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Synthesis, crystal structure, infrared and Raman spectra of $Sr_5(As_2O_7)_2(AsO_3OH)$

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Abstract

The new compound $Sr_5(As_2O_7)_2(AsO_3OH)$ was synthesized under hydrothermal conditions. It represents a previously unknown structure type and belongs to a group of a few compounds in the system SrO–As_2O_5–H_2O; $(As_2O_7)^{4-}$ besides $(AsO_3OH)^{2-}$ groups have not been described yet. The crystal structure of $Sr_5(As_2O_7)_2(AsO_3OH)$ was determined by single-crystal X-ray diffraction (space group $P2_1/n$, $a = 7.146(1)$, $b = 7.142(1)$, $c = 32.750(1)$ Å, $\beta = 93.67(3)°$, $V = 1668.0(5)$ Å^3, $Z = 4$). One of the five symmetrically unique Sr atoms is in a trigonal antiprismatic (Inorg. Chem. 35 (1996) 4708)—coordination, whereas the other Sr atoms adopt the commonly observed ("Collect" data collection software, Delft, The Netherlands, 1999; Methods Enzymol. 276 (1997) 307)—coordination. The position of the hydrogen atom was located in a difference Fourier map and subsequently refined with an isotropic displacement parameter. Worth mentioning is the very short hydrogen bond length O_h–H$\cdots$O(1) of 2.494(4) Å; it belongs to the shortest known examples where the donor and acceptor atoms are crystallographically different. This hydrogen bond was confirmed by IR spectroscopy. In addition, Raman spectra were collected in order to study the arsenate groups.

Keywords: $Sr_5(As_2O_7)_2(AsO_3OH)$; Hydrothermal synthesis; Raman; Infrared; Crystal structure investigation; Pyroarsenate; Protonated arsenate

1. Introduction

Arsenates(V) as well as biarsenates (pyroarsenates) (V) are well known anion groups among natural and particularly synthetic compounds. Sometimes they occur in a mono-, bi- or tri-protonated form. Compounds containing both anion groups $(AsO_4)^{3-}$ and $(As_2O_7)^{4-}$ were rarely found. $KNi_3(AsO_4)(As_2O_7)$ [1], $Na_5Bi_2(AsO_4)(As_2O_7)_2$ [2] and $Ba(VO)_4(AsO_4)_2(As_2O_7)$ [3], were synthesized by solid-state reactions. The latter compound contains also V_2O_8 divanadyl groups formed by face sharing VO_6 octahedra. $Ag_5Cu(AsO_4)(As_2O_7)$ [4] was hydrothermally synthesized. $K_8H_2(AsO_4)_2As_2O_7$ [5], is formed as a reaction product of $K_4As_2O_7$ and $KHAsO_4$. Only hydrothermally synthesized $BaZn_2(As_2O_6OH)(AsO_4)$ [6] contains $(AsO_4)^{3-}$ besides $(As_2O_6OH)^{3-}$ groups, with the $(As_2O_6OH)^{3-}$ groups linked to infinite chains by hydrogen bonds. It represents the first substance in the BaO–ZnO–As_2O_5–H_2O system and the first structurally characterized compound which contains protonated diarsenate groups. However, until now there was no evidence for the occurrence of protonated $(AsO_3OH)^{2-}$ anions besides $(As_2O_7)^{4-}$.

This work deals with the hydrothermal synthesis and structural characterization of $Sr_5(As_2O_7)_2(AsO_3OH)$, which contains both $(AsO_3OH)^{2-}$ and $(As_2O_7)^{4-}$ groups. Furthermore this compound represents a new structure type. To obtain further information on both anion groups and especially on the very short hydrogen bond, where the donor and acceptor atoms are not equal due to (average) space-group symmetry, Raman and infrared spectra were acquired. Continuous investigations on the crystal chemistry of the arsenates are performed because arsenic is at the top of the priority of

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the most hazardous substances, but less is known about its crystal structures.

2. Experimental

2.1. Synthesis

During work aimed at hydrothermal preparation of synthetic compounds with the general formula $M(1)^{1+,2+}M(2)^{2+,3+}(OH,O)[X^{4+,5+,6+}(O_4,O_3OH)]$ (mineral group descloizite-adelite, where $M(1)=Na^+$, Ca^{2+}, Cd^{2+}, Pb^{2+}; $M(2)=Mg^{2+}$, Al^{3+}, $Mn^{2+,3+}$, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}; $X=Si^{4+}$, P^{5+}, V^{5+}, As^{5+}, Mo^{6+}), single crystals of $Sr_5(As_2O_7)_2(AsO_3OH)$ were synthesized in Teflon-lined stainless-steel autoclaves. Crystals of the title compound were prepared from a mixture of Ni-powder, $Sr(OH)_2 \cdot 8H_2O$, H_3AsO_4 and distilled H_2O as the solvent. The autoclaves were heated under autogeneous pressure from 20 to 220 °C (2 h), held at 220 °C (24 h), cooled to 120 °C (14 h), kept at this temperature (24 h), and finally cooled to room temperature (4 h). At the end of the reaction the pH of the solvent showed a weakly acid character (pH = 6.4–6.7). The reaction product was filtered and washed thoroughly with distilled water. $Sr_5(As_2O_7)_2(AsO_3OH)$ crystallizes in the form of transparent, colorless, prismatic crystals up to 0.25 mm in length. In addition, the reaction product contained the new triclinic Sr–arsenate $Sr(AsO_3OH)$ (Mihajlović et al., in preparation) in a similar quantity.

