The first proof of protonated anion tetrahedra in the tsumcorite-type compounds

T. Mihajlović* and H. Effenberger

Institut für Mineralogie und Kristallographie, Universität Wien, Geozentrum, Althanstr. 14, A-1090 Wien, Austria

ABSTRACT

Hydrothermal synthesis produced the new compound $SrCo_2(AsO_4)(AsO_3OH)(OH)(H_2O)$. The compound belongs to the tsumcorite group (natural and synthetic compounds with the general formula $M(1)M(2)_2(XO_4)_2(H_2O,OH)_2$; $M(1)^{1+,2+,3+}$ = Na, K, Rb, Ag, NH_4, Ca, Pb, Bi, Tl; $M(2)^{2+,3+}$ = Al, Mn^{3+}, Fe^{3+}, Co, Ni, Cu, Zn; and $X^{5+,6+}$ = P, As, V, S, Se, Mo). It represents (1) the first Sr member, (2) the until now unknown [7]-coordination for the $M(1)$ position, (3) the first proof of (partially) protonated arsenate groups in this group of compounds, and (4) a new structure variant.

The crystal structure of the title compound was determined using single-crystal X-ray diffraction data. The compound is monoclinic, space group $P2_1/a$, with a = 9.139(2), b = 12.829(3), c = 7.522(2) Å, β = 114.33(3)°, V = 803.6(3) Å^3, Z = 4 [w$R2$ = 0.065 for 3530 unique reflections]. The hydrogen atoms were located experimentally.

Introduction

The minerals of the tsumcorite group and synthetic isostructural compounds show great compositional and structural variety. To date, >30 natural and synthetic representatives of the group have been recognized (cf. Tillmanns and Gebert, 1973; Giester and Zemann, 1987; Beran *et al.*, 1997; Krause *et al.*, 1998, 2002; Effenberger *et al.*, 2000; Brugger *et al.*, 2002, and references therein). The general formula of the group is: $M(1)M(2)_2(XO_4)_2(H_2O,OH)_2$: $M(1)^{1+,2+,3+}$ = Na, K, Rb, Ag, NH_4, Ca, Pb, Bi, Tl; $M(2)^{2+,3+}$ = Al, Mn^{3+}, Fe^{3+}, Co, Ni, Cu, Zn; $X^{5+,6+}$ = P, As, V, S, Se, Mo. The $M(2)O_6$ polyhedra are edge-connected to chains which are linked by XO_4 tetrahedra to layers. They are connected by $M(1)^{[6+2]}$ or $M(1)^{[8]}$ atoms and by hydrogen bonds. For each of the cation sites $M(1)$, $M(2)$ and X, at least two different valences are possible; the coupled exchange at these cation

positions ensures electroneutrality. Furthermore, charge balance is also realized by adjusting the ratio $OH:H_2O$.

Most members of the tsumcorite group crystallize in space group $C2/m$ (Z = 2). The structure type was determined by Tillmanns and Gebert (1973). It represents the parent structure of the group referred to as 'tsumcorite type'. This requires point symmetry $2/m$ for the $M(1)$ atom, $\bar{1}$ for the $M(2)$ position as well as m for the XO_4 group. In addition, there is a strong symmetry-restricted hydrogen bond between two OH groups linked by a centre of inversion. As a consequence, H_3O_2 groups are formed. The hydrogen bonding scheme is $O(4)\cdots H(2)-O(1)-H(1)\cdots O(1)-H(2)\cdots O(4)$ ↔ $O(4)\cdots H(2)-O(1)\cdots H(1)-O(1)-H(2)\cdots O(4)$. The ratio $OH:H_2O$ is mostly ~1:1; the structure type requires a content of $OH:H_2O \geqslant 1:1$.

Two different structure variants with lower symmetry have been known to date. They are caused by distinct crystal-chemical requirements. (1) In the 'helmutwinklerite type' ($P\bar{1}$, Z = 4), the symmetry is reduced to triclinic primitive with the unit cell twice as large as that of the 'tsumcorite

type': two H_2O molecules p.f.u. (per formula unit) require an avoidance of the symmetry-restricted hydrogen bond. For the two representatives (helmutwinklerite and rappoldite), only twinned samples are known to date. The twin plane corresponds to the mirror plane of the space group $C2/m$ in the average (parent) cell. (2) In gartrellite, zincgartrellite, phosphogartrellite and lukrahnite, each half of the $M(2)$ atoms shows a distinct crystal-chemical behaviour: the Jahn-Teller effect causes a $Cu^{[4+2]}O_6$ polyhedron besides $Fe^{[6]}O_6$ or $Zn^{[6]}O_6$ octahedra. The order of the different $M(2)$ cations causes the reduction of the symmetry to $P\bar{1}$ ('gartrellite type', $Z = 1$).

A further structure variant was found in $SrCo_2(AsO_4)(AsO_3OH)(OH)(H_2O)$ during the present work. Monoclinic symmetry is maintained but the cell volume is doubled. In addition, the C-centering is avoided and the space-group symmetry is lowered to the subgroup $P2_1/a$. It is essential for this 'Sr-Co type' that the As position is split into two crystallographically independent sites and that the O(1) atoms are no longer linked by an inversion centre; consequently, the symmetry restriction of the hydrogen bond $O(1)\cdots H\cdots O(1)$ is given up. The hydrogen bonding scheme is reorganized as compared to the 'tsumcorite type'. These reduce the point symmetry of the $M(1)$ position from $2/m$ to 1. The $M(2)$ position is split into three positions of which

two have site symmetry $\bar{1}$, and one only 1. Figure 1 compares the unit cells of the four structure types of compounds belonging to the tsumcorite group.

