass G., Bernhardt H.-J. and Effenberger H. (2001b) Lukrahinite, CaCuFe_2^2+(AsO_4)\cdot (H_2O,OH), the calcium analogue of gartrellite. *Neues Jahrbuch für Mineralogie, Monatshefte*, 11, 481–492.

Krause W., Bernhardt H.-J., Effenberger H. and Witzke T. (2002) Schneebergite and nickelschneebergite from Schneeberg, Saxony, Germany; the first Bi-bearing members of the tsumcorite group. *European Journal of Mineralogy*, 14, 115–126.

Krickl R. and Wildner M. (2007) Crystal chemistry of synthetic Co- and Ni-analogues of natrocalcite – the shortest known hydrogen bonds among mineral-type compounds, Part I: Single-crystal X-ray structures. *European Journal of Mineralogy*, 19, 805–816.

Lafuente B. and Downs R.T. (2016) Redetermination of brackebusche, $PbMn^{2+}(VO_4)(OH)$. *Acta Crystallographica*, E72, 293–296.

Libowitzky E. (1999) Correlation of O–H stretching frequencies and O–H–O hydrogen bond lengths in minerals. *Monatshefte für Chemie*, 130, 1047–1059.

Millhøjovic T. and Effenberger H. (2004) The first proof of protonated anion tetrahedra in the tsumcorite-type compounds. *Mineralogical Magazine*, 68, 757–767.

Mills S.J., Birch W.D.; Kampf A.R., Christy A.G., Pluth J.J., Pring A., Raudsepp M. and Chen Y.S. (2010a) Kapundite, (Na,Ca)$_2$Fe$_2^2+$$(PO_4)(OH)\cdot 5\text{H}_2\text{O}$, a new phosphate species from Toms quarry, South Australia: Description and structural relationship to melanojosephite. *American Mineralogist*, 95, 754–760.

Elliot P. and Pring A. (2015) Yancowinnite, a new mineral from the Kintore Opencut, Broken Hill, New South Wales. *Australian Journal of Mineralogy*, 17, 73–76.

Farrugia L.J. (2012) WinGX and ORTEP for Windows: an update. *Journal of Applied Crystallography*, 45, 849–854.

Finney J.J. (1963) The crystal structure of carminite, *American Mineralogist*, 48, 1–13.

Foley J.A., Hughes J.M. and Lange D. (1997) The atomic arrangement of brackebusche, redefined as $Pb_2(Mn,Fe)(VO_4)\cdot OH$, and comments on Mn octahedra. *The Canadian Mineralogist*, 35, 1027–1033.

Gagne O.C. and Hawthorne F.C. (2016) Bond lengths for ions bonded to oxygen. *Acta Crystallographica*, B72, 602–625.

Gonzalez del Tanago J., La Iglesia A., Rius J. and Fernandez Santin S. (2003) Calderonite, a new lead-iron-vanadate of the brackebusche group. *American Mineralogist*, 88, 1703–1708.

Hawthorne F.C. (2014) The structure hierarchy hypothesis. *Mineralogical Magazine*, 78, 957–1027.

Hawthorne F.C., Kridrovich S.V. and Burns P.C. (2000) The crystal chemistry of sulfate minerals. Pp. 1–101 in: *Sulfate Minerals – Crystallography, Geochemistry and Environmental Significance* (C.N. Alpers, J.L. Jambor and D.K. Nordstrom, editors). Reviews in Mineralogy and Geochemistry, 40. Mineralogical Society of America and the Geochemical Society, Chantilly, Virginia, USA.
Mills S.J., Kolitsch U., Miyawaki R., Hatert F., Poirier G., Kampf A.R., Matsubara S. and Tillmanns E. (2010b) Pb$_3$Fe$_3^{2+}$(PO$_4$)$_4$·(H$_2$O), a new octahedral-tetrahedral framework structure with double-strand chains. European Journal of Mineralogy, 22, 595–604.

Momma K. and Izumi F. (2011) VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. Journal of Applied Crystallography, 44, 1272.

Nonius (2005–2007) COLLECT data collection software. Nonius BV, Delft, The Netherlands.

O’Day P.A. (2006) Chemistry and mineralogy of arsenic. Elements, 2, 77–83.

Olmi F. and Sabelli C. (1995) Carminite from three localities of Sardinia (Italy). Crystal structure refinements. Neues Jahrbuch für Mineralogie, Monatshefte, 1995, 553–562.

Otwinowski Z., Borek D., Majewski W. and Minor W. (2003) Multiparametric scaling of diffraction intensities. Acta Crystallographica, A59, 228–234.

Pekov I.V., Chukanov N.V., Varlamov D.A., Belakovskiy D.I., Turchkova A.G., Voudouris P., Katerinopoulos A. and Magganas A. (2016) Nickeltsumcorite, Pb(Ni,Fe$_3^{2+}$)(AsO$_4$)$_2$(H$_2$O,OH)$_2$, a new tsumcorite-group mineral from Lavrion, Greece. Mineralogical Magazine, 80, 337–346.

Pring A., McBriar E.M. and Birch W.D. (1989 ) Mawbyite a new arsenate of lead and iron related to tsumcorite and carminite from Broken Hill New South Wales. American Mineralogist, 74, 1379–1381.

Roberts A.C., Cooper M.A., Hawthorne F.C., Criddle A.J. and Stirling J.A.R. (2002) Sewardite, CaFe$^{2+}$(AsO$_4$)$_2$(OH)$_2$, the Ca-analogue of carminite, from Tsumeb, Namibia: description and crystal structure. The Canadian Mineralogist, 40, 1191–1198.

Sanjeeva L.D., McGuire M.A., Garlea V.O., Hu L., Chumanov G., McMillen C.D. and Kolis J.W. (2015) Hydrothermal synthesis and characterization of novel brackebuschite-type transition metal vanadates: Ba$_3$M (VO$_4$)$_2$(OH), M = V$^{3+}$, Mn$^{3+}$, and Fe$^{3+}$, with interesting Jahn–Teller and spin-liquid behaviour. Inorganic Chemistry, 54, 7014–7020.

Shannon R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica, A32, 751–767.

Sheldrick G.M. (2015a) SHELXT – Integrated space-group and crystal structure determination. Acta Crystallographica, A71, 3–8.

Sheldrick G.M. (2015b) Crystal structure refinement with SHELXL. Acta Crystallographica, C71, 3–8.

Stoe (2013) X-AREA and X-RED32. Stoe & Cie, Darmstadt, Germany.

Tillmanns E. and Gebert W. (1973) The crystal structure of tsumcorite, a new mineral from the Tsumeb Mine, S.W. Africa. Acta Crystallographica, B29, 2789–2794.

Wills A.S. (2010) VaList – Bond Valence Software for Windows. http://www.CCP14.ac.uk

Xu W.Q. and Parise J.B. (2011) Synthetic ferric sulfate trihydrate Fe$_2$(SO$_4$)$_3$·3H$_2$O, a new ferric sulfate salt. Acta Crystallographica, C67, i30–i32.

Yang Y.W., Evans S.H., Downs R.T. and Yang H. (2012) Lotharmeyerite, Ca (Zn,Mn)$_3$(AsO$_4$)$_2$(H$_2$O,OH)$_2$, Acta Crystallographica, E68, i9–i10.