2.2. X-ray diffraction experiments and crystal structure solution

Several single crystals of $Sr_5(As_2O_7)_2(AsO_3OH)$ were studied with an automatic four-circle X-ray diffractometer. Preliminary measurements showed a primitive monoclinic unit cell. A sample exhibiting sharp reflection spots was chosen for data collection. The crystal structure was solved by direct methods and refined using standard procedures. The space-group symmetry $P2_1/n$ was found from the extinction rules and confirmed by structure refinements. The H atom was located in a difference Fourier map; its isotropic displacement parameter was considered besides the atomic

Table 1
Crystal data, data collection and structure refinement details for $Sr_5(As_2O_7)_2(AsO_3OH)$

Crystal data	
Formula	$Sr_5(As_2O_7)_2(AsO_3OH)$
Space group	$P2_1/n$
a (Å)	7.146(1)
b (Å)	7.142(1)
c (Å)	32.750(1)
β (Å)	93.67(3)
V (Å^3)	1668.0(5)
Z	4
F (000), ρ_{calc} (g cm^{-3})	2004, 4.39
μ (mm^{-1})	26
Crystal dimensions (mm^3)	0.08 × 0.10 × 0.10
Data collection and processing: single-crystal four-circle diffractometer Nonius KappaCCD, frame size: 621 × 576 pixels (binned mode), Mo tube, graphite monochromator, 300 μm diameter capillary-optics collimator, program COLLECT [7], scan mode: φ-scans for distinct ω values, $\Delta\varphi = 0.8°$, crystal-to-detector distance 40 mm, $2\theta_{max} = 60°$, $T = 293$ K, Nonius program suite DENZO-SMN [8], corrections were applied for Lorentz and polarization effects as well as for background, the absorption was corrected according to the multi-scan method.	
Total no. of frames measured	1210
Collection time per degree(s)	140
h, k, l ranges	−10→10, 0→10, −46→46
Total reflections measured	9352
Unique reflections	4872
$R_{int}=\sum\lvert F_o^2-F_o^2(\text{mean})\rvert/\sum F_o^2$	0.0302
'Observed' reflections, $F_o>4\sigma(F_o)$	3896
Structure solution and refinement: Neutral-atomic complex scattering functions [9], programs [10,11], 258 variable parameters, $\Delta/\sigma<0.001$.	
$R_1(F)$, w$R_2(F^2)$[a], unique reflections	0.0429, 0.0558
$R_1(F)$ 'observed' reflections	0.0262
Extinction coefficient	0.00058(4)
GooF = $\{\sum[w(F_o^2-F_c^2)^2]/(n-p)\}^{0.5}$	1.032
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e/Å^3)	−1.295, 0.894

[a] $R_1(F)=\sum(\lvert\lvert F_o-\lvert\lvert F_c\rvert\rvert)/\sum F_o$; $wR_2(F^2)=[\sum w(F_o^2-F_c^2)^2/\sum wF_o^4]^{1/2}$, $w=1/\{\sigma^2(F_o^2)+[0.0212*P]^2+[0.4832*P]\}$, $P=[max(0,F_o^2)]+2*F_c^2)/3]$.

Table 2
Fractional atomic coordinates and displacement parameters for $Sr_5(As_2O_7)_2(AsO_3OH)$

Atom	x	y	z	$U_{\mathrm{equiv}}/U_{\mathrm{iso}}$
Sr(1)	0.08672(5)	0.34759(5)	0.254005(12)	0.01049(8)
Sr(2)	0.38754(5)	0.09618(5)	0.056960(12)	0.01075(9)
Sr(3)	0.73314(5)	0.65933(6)	0.054452(12)	0.01388(9)
Sr(4)	0.15534(5)	0.61763(5)	0.144821(12)	0.01120(9)
Sr(5)	0.69900(5)	0.27767(5)	0.156464(12)	0.01137(9)
As(1)	0.83494(5)	0.15848(5)	0.041605(12)	0.00951(9)
As(2)	0.77347(6)	0.40474(6)	−0.039371(12)	0.00959(9)
As(3)	0.92564(5)	0.84003(6)	0.233298(12)	0.00862(9)
As(4)	0.65902(5)	0.79596(5)	0.151923(12)	0.00894(9)
As(5)	0.24153(6)	0.17314(6)	0.157063(13)	0.01003(9)
O(1)	1.0321(4)	0.0701(4)	0.06255(9)	0.0167(7)
O(2)	0.7126(4)	0.2989(4)	0.07090(9)	0.0151(6)
O(3)	0.6945(4)	−0.0093(4)	0.02154(8)	0.0143(6)
O(4)	0.9081(4)	0.2950(4)	0.00117(8)	0.0138(6)
O(5)	0.6825(4)	0.5966(4)	−0.02029(8)	0.0152(6)
O(6)	0.9386(4)	0.4335(4)	−0.07221(8)	0.0161(6)
O(7)	0.6071(4)	0.2605(4)	−0.05820(9)	0.0184(7)
O(8)	0.7887(4)	0.6221(4)	0.13395(9)	0.0142(6)
O(9)	0.6234(4)	0.9610(4)	0.11640(8)	0.0158(6)
O(10)	0.4771(4)	0.7049(4)	0.17395(8)	0.0145(6)
O(11)	0.7949(4)	0.9270(4)	0.18894(8)	0.0126(6)
O(12)	0.7613(4)	0.8034(4)	0.26607(8)	0.0149(6)
O(13)	1.0847(4)	1.0001(4)	0.24667(9)	0.0153(6)
O(14)	1.0396(4)	0.6564(4)	0.21552(8)	0.0155(6)
O(15)	0.0608(4)	0.2982(4)	0.17275(8)	0.0130(6)
O(16)	0.4014(4)	0.1137(4)	0.19347(9)	0.0152(6)
O(17)	0.3487(4)	0.3043(4)	0.12281(8)	0.0128(6)
O_h	0.1516(4)	−0.0258(4)	0.13267(9)	0.0160(6)
H	0.120(10)	−0.005(10)	0.104(2)	0.10(3)