Experimental

Synthesis

During work aimed at the hydrothermal preparation of synthetic members of the descloizite–adelite group of minerals, single crystals of the title compound were obtained. For synthesis, a mixture of $Co(OH)_2$, $Sr(NO_3)_2$ and H_3AsO_4 was transferred into a stainless steel autoclave with a Teflon liner, tightly closed and heated up to 493 K for 3 days, before cooling to room temperature. Within the reaction space appeared autogenous pressure. The final product was filtered and washed thoroughly with distilled water. It contained single crystals of the title compound besides other Sr and Co arsenates. The title compound crystallized as transparent pale pinkish, prismatic crystals up to 0.14 mm in length. $Co_2(AsO_4)(OH)$ (Keller *et al.*, 1979) crystallized in a much larger quantity than the tsumcorite-group representative. Other synthesis runs have shown that $SrCo_2(AsO_4)(AsO_3OH)$ $(OH)(H_2O)$ can also be obtained using $Sr(OH)_2 \cdot 8H_2O$ instead of $Sr(NO_3)_2$, but then the single crystals were quite small (<0.06 mm). The
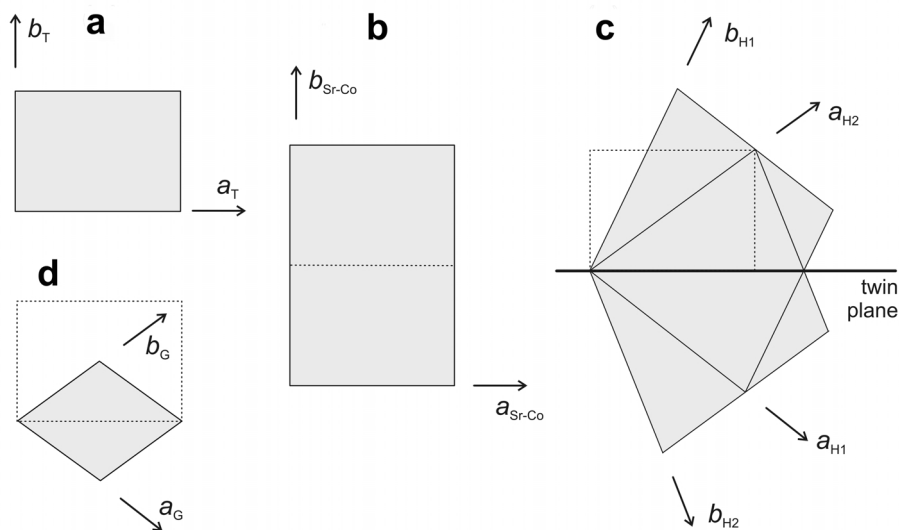

FIG. 1. Comparison of the unit cells in the four structure variants of the tsumcorite group: (*a*) the monoclinic C-centred 'tsumcorite type', (*b*) the monoclinic primitive 'Sr-Co type', (*c*) the 'helmutwinklerite type' (two twin components), and (*d*) the 'gartrellite type'. The 'tsumcorite type' cell is dashed.

chemical reaction requires a moderate acid condition; the post-synthesis pH value of the liquid phase was ~4.

Single crystal X-ray diffraction experiments and crystal-structure refinement

Several single crystals of the title compound were studied by X-ray diffraction techniques. The measured intensity data were corrected for Lorentz, polarization, background and absorption effects. From cell metrics and intensity distribution a close structural relationship with the 'tsumcorite type' was expected. The atomic arrangement of the title compound was found by an appropriate transformation of the atomic coordinates of tsumcorite (Tillmanns and Gebert, 1973) followed by full matrix least-squares refinements on F^2. From subsequent difference Fourier syntheses all the hydrogen atoms were located. Initial attempts to determine the crystal structure from a very small crystal (<0.05 mm) yielded a partly incorrect chemical formula of the title compound (Mihajlović, 2003) because of poor counting statistics and therefore, inaccurately determined atomic coordinates. During further syntheses, larger crystals of higher quality were obtained. They were successfully investigated. Crystal data, information on data collection and the results of the final structure refinement are compiled in Table 1.

The space-group symmetry of $SrCo_2(AsO_4)$ $(AsO_3OH)(OH)(H_2O)$ is $P2_1/a$. The structure was refined using anisotropic displacement parameters for all atoms except H. $R1$ is 0.035 ($wR2$ = 0.065) for all 3530 unique reflections and $R1$ is 0.025 for 2872 observed reflections using 156 variable parameters. Refined single-crystal cell parameters are: a = 9.139(2), b = 12.829(3), c = 7.522(2) Å, β = 114.33(3)°, V = 803.6(3) Å^3 (Z = 4). The final positional and displacement parameters are given in Tables 2 and 3.

An analysis of the observed reflections showed that all with $k = 2n+1$ are weak but could clearly be seen. Omitting these weak reflections results in a subcell with a' = a, b' = ½ × b, c' = c, β' = β and the centrosymmetric space group $C2/m$. This average cell corresponds to the 'tsumcorite-type' structure (Tillmanns and Gebert, 1973): a = 9.139(2), b = 6.415(1), c = 7.522(2) Å, β = 114.33(3)°, V = 401.8(2) Å^3 (Fig. 2). The structure refinement in the subcell yielded $R1$ = 0.019 ($wR2$ = 0.044) for 990 unique reflections and $R1$ = 0.018 for 959 observed reflections using 47 variable parameters.

Despite the small R values, the anisotropies of the displacement parameters of some O atoms were unusually large, clearly indicating an insufficient structure model.

Figure 3 compares the reciprocal lattices of the tsumcorite-group structures. As in the title compound, in the 'helmutwinklerite-type' weak reflections are responsible for the larger unit cell. The superstructure reflections obtained in the two structure variants are distinct from each other. Faint streaks like those observed in the 'helmutwinklerite type' could not be seen in the 'Sr-Co type'.

It is worth mentioning that $SrCo_2(AsO_4)$ $(AsO_3OH)(OH)(H_2O)$ represents a relatively rare case where the lattice symmetry is higher than the symmetry of the atomic arrangement. Using the transformation matrix (2 0 1/0 1 0/0 0 1) the monoclinic cell parameters of the true cell (space group $P2_1/a$) can be transformed into a B-centred, metrically orthorhombic lattice with unit-cell parameters a = 16.657, b = 12.829, c = 7.522 Å, α = 90, β = 90.03, γ = 90° and V = 1607.2 Å^3. However, the true symmetry of the crystal structure is clearly monoclinic.

Discussion

The M(1) position

The title compound represents the first member of the tsumcorite group with Sr atoms occupying the $M(1)$ position. The Sr atom is coordinated by seven oxygen atoms with an average Sr−O bond length of 2.604 Å (for interatomic bond lengths and bond angles see Table 4); the individual bond lengths range from 2.500(2) to 2.785(2) Å. They are split to five nearest and two next nearest neighbours with a gap of ~0.13 Å in between. The coordination polyhedron is a mono-capped octahedron with the atom O(2a) above the face O(3b2)−O(3a2)−O(4a). The eighth oxygen atom already exhibits a Sr−O(2b) distance of 3.203 Å indicating weak chemical interactions only. The [7]-coordination is new for the $M(1)$ position in the tsumcorite structure; to date, only [4+2+2]-, [6+2]- and [8]-coordinations have been found. The SrO_7 polyhedron seems to be caused by the structure type rather than by the crystal-chemical behaviour of the Sr atom. An [8]-coordination would also be compatible with the stereochemical requirements of Sr atoms; [7]-coordination is well known for most of the other cations occupying the $M(1)$ site in the tsumcorite structure (Na, K, Rb, Ag, NH_4, Ca, Pb, Bi, Tl).

TABLE 1. Crystal data, data collection and structure-refinement details for $SrCo_2(AsO_4)(AsO_3OH)(OH)(H_2O)$.

Crystal data	
Formula	$SrCo_2(AsO_4)(AsO_3OH)(OH)(H_2O)$
Space group	$P2_1/a$
a, b, c (Å)	9.139(2), 12.829(3), 7.522(2)
β (º)	114.33(3)
V (Å^3), Z	803.6(3), 4
F (000); ρ_{calc} (g cm^{-3})	968; 4.29
μ (mm^{-1})	18.9
Crystal dimensions (mm^3)	$0.10 \times 0.12 \times 0.14$
Data collection	
Diffractometer	Nonius KappaCCD system
Equipment	300 μm diameter capillary-optics collimator
Program	COLLECT, Nonius (1999)
T (K); λ (Mo-$K\alpha$) (Å)	293; 0.71073
Crystal–detector distance (mm)	30
Scan mode; rotation width (º)	φ-scans for distinct ω values; 1.5
Total no. of frames	743
Collection time per frame (s)	125
Collection mode; $2\theta_{max}$	triclinic, full sphere; 70
h, k, l ranges	$-14 \to 14, -20 \to 20, -12 \to 12$
Total reflections measured	13400
Unique reflections	3530
$R_{int} = \Sigma|F_o^2 - F_o^2(mean)|/\Sigma F_o^2$	0.031
'Observed' reflections	2872 [$F_o > 4\sigma(F_o)$]
Data processing	Nonius program suite DENZO-SMN (Otwinowski and Minor, 1997)
Absorption correction	multi-scan method
Refinement	
$R1(F)$, $wR2(F^2)$*, unique reflections	0.035, 0.065
$R1(F)$, observed reflections	0.025 [$F_o > 4\sigma(F_o)$]
Extinction coefficient	0.00231(16)
No. of refined parameters	156
GooF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{0.5}$; $(\Delta/\sigma)_{max}$	1.038, 0.002
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e/Å^3)	-1.07, 0.82
Program for structure refinement	SHELXL-97 (Sheldrick, 1997)

* $w = 1/[\sigma^2(F_o^2) + (0.0281 \times P)^2 + 0.48 \times P]$, where $P = (max (F_o^2, 0) + 2F_c^2)/3$
$R1(F) = \Sigma(||F_o| - |F_c||)/\Sigma F_o$
$wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w F_o^4]^{1/2}$