U_{equiv} according to [12]. For the H atom U_{iso} is shown.

coordinate. Anisotropic displacement parameters for all the other atoms were allowed to vary. The anisotropies were found to be only moderate. The principle mean square displacements are ⟨0.019 Å⟩ for the Sr atoms, ⟨0.011 Å⟩ for the As atoms, and ⟨0.031 Å⟩ for the O atoms. The ratios longest:shortest of the axes are $\leqslant 2.10$ for the Sr and As atoms, but they vary from 1.78 to 5.70 for the O atoms. Crystal data, information on the data collection and results of the final structure refinement are compiled in Table 1. The positional and displacement parameters are given in Table 2, selected bond distances in Table 3.

2.3. Infrared and Raman spectra

Fourier transform infrared (FTIR) absorption spectra of $Sr_5(As_2O_7)_2(AsO_3OH)$ were recorded with a Perkin Elmer FTIR instrument 1760X at a resolution of $4\,\mathrm{cm}^{-1}$ (Fig. 1). For powder measurements the sample was prepared as a KBr pellet. A TGS detector was used to collect a total of 128 scans in the range $4000–400\,\mathrm{cm}^{-1}$. Investigations of polarized single-crystal spectra were performed with an attached Perkin Elmer FTIR microscope (circular sample aperture 100 μm diameter, 6×/0.60 N.A. mirror lenses (Cassegrains), N_2 cooled wide-range MCT detector, gold-wire grid-polarizer with an extinction ratio better than 100:1 at $<3500\,\mathrm{cm}^{-1}$). A total of 128 scans were accumulated between 4000 and $600\,\mathrm{cm}^{-1}$.

The Raman spectrum of $Sr_5(As_2O_7)_2(AsO_3OH)$ was measured with a Renishaw RM1000 notch filter-based micro-Raman system in the spectral range from 4000 to $200\,\mathrm{cm}^{-1}$ (Fig. 2). The 488.0 nm excitation line of a 20 mW Ar ion laser was focused with a 50×/0.75 objective on the (001) face of a single crystal. The backscattered radiation (180° configuration) was analyzed with a 1200 lines/mm grating monochromator in the non-confocal/continuous extended scan mode. Raman intensities were collected with a thermo-electrically cooled CCD array. The resolution of the system (i.e., the instrument function) was $5\,\mathrm{cm}^{-1}$, the wavenumber accuracy was $\pm 1\,\mathrm{cm}^{-1}$ (both calibrated with the Rayleigh line and the $520.5\,\mathrm{cm}^{-1}$ line of a Si standard). The sample spectra were acquired with a nominal exposure time of 120 s.