The M(2) positions

The $M(2)$ position of the parental structure is split into three symmetrically independent positions Co(a), Co(b) and Co(c) in the title compound. Two of them have point symmetry $\bar{1}$ and the third one is on a general position. The three Co atoms are all [6]-coordinated by four oxygen atoms belonging to arsenate tetrahedra and by two O(1) atoms; the CoO$_6$ polyhedra are fairly regular octahedra. However, the three environments are distinct from each other with respect to the function of the O(1) atom: the Co(a) atom is coordinated by two water molecules, the Co(b) atom by two hydroxyl groups, and the Co(c) atom by one water molecule and one hydroxyl group. The average Co–O bond lengths are 2.097, 2.122 and 2.112 Å respectively; the individual bond distances vary from 2.010(1) to 2.217(1) Å. According to the formula $\Delta_{oct} = 1/6 \Sigma[(d_i - d_m)/d_m]^2$ (Robinson et al., 1971, Fleet, 1976), the bond-length distortions for the three Co atoms amount to 8.40×10^{-5}, 1.54×10^{-3}, 8.94×10^{-4} and indicate only moderate distortions. These results compare well with the values compiled by

TABLE 2. Fractional atomic coordinates and displacement parameters for $SrCo_2(AsO_4)(AsO_3OH)(OH)(H_2O)$. U_{equiv} according to Fischer and Tillmanns (1988).

Atom	x	y	z	U_{equiv}/U_{iso}
Sr	0.253734(18)	0.128541(11)	0.00470(2)	0.00959(6)
Co(a)	0.0	0.0	0.5	0.00617(7)
Co(b)	0.5	0.0	0.5	0.00679(7)
Co(c)	0.00281(2)	0.749252(15)	0.50613(3)	0.00677(6)
As(a)	0.32249(2)	0.880584(12)	0.78125(3)	0.00582(5)
As(b)	0.66898(2)	0.631403(12)	0.21897(3)	0.00600(5)
O(1a)−OH	0.60887(18)	0.87567(8)	0.4454(2)	0.0114(3)
O(1b)−H₂O	−0.08549(18)	0.87530(8)	0.6137(2)	0.0108(3)
O(2a)	0.45118(17)	0.87682(8)	0.6736(2)	0.0113(3)
O(2b)	0.57867(19)	0.62344(8)	0.3757(2)	0.0137(3)
O(3a1)	0.21558(16)	0.99132(9)	0.74396(19)	0.0105(2)
O(3a2)	0.21442(16)	0.77269(10)	0.75594(19)	0.0108(2)
O(3b1)	0.78433(16)	0.74056(9)	0.26569(19)	0.0119(3)
O(3b2)	0.79054(16)	0.52872(10)	0.23622(19)	0.0136(3)
O(4a)−OH	0.45899(18)	0.88587(10)	1.0254(2)	0.0156(3)
O(4b)	0.51975(18)	0.63817(11)	−0.0038(2)	0.0181(3)
H(1)	0.598(3)	0.8716(15)	0.335(4)	0.012(6)
H(2)	−0.046(4)	0.8718(18)	0.739(5)	0.040(10)
H(3)	−0.207(6)	0.874(2)	0.554(7)	0.077(14)
H(4)	0.413(5)	0.903(3)	0.113(7)	0.115(16)

Wildner (1992) for CoO₆ octahedra in accurately determined crystal structures, who found 672 Co−O bond lengths between 1.959 and 2.517 Å. The average <Co−O> bond lengths for 112 polyhedra are in the range of 2.054 to 2.182 Å; the overall mean value is 2.1115 Å.

The CoO₆ octahedra are edge-linked to chains parallel to [010]. The sequence is

TABLE 3. Anisotropic displacement parameters for $SrCo_2(AsO_4)(AsO_3OH)(OH)(H_2O)$. The anisotropic dislocation parameters are defined as $exp\,[-2\pi^2\,\Sigma^3_{i=1}\,\Sigma^3_{j=1}\,U_{ij}\,a^*_i\,a^*_j\,h_i\,h_j]$.

| Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sr	0.01127(10)	0.00889(9)	0.00961(9)	−0.00037(5)	0.00539(7)	0.00061(5)
Co(a)	0.00620(16)	0.00513(13)	0.00680(15)	−0.00003(10)	0.00230(12)	0.00067(10)
Co(b)	0.00720(16)	0.00511(13)	0.00793(15)	0.00039(10)	0.00298(12)	0.00032(10)
Co(c)	0.00635(13)	0.00524(11)	0.00818(12)	0.00007(7)	0.00245(10)	−0.00016(8)
As(a)	0.00522(9)	0.00596(8)	0.00643(9)	0.00011(5)	0.00255(7)	−0.00023(5)
As(b)	0.00483(9)	0.00756(8)	0.00569(9)	−0.00003(5)	0.00224(7)	0.00008(5)
O(1a)−OH	0.0112(6)	0.0090(6)	0.0167(6)	0.0004(4)	0.0086(5)	0.0004(4)
O(1b)−H₂O	0.0079(6)	0.0099(6)	0.0159(7)	0.0011(4)	0.0063(5)	0.0007(4)
O(2a)	0.0118(6)	0.0085(5)	0.0188(7)	0.0010(4)	0.0117(5)	0.0010(4)
O(2b)	0.0216(7)	0.0081(6)	0.0208(7)	−0.0011(4)	0.0182(6)	−0.0019(4)
O(3a1)	0.0099(6)	0.0078(5)	0.0114(6)	−0.0022(4)	0.0019(5)	0.0022(4)
O(3a2)	0.0084(6)	0.0088(5)	0.0123(6)	0.0032(4)	0.0015(5)	−0.0024(4)
O(3b1)	0.0093(6)	0.0100(5)	0.0142(6)	0.0036(4)	0.0026(5)	−0.0036(4)
O(3b2)	0.0099(6)	0.0133(6)	0.0143(6)	−0.0057(5)	0.0016(5)	0.0039(5)
O(4a)−OH	0.0111(6)	0.0220(7)	0.0090(6)	−0.0002(5)	−0.0007(5)	0.0001(5)
O(4b)	0.0107(6)	0.0295(7)	0.0090(6)	0.0009(5)	−0.0011(5)	0.0017(5)
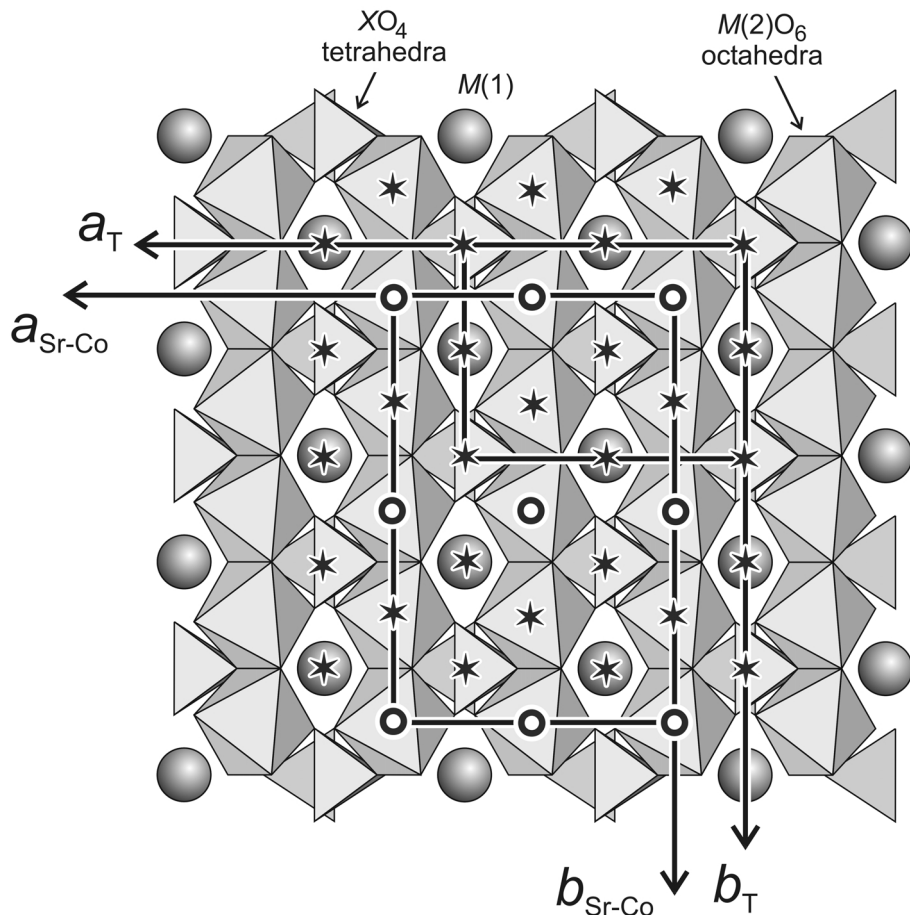
FIG. 2. Symmetry relations between the 'tsumcorite type' and the 'Sr-Co type'. The inversion centres occurring in both structures are indicated by a circle, those verified only in the 'tsumcorite type' are indicated by a star (program ATOMS; Dowty, 1999).

$-Co(a)O_6-Co(c)O_6-Co(b)O_6-Co(c)O_6-$. The shared edges $O(1a)-O(2a)$ and $O(1b)-O(2b)$ have lengths of 2.658(2) and 2.770(2) Å. Due to this connection, the angular distortion is large: $\sigma_{oct}^2 = 1/11 \, \Sigma(\angle_i - 90)^2$ is 24.3, 65.8 and 57.1 for the three CoO_6 octahedra (Robinson et al., 1971; Fleet, 1976). As expected, the smallest $O-Co-O$ angles occur in case of shared edges between the CoO_6 octahedra (77.5º to 82.0º), while for the other O atoms in cis-arrangement $O-Co-O$ varies from 84.17º to 102.89º.

While Sr atoms were not known on the M1 position in the tsumcorite-group up to now, Co at M2 is well known. However, most natural samples exhibit an extensive solid solution at the M(2) site, especially for (Fe,Co,Ni), (Fe,Zn)