3. Results and discussion

The new structure type of $Sr_5(As_2O_7)_2(AsO_3OH)$ is built from five crystallographically unique SrO_x ($x = 6-8$) polyhedra (see Fig. 3) and arsenate(V) tetrahedra. Despite the three-dimensional connection of the SrO_x polyhedra, a layer-like arrangement of the Sr atoms as well as of the centers of the arsenate tetrahedra in $z \sim (2n+1)/20$ ($n \in \mathbb{N}$) is to be mentioned. The sequence is Sr(2) + Sr(3) in $z \sim 0.05$, 0.45, 0.55, and 0.95, Sr(4) + Sr(5) in $z \sim 0.15$, 0.35, 0.65, and 0.85, but only Sr(1) atoms in $z \sim 0.25$ and 0.75. The Sr(1) and Sr(4) atoms are coordinated by seven oxygen atoms with average ⟨Sr–O⟩ bond lengths of ⟨2.580 Å⟩ and ⟨2.571 Å⟩, respectively; the individual bond lengths range from 2.439(3) to 2.750(3) Å. The $Sr(1)O_7$ polyhedron is a distorted pentagonal bipyramid with the basal plane $O(10)^{x}$–$O(13)^{xi}$–O(15)–$O(14)^{iv}$–$O(16)^{ix}$ and the atoms $O(12)^{x}$ and $O(13)^{xi}$ as the two apices. The $Sr(4)O_7$ polyhedron represents a mono-capped octahedron with the atom O(17) above the face $O(6)^{vii}$–O(10)–O(15). Each of the $Sr(2)O_8$ and $Sr(5)O_8$ polyhedra are square antiprisms with average ⟨Sr(2/5)–O⟩ bond lengths of ⟨2.631 Å⟩ and ⟨2.689 Å⟩, respectively; the individual values range from 2.536(3) to 2.814(3) Å. The top and bottom faces of the $Sr(2/5)O_8$ polyhedra are formed by the atoms O(2)–$O(5)^{vii}$–$O(3)^{vi}$–O(3) and $O(7)^{vi}$–$O(9)^{ii}$–O(17)–$O(1)^{iv}$/O(2)–$O(9)^{ii}$–$O(11)^{ii}$–$O(15)^{iii}$ and O(8)–$O(12)^{xi}$–O(16)–O(17), respectively. Unusual for a cation with the ionic radius as large as 1.18 Å [14] is the [6] coordination observed for the Sr(3) atom. The individual Sr(3)–O bond lengths range from 2.471(3) to 2.637(3) Å; a seventh ligand is at

Table 3
Selected bond distances (Å) and bond angles (deg) for the coordination polyhedra in $Sr_5(As_2O_7)_2(AsO_3OH)$

Sr(1)–O(13)^{v}	2.494(3)	Sr(4)–O(6)^{vii}	2.457(3)	As(1)–O(1)	1.652(3)	
–O(12)^{x}	2.551(3)	–O(10)	2.511(3)	–O(3)	1.671(3)	
–O(14)^{iv}	2.552(3)	–O(14)^{iv}	2.523(3)	–O(2)	1.673(3)	
–O(16)^{ix}	2.561(3)	–O(15)	2.565(3)	–O(4)	1.751(3)	
–O(13)^{xi}	2.590(3)	–O_h^{i}	2.577(3)	〈As(1)–O〉	1.687	
–O(10)^{x}	2.637(3)	–O(8)^{iv}	2.622(3)			
–O(15)	2.679(3)	–O(17)	2.750(3)	As(2)–O(5)	1.656(3)	
〈Sr(1)–O〉	2.580	〈Sr(4)–O〉	2.572	–O(6)	1.659(3)	
				–O(7)	1.662(3)	
Sr(2)–O(5)^{vii}	2.536(3)	Sr(5)–O(12)^{xi}	2.542(3)	–O(4)	1.772(3)	
–O(7)^{vi}	2.548(3)	–O(15)^{iii}	2.610(3)	〈As(2)–O〉	1.687	
–O(1)^{iv}	2.565(3)	–O(9)^{ii}	2.653(3)			
–O(17)	2.648(3)	–O(8)	2.658(3)	As(3)–O(13)	1.651(3)	
–O(3)	2.656(3)	–O(17)	2.677(3)	–O(12)	1.662(3)	
–O(9)^{ii}	2.672(3)	–O(16)	2.774(3)	–O(14)	1.668(3)	
–O(3)^{vi}	2.673(3)	–O(11)^{ii}	2.790(3)	–O(11)	1.788(3)	
–O(2)	2.750(3)	–O(2)	2.814(3)	〈As(3)–O〉	1.692	
〈Sr(2)–O〉	2.631	〈Sr(5)–O〉	2.689			
				As(4)–O(10)	1.660(3)	
Sr(3)–O(6)^{viii}	2.471(3)	As(5)–O(16)	1.653(3)	–O(9)	1.664(3)	
–O(5)	2.492(3)	–O(15)	1.678(3)	–O(8)	1.678(3)	
–O(7)^{vii}	2.508(3)	–O(17)	1.683(3)	–O(11)	1.771(3)	
–O(3)^{i}	2.608(3)	–O_h	1.733(3)	〈As(4)–O〉	1.693	
–O(8)	2.622(3)	〈As(5)–O〉	1.687			
–O(2)^{i}	2.637(3)					
〈Sr(3)–O〉	2.556					
Hydrogen bonds						
Donor (D)	Hydrogen atom	Acceptor (A)	D–H	H···A	D–H···A	D···A
O_h	H	O(1)^{iv}	0.95(6)	1.56(7)	164(7)	2.494(4)

Symmetry codes: $^{i}x, y+1, z$; $^{ii}x, y-1, z$; $^{iii}x+1, y, z$; $^{iv}x-1, y, z$; $^{v}x-1, y-1, z$; $^{vi}-x+1, -y, -z$; $^{vii}-x+1, -y+1, -z$; $^{viii}-x+2, -y+1, -z$; $^{ix}-x+1/2, y+1/2, -z+1/2$; $^{x}-x+1/2, y-1/2, -z+1/2$; $^{xi}-x+3/2, y-1/2, -z+1/2$.