and (Zn,Cu). Structure investigations of tsumcorite-group minerals with a pure occupation of the M(2) site by Co atoms are unknown. Dominant Co contents at the M(2) position were described in schneebergite ($<(Co_{1.04}Ni_{0.60}Fe_{0.36})-O>$ = 2.069 Å, Krause et al., 2002), cobaltlotharmeyerite ($<(Co_{0.97}Ni_{0.36}Fe_{0.67})-O>$ = 2.060 Å, Krause et al., 1999), cobalttsumcorite ($<(Co_{0.79}Ni_{0.40}Fe_{0.73}Zn_{0.04}Al_{0.04})-O>$ = 2.060 Å, Krause et al., 2001), and rappoldite ($<(Co_{0.99}Ni_{0.62}Zn_{0.35}Fe_{0.02})-O>$ = 2.101 and 2.096 Å, Effenberger et al., 2000). The size of the CoO_6 polyhedra in these minerals is somewhat smaller as compared to the title compound. This observation correlates well with the distinct ionic radii given by Shannon (1976) for Co (0.745 Å), Fe^{3+} (0.645 Å), Ni (0.690 Å) and Zn (0.740 Å).
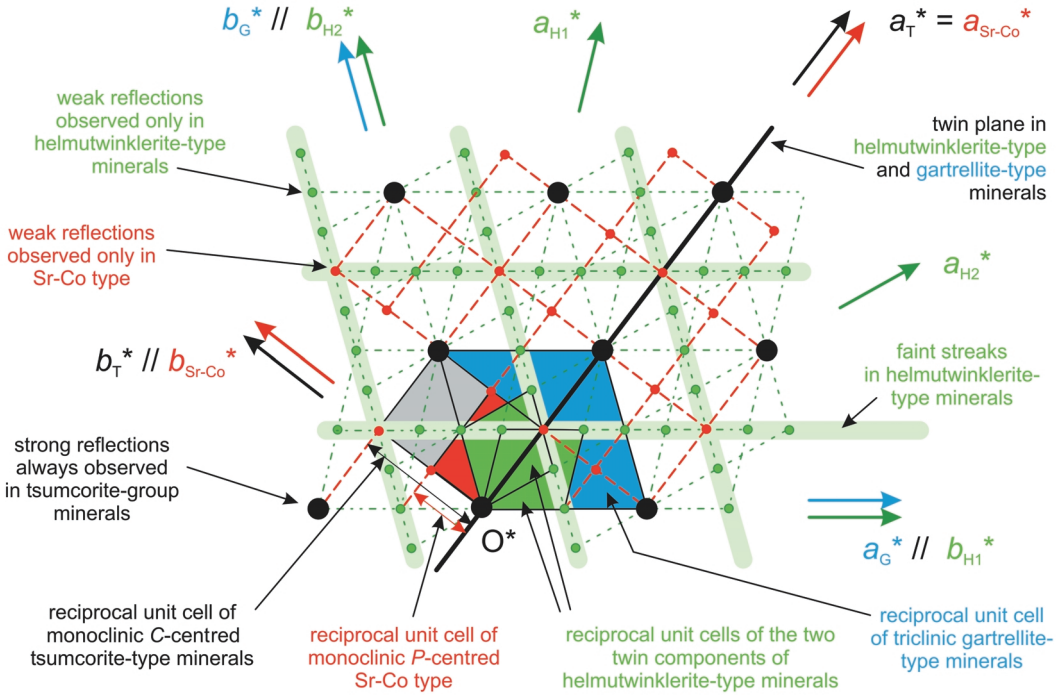
FIG. 3. Relation between the reciprocal unit cells and lattices observed in the tsumcorite group: 'tsumcorite type' (a_T^*, b_T^*), 'Sr-Co type' (a_{Sr-Co}^*, b_{Sr-Co}^*), 'helmutwinklerite type' (a_{H1}^*, b_{H1}^* and a_{H2}^*, b_{H2}^*), and 'gartrellite type' (a_G^*, b_G^*). The superstructure reflections observed in the 'Sr-Co type' (red dots) as well as in the 'helmutwinklerite type' (green dots) are shown.

The AsO₄ and AsO₃OH group

The coordination figures around the X = As atoms in the title compound represent two distinct tetrahedra. Both arsenate tetrahedra have site symmetry 1. The average As–O bond lengths are practically equivalent: 1.693 and 1.691 Å, respectively. However, the individual As–O bond lengths vary from 1.665(2) to 1.700(1) Å, but the

TABLE 4. Selected bond distances (Å) for SrCo₂(AsO₄)(AsO₃OH)(OH)(H₂O).

Sr –O(4b)	2.4996(17)	As(a)–O(3a2)	1.6651(13)	As(b)–O(4b)	1.6709(16)
–O(3a2)	2.5129(13)	–O(2a)	1.6810(14)	–O(3b2)	1.6934(13)
–O(3b1)	2.5485(13)	–O(3a1)	1.6811(13)	–O(2b)	1.6979(14)
–O(3a1)	2.5502(13)	–O(4a)	1.7452(16)	–O(3b1)	1.7002(13)
–O(3b2)	2.5949(13)	<As(a)–O>	1.6931	<As(b)–O>	1.6906
–O(4a)	2.7328(17)				
–O(2a)	2.7849(19)				
<Sr–O>	2.6029				
Co(a)–O(3a1) 2 ×	2.0694(16)	Co(b)–O(1a) 2 ×	2.0100(12)	Co(c)–O(1a)	2.0203(13)
–O(1b) 2 ×	2.1101(13)	–O(3b2) 2 ×	2.1465(16)	–O(3b1)	2.0724(16)
–O(2b) 2 ×	2.1102(12)	–O(2a) 2 ×	2.2095(12)	–O(3a2)	2.0897(16)
<Co(a)–O>	2.0966	<Co(b)–O>	2.1220	–O(1b)	2.1117(13)
				–O(2b)	2.1611(12)
				–O(2a)	2.2170(12)
				<Co(c)–O>	2.1120

TABLE 5. Hydrogen bonds in $SrCo_2(AsO_4)(AsO_3OH)(OH)(H_2O)$.

Donor atom	Hydrogen atom	Acceptor atom	D−H (Å)	H···A (Å)	D···A (Å)	D−H···A (°)
O(1a) OH	H(1)	O(4a) O(3b1) O(3a1)	0.80(3)	2.15(3) 2.59(2) 2.68(2)	2.882(2) 3.098(2) 3.065(2)	152(3) 116(2) 112(2)
O(1b) H_2O	H(2) H(3)	O(4b) O(1a)	0.86(3) 1.01(5)	1.78(3) 1.54(5)	2.637(2) 2.548(2)	175(3) 175(4)
O(4a) OH	H(4)	O(3b2) O(1a)	0.94(5)	1.93(5) 2.42(4)	2.846(2) 2.882(2)	162(4) 110(3)

H(2)−O(1b)−H(3) = 112(3)°   O(4b)···O(1b)···O(1a) = 112.02(8)°

As(a)−O(4a) bond is distinctly longer: 1.745(2) Å. Accordingly, a protonated arsenate group $[As(a)O_3OH]^{2-}$ beside a pure arsenate tetrahedron $[As(b)O_4]^{3-}$ is indicated. The crystal-chemical environment is in agreement with the experimentally determined location of the hydrogen atoms: the hydrogen atom H(4) is covalently bonded to the O(4a) atom (see Table 5). Ferraris and Ivaldi (1984) found for 36 well-determined AsO₃OH groups an average

As−OH distance of 1.731(2) Å which is somewhat shorter than the As(a)−O(4a) bond length. The O(4a) atom represents one ligand of the Sr atom and it is an acceptor atom of a further hydrogen bond which provides a comparably large contribution to the bond valence (Table 6); the bond valence sum for the O(4a) atom is slightly oversaturated (2.08 v.u.). As a consequence, a relatively long As−OH bond is caused in the title compound. The O−As−O angles are

TABLE 6. Bond-valences v_{ij} (valence units) for $SrCo_2(AsO_4)(AsO_3OH)(OH)(H_2O)$. The calculation is based on the parameters given by Brese and O'Keeffe (1991), for the hydrogen bonds according to Ferraris and Ivaldi (1988).

	Sr	Co(a)	Co(b)	Co(c)	As(a)	As(b)	Σv_{ij}*	H(1)	H(2)	H(3)	H(4)	Σv_{ij}†
O(1a)−OH	–	–	0.43 ×2 ↓	0.41	–	–	0.84	0.61	–	0.33	0.16	1.94
O(1b)−H_2O	–	0.33 ×2 ↓	–	0.32	–	–	0.65	–	0.74	0.67	–	2.06
O(2a)	0.16	–	0.25 ×2 ↓	0.24	1.26	–	1.91	–	–	–	–	1.91
O(2b)	–	0.32 ×2 ↓	–	0.28	–	1.21	1.81	–	–	–	–	1.81
O(3a1)	0.31	0.36 ×2 ↓	–	–	1.26	–	1.93	0.12	–	–	–	2.05
O(3a2)	0.34	–	–	0.34	1.32	–	2.00	–	–	–	–	2.00
O(3b1)	0.31	–	–	0.36	–	1.21	1.88	0.11	–	–	–	1.99
O(3b2)	0.27	–	0.30 ×2 ↓	–	–	1.22	1.79	–	–	–	0.17	1.96
O(4a)−OH	0.19	–	–	–	1.06	–	1.25	0.16	–	–	0.67	2.08
O(4b)	0.36	–	–	–	–	1.28	1.64	–	0.26	–	–	1.90
Σv_{ij}	1.94	2.02	1.96	1.95	4.90	4.92		1.00	1.00	1.00	1.00	

* ignoring the contribution from the hydrogen bonds
† including the contribution from the hydrogen bonds

consistent with this interpretation. As compared with the ideal tetrahedral angle of 109.47°, O−As(a)−O(4a) angles are slightly decreased (O−As(a)−O(4a) is 99.74(8) to 106.60(7)°) and the other O−As(a)−O angles are slightly increased (113.98(7) to 114.92(6)°). A similar crystal-chemical behaviour was found for protonated phosphates (Baur, 1974). The As(b)O₄ tetrahedron is much more regular than the protonated one, O−As(b)−O angles range between 105.66(8)° and 113.03(6)° only.

Hydrogen bonds

Due to the fact that all H atoms were located experimentally in the title compound, the hydrogen bonding scheme can be discussed in detail (Table 5). There are four hydrogen atoms p.f.u., and the hydrogen bonding network is responsible for the new structure variant. More than three H atoms p.f.u. are incompatible with the 'tsumcorite type' or the 'gartrellite type'. Four H atoms p.f.u. may form two water molecules as in the 'helmutwinklerite type'. A further possibility was found during the present investigations: only one water molecule but two hydroxyl groups are formed. Whereas in the other tsumcorite-structure variants the donor oxygen atom is the

O(1) atom, in the 'Sr-Co type' one of the OH groups represents a ligand to the As atom. The title compound is the first example of a tsumcorite group compound where the presence of a protonated arsenate group is proven by X-ray structure investigations. However, [AsO₂(OH)₂]¹⁻ groups were discussed by Brugger *et al.* (2002) in manganlotharmeyerite: Approximately ¼ of the $M(2)$ site is described as vacant; instead OH groups are postulated at the O(2) and O(3) sites. Earlier, protonated AsO₃OH groups were proposed for lotharmeyerite and ferrilotharmeyerite (Kampf *et al.*, 1984, Ansell *et al.*, 1992), but Krause *et al.* (1998) proved that pure arsenate tetrahedra exist in these two minerals.