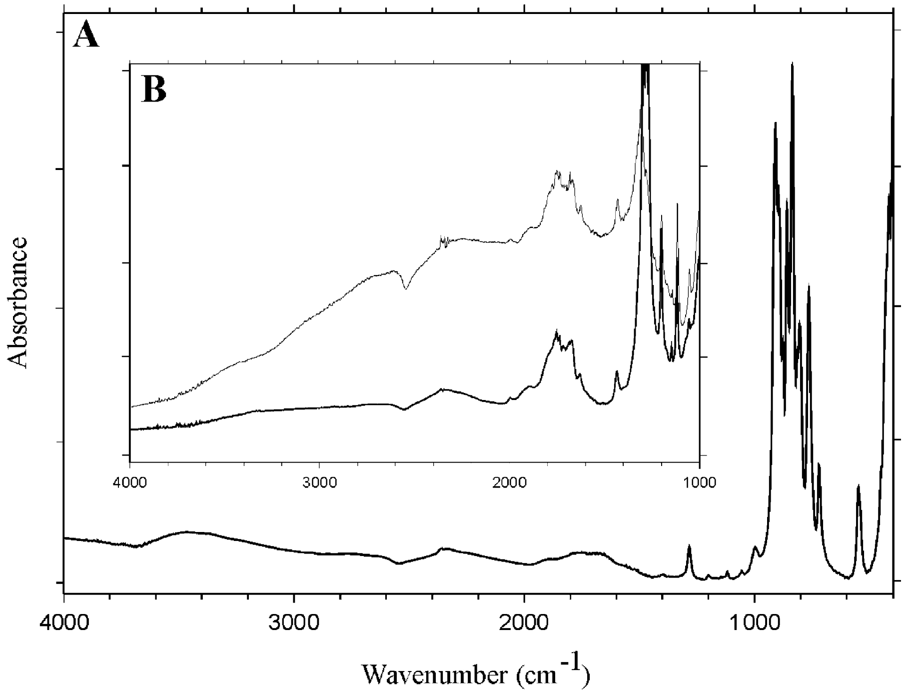

Fig. 1. Infrared spectra of $Sr_5(As_2O_7)_2(AsO_3OH)$. (A) Powder spectrum; (B) polarized single-crystal infrared spectra on a (001) face. Bands at ~1250–1300 and <1000 cm^{-1} truncated due to strong absorption.

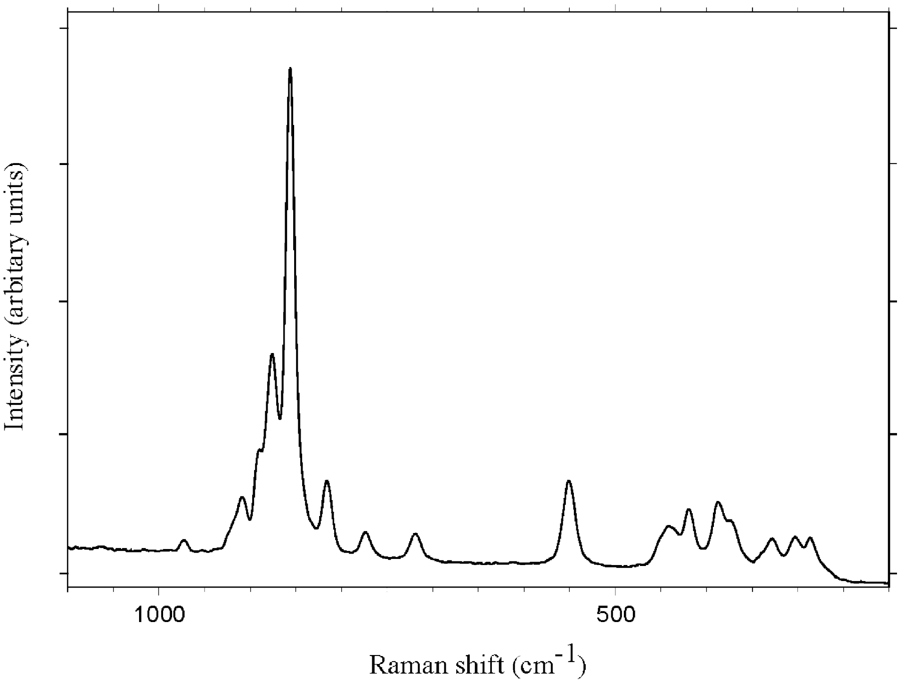

Fig. 2. Raman spectrum of a (001) face of $Sr_5(As_2O_7)_2(AsO_3OH)$ without features $>1100\,cm^{-1}$.