As mentioned above, in the 'tsumcorite type' a hydrogen bond restricted by an inversion centre is formed between two O(1) atoms. In the title compound these O(1) atoms are split into two sites O(1a) and O(1b). The O(1a) atom strictly belongs to a hydroxyl group, whereas the O(1b) atom is part of a water molecule (Fig. 4). The former statistical occupation of two sites along the O(1)···O(1) distance by one H atom is ordered now. However, the short distance O(1b)−H(3)···O(1a) is maintained (2.55 Å); this is conspicuous for a hydrogen bond which is not

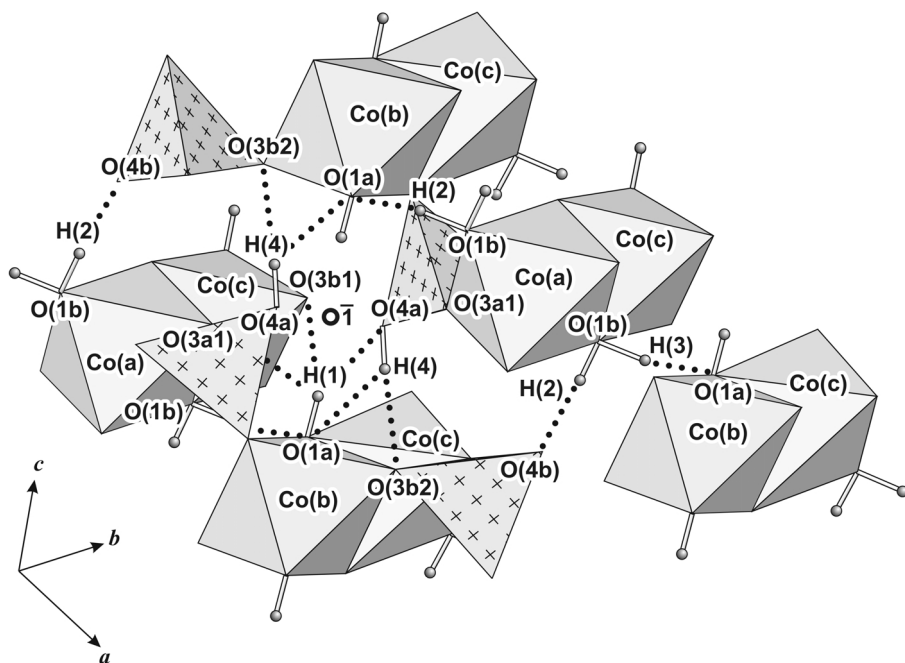

FIG. 4. The hydrogen bonds in SrCo₂(AsO₄)(AsO₃OH)(OH)(H₂O) (program ATOMS; Dowty, 1999).

restricted by any symmetry element (Jeffrey, 1997; Steiner, 2002; Lutz, 2003; Mörtel and Lutz, 2003; Poater *et al.*, 2003). It is worth mentioning that symmetrically restricted O(1)···O(1) distances are 2.44 to 2.64 Å in the tsumcorite group. The structure type allows that some members exhibit longer symmetry-restricted hydrogen bonds as compared to the ordered one in the title compound. The two hydrogen bonds of the water molecule in $SrCo_2(AsO_4)$ $(AsO_3OH)(OH)(H_2O)$ are of different strengths; the second hydrogen bond O(1b)−H(2)···O(4b) is somewhat longer (2.64 Å). Both hydrogen bonds involving the water molecule are more or less linear. The interaction with each acceptor atom is evident. Despite the inaccuracy in the location of hydrogen atoms by X-rays we note that O(1b)−H(3) = 1.05 Å is exceptionally large as compared with usual experiments but correlates with the short O(1)···O(1) distance. The three other O−H bonds range from 0.80(3) to 0.94(5) Å. However, a detailed discussion of the O−H bond lengths and O···H distances is impossible because of the large standard deviations. It is noteworthy that the location of hydrogen atoms in inorganic compounds beside Sr, As and Co atom does not allow a greater significance.

The hydrogen bonds of both the OH groups with donor atoms O(1a) and O(4a) have several O···O distances above 2.85 Å. They can be described as tri- and bifurcated. Acceptor atoms are the atoms O(4a) and O(1a) besides distinct O(3) atoms.

This hydrogen bonding scheme is in accordance with the bond valences (Table 6). Considering the contributions of the non-hydrogen atoms only, the three oxygen atoms O(1b), O(1a), and O(4a) are very undersaturated and are associated with the one water molecule and the two hydroxyl groups, respectively. Taking into account that the atoms O(1a) and O(4b) are also acceptors of strong hydrogen bonds, whereas O(4a), O(3b1), O(3a1), O(3b2) and O(1a) are acceptors of weak hydrogen bonds, the bond valences are balanced satisfactorily.

Acknowledgements

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