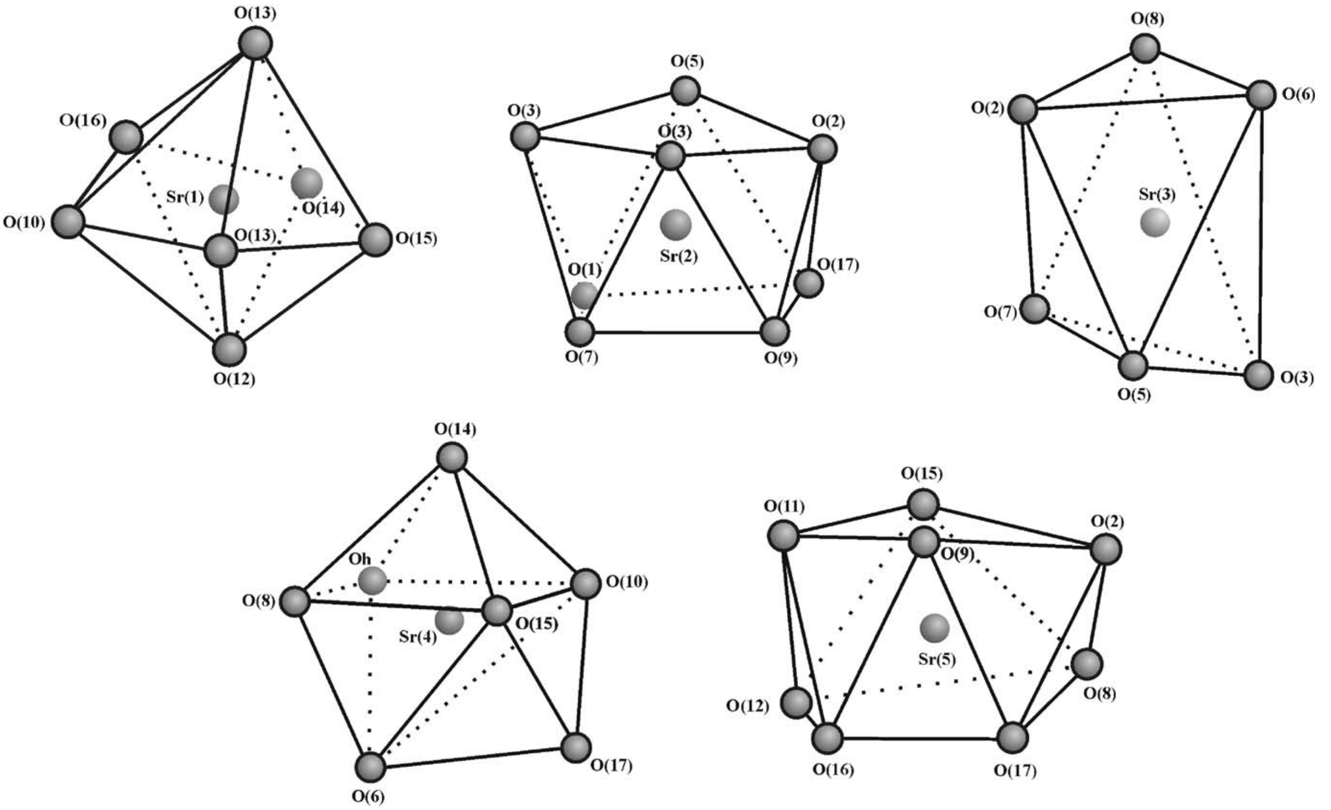

Fig. 3. The five distinct SrO_x ($x = 6-8$) coordination polyhedra in $Sr_5(As_2O_7)_2(AsO_3OH)$ [13].

a distance of 3.095(3) Å suggesting only weak chemical interactions. ⟨Sr(3)–O⟩ is shorter (⟨2.556 Å⟩) than the four other ⟨Sr–O⟩ bond lengths. The $Sr(3)O_6$ polyhedron is a trigonal antiprism with O(2)–O(8)–O(6)^{viii} and O(7)^{vii}–O(5)–O(3)^{i} representing the top and bottom faces, respectively.

The two pyroarsenate groups in $Sr_{5(As2O_7)_2(AsO3}OH)$ are formed by four crystallographically non-equivalent AsO_4 tetrahedra (Table 4). As expected, the longest As–O bond lengths are to the bridging oxygen atoms. The bond angles $O_{terminal}$–As–$O_{terminal}$ are significantly larger than $O_{bridging}$–As–$O_{terminal}$. The As–$O_{bridging}$–As angles are 129.7(2)° and 127.4(2)° which compares well with the average value for acentric pyroarsenate groups [4]. Besides these pyroarsenate groups, a protonated arsenate group $[As(5)O_3OH]^{2-}$ is embedded in the crystal structure with an average ⟨As(5)–O⟩ bond length of 1.687 Å. The As(5)–O_h bond is 1.734(3) Å, while the other individual bond lengths are distinctly shorter and range from 1.653(3) to 1.683(3) Å. It agrees with the average As–O_h bond length of 1.731(2) Å recalculated from 36 well-determined *mono*-protonated arsenate groups [16].

Table 4
As_2O_7 groups: interatomic distances (Å), bond angles (°) and distortion parameters (DI) [15] re-calculated from the atomic coordinates

Atom	As(1)	As(2)	As(3)	As(4)
As–O_b–As	129.7(2)		127.4(2)	
⟨As–O⟩	1.687	1.688	1.692	1.694
As–O_b	1.751(3)	1.772(3)	1.787(3)	1.772(3)
⟨As–O_t⟩	1.666	1.660	1.661	1.667
DI(As–O)	0.01882	0.02503	0.02793	0.02332
⟨O–As–O⟩	109.37	109.34	109.22	109.37
⟨O_b–As–O_t⟩	106.18	105.55	104.41	105.85
⟨O_t–As–O_t⟩	112.57	113.12	114.03	112.89
DI(O–As–O)	0.02919	0.03698	0.05062	0.03435
⟨O–O⟩	2.751	2.750	2.766	2.754
⟨O_b–O_t⟩	2.732	2.731	2.742	2.725
⟨O_t–O_t⟩	2.770	2.769	2.791	2.783
DI(O–O)	0.01169	0.01824	0.02483	0.02179

O, any oxygen atom in the As_2O_7 group; the atom O_b bridges between two AsO_4 tetrahedra in the As_2O_7 group; O_t are the other (terminal) O atoms of the As_2O_7 group.

As compared to the common experience for the non-symmetrically restricted hydrogen bonds, O_h–H$\cdots$O(1)^{iv} = 2.494(4) Å is remarkably short. Considering the contribution of non-hydrogen atoms only, the O_h and O(1) atoms are both undersaturated (i.e., $v_{ij}(O_h)$ and v_{ij}(O(1)) are 1.39 and 1.66 v.u., see Table 5), respectively. Taking into account that the O_h and the O(1) atoms are the donor and acceptor atoms of a very strong hydrogen bond, the bond valences are well balanced. The total amount of the bond strengths including the contribution of the hydrogen bond is in excellent agreement with the expectations: $\sum v_{ij}$ ($i = O_h$, O(1); j = Sr, As, H) is 4.05 v.u. Despite of an only inaccurate location of H atoms by X-ray experiments it should be mentioned that the O(5)–H bond length of 0.95(6) Å observed for the title compound is relatively long as compared to the formal donor–proton distance determined usually by this techniques. It indicates a significant contribution of the hydrogen atom also to the bond valence of the acceptor atom O(1) as expected for short and very short hydrogen bonds. The angle O_h–H$\cdots$O(1) of 164(7)° accords with an only slightly bent hydrogen bond. The direction of the O–H vector is approximately parallel to [001] and the angle between $O_h\cdots$O(1) and [001] amounts 26.0°. Considering the layer-like atomic arrangement with the slabs {Sr(2)Sr(3)[As(1)As(2)O_7]} and {Sr(1)Sr(4)Sr(5)[As(3)

Table 5
Bond-valences v_{ij} (valence units) according to [17] for $Sr_5(As_2O_7)_2(AsO_3OH)$

	Sr(1)	Sr(2)	Sr(3)	Sr(4)	Sr(5)	As(1)	As(2)	As(3)	As(4)	As(5)	$\sum v_{ij}$
O(1)	—	0.30	—	—	—	1.36	—	—	—	—	1.66
O(2)	—	0.18	0.25	—	0.15	1.29	—	—	—	—	1.87
O(3)	—	0.22/0.23	0.27	—	—	1.30	—	—	—	—	2.02
O(4)	—	—	—	—	—	1.04	0.99	—	—	—	2.03
O(5)	—	0.32	0.36	—	—	—	1.35	—	—	—	2.03
O(6)	—	—	0.38	0.40	—	—	1.34	—	—	—	2.12
O(7)	—	0.31	0.35	—	—	—	1.33	—	—	—	1.99
O(8)	—	—	0.26	0.26	0.23	—	—	—	1.27	—	2.02
O(9)	—	0.22	—	—	0.24	—	—	—	1.32	—	1.78
O(10)	0.25	—	—	0.35	—	—	—	—	1.34	—	1.94
O(11)	—	—	—	—	0.16	—	—	0.95	0.99	—	2.10
O(12)	0.31	—	—	—	0.32	—	—	1.32	—	—	1.95
O(13)	0.36/0.28	—	—	—	—	—	—	1.37	—	—	2.01
O(14)	0.31	—	—	0.33	—	—	—	1.31	—	—	1.95
O(15)	0.22	—	—	0.30	0.26	—	—	—	—	1.27	2.05
O(16)	0.30	—	—	—	0.17	—	—	—	—	1.36	1.83
O(17)	—	0.24	—	0.18	0.22	—	—	—	—	1.25	1.89
O_h	—	—	—	0.29	—	—	—	—	—	1.10	1.39
$\sum v_{ij}$	2.03	2.02	1.87	2.11	1.75	4.99	5.01	4.95	4.92	4.98	

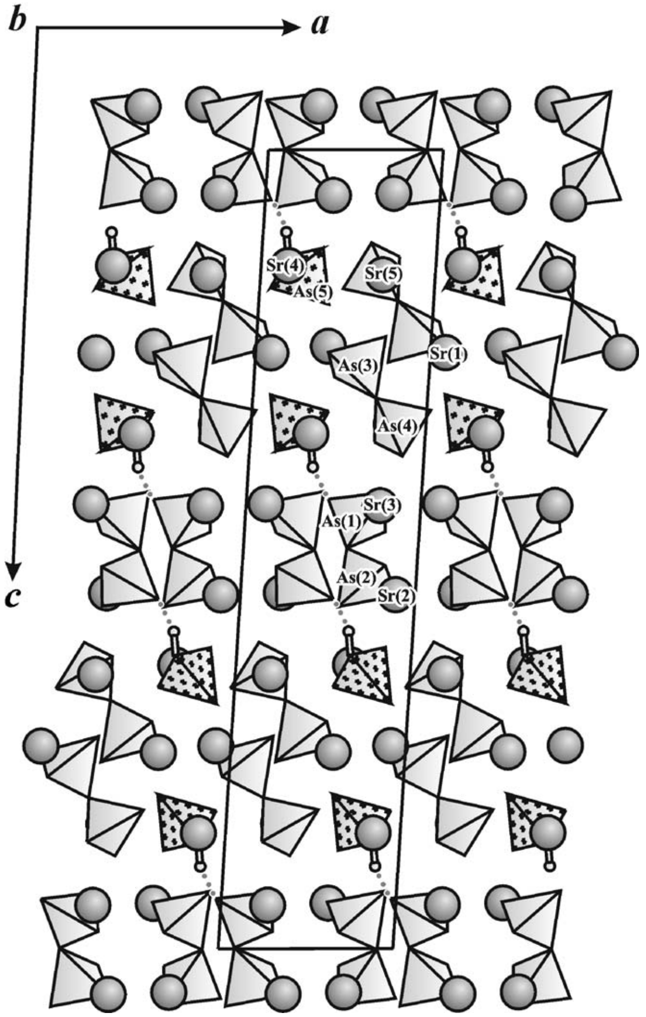

Fig. 4. The crystal structure of $Sr_5(As_2O_7)_2(AsO_3OH)$ in a projection parallel to [010] [13].

$As(2)O_7][As(5)O_3OH]\}$ parallel to (001), the hydrogen bonds link between them (Fig. 4).

Both the IR and the Raman spectra reflect the complexity of the crystal structure. The considerably large number of bands which cannot be certainly specified are caused by the five crystallographically different AsO_4 tetrahedra (two As_2O_7 groups and one protonated AsO_3OH group). Spectral data on orthoarsenates and biarsenates that have been previously published are so far rather incomplete [18] 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:

The spectral region between 3500 and 1000 cm^{-1} shows a peculiar increase in "background absorption" (Fig. 1), which is a typical feature of compounds with very short, i.e., very strong hydrogen bonds (e.g., mozartite [19], pectolite and serandite [20], natrochalcite-type compounds [21], and organic compounds [22]). It represents an extremely broad (FWHM~1000 cm^{-1}) and low-energetic band that is assigned to the OH stretching mode of the $(AsO_3OH)^{2-}$ group. It is quite characteristic that this band can be observed only in one of the polarized spectra, whereas it is absent in the other polarization directions and almost invisible in powder spectra. The former is caused by the preferred orientation of the OH vectors in the structure, the latter is a phenomenon of absorbance attenuation in powder spectra of optically anisotropic materials [23]. The peculiar shape of the band (large FWHM, wavy appearance, transmission window at ~2550 cm^{-1}) is caused by resonance and interference phenomena enhanced by the strong anharmonicity [24] of this vibration. Because of the broad band shape, As–O tetrahedral stretching vibrations and lattice modes are superimposed in the low-energy region of the spectrum. The large FWHM aggravates a precise determination of the band center, which is estimated to be roughly at $\sim 1600 \pm 200\,cm^{-1}$. According to the *d*–*v* correlation for hydrogen bonds this wavenumber is in excellent agreement with the refined $O_h–H \cdots O(1)^{iv}$ bond length of 2.494(4) Å [22,25]. The sharp and truncated band (Fig. 1B) at ~1250–1300 cm^{-1} in the IR spectrum is assigned to the bending mode of the OH group and it corresponds with typical bending frequencies of strongly H bonded hydroxyl groups [22,26].

The 1100–700 cm^{-1} range shows the As–O stretching modes of the $(AsO_3OH)^{2-}$ and $(As_2O_7)^{4-}$ groups. As already mentioned, the complexity of the crystal structure does not allow to be more specific. The strong and sharp band in infrared and the weak one in Raman spectra around 909 cm^{-1} could be attributed to the antisymmetric bridge stretching vibration, ν_{as} (As–O–As) of pyroarsenate groups [27]. The most intense Raman bands around 876 cm^{-1} (very weak in IR) and 857 cm^{-1} correspond to the symmetric stretching vibrations of $(AsO_3OH)^{2-}$ and $(As_2O_7)^{4-}$ groups, respectively. In infrared spectra, the modes around 860 and 836 cm^{-1} may be assigned to antisymmetric stretching vibrations of the $(As_2O_7)^{4-}$ groups. The modes around 804 and 764 cm^{-1} represent antisymmetric stretching modes of the protonated arsenate group. It is suggested that the $(AsO_4)^{3-}$ group is the only tetrahedral oxyanion of the main group elements in which $\nu_s > \nu_{as}$ [18]. However, because of five crystallographically different As sites, additional stretching modes can be expected.

The band near 550 cm^{-1} (both in IR and Raman) is the symmetric bridge stretching vibration, ν_s (As–O–As) and it is characteristic of the $(As_2O_7)^{4-}$ group with a non-linear As–O–As bond [18,27]. In the region below 450 cm^{-1} appear the bending modes of the $(AsO_3OH)^{2-}$ and $(As_2O_7)^{4-}$groups, and various lattice modes of the compound.

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