

Synthesis and characterization of 2-phosphonoethanesulfonic acid and a barium-hydrogenphosphonatoethanesulfonate — $\text{BaH}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)$

Andreas Sonnauer, Norbert Stock*

Institute of Inorganic Chemistry, Christian-Albrechts-University, Otto-Hahn-Platz 6/7, D 24118 Kiel, Germany

Received 17 October 2007; received in revised form 7 December 2007; accepted 7 December 2007

Available online 15 December 2007

Abstract

Following the strategy of using polyfunctional phosphonic acids for the synthesis of new metal phosphonates, the organic linker molecule 2-phosphonoethanesulfonic acid, $\text{H}_2\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3\text{H}$ (**1**) (H_3L), was synthesized and characterized in detail. The acid was used in a high-throughput (HT) investigation of the system $\text{BaCl}_2/\text{H}_3\text{L}/\text{NaOH}/\text{H}_2\text{O}$. The HT experiments comprising 48 individual hydrothermal reactions were performed to systematically investigate the influence of pH of the starting mixture as well as the molar ratio $\text{Ba}^{2+}:\text{H}_3\text{L}$. Only two reaction products were observed: small amounts of BaCO_3 under basic conditions and $\text{BaH}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)$ (**2**). For compounds **1** and **2** the crystal structures were determined from single-crystal X-ray diffraction data ($\text{H}_2\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3\text{H}$: trigonal, $P3_2$, $a = 814.58(1)$, $c = 861.20(2)$ pm, $Z = 3$, $R_1 = 0.0254$, $wR_2 = 0.0758$ for $I > 2\sigma(I)$; $\text{BaH}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)$: orthorhombic, $Ibam$, $a = 953.39(19)$, $b = 855.55(17)$, $c = 867.82(17)$ pm, $Z = 4$, $R_1 = 0.0162$, $wR_2 = 0.0417$ for $I > 2\sigma(I)$). The structure of H_3L (**1**) is stabilized exclusively by strong hydrogen bonds. Compound **2** is built up by chains of edge sharing BaO_8 polyhedra. These chains are connected to a three-dimensional network by the $-\text{CH}_2\text{CH}_2-$ linker of the ligand. Thermogravimetric investigation of compound **2**, as well as IR spectra of **1** and **2** are presented.

© 2007 Elsevier Inc. All rights reserved.

Keywords: Metal phosphonates; 2-Phosphonoethanesulfonic acid; Inorganic–organic hybrid compounds; Crystal structure; Barium

1. Introduction

Many inorganic–organic hybrid compounds are well known. They can be classified according to interactions and arrangement of the inorganic and organic building units [1]. The classes of inorganic–organic hybrids range from amorphous nanocomposites such as self-assembled mesoporous, to crystalline hybrid materials. These compounds are mostly based on metal carboxylates, sulfonates and phosphonates and are intensively investigated due to their potential applications as sorbents, ion exchangers, catalysts, or charge-storage materials [2,3]. Porous hybrid compounds based on metal carboxylates [4–7] and phosphonates [8] have attracted widespread interest in the past few years. We are interested in the use of organic ligands containing two or more different functional groups

for the synthesis of functionalized porous hybrid compounds or bimetallic hybrid systems. So far our focus has been on the use of phosphonocarboxylic [8], iminobis (methylphosphonic) ($(\text{H}_2\text{O}_3\text{P}-\text{CH}_2)_2\text{N}-\text{CH}_2\text{C}_6\text{H}_4-\text{COOH}$) [9] as well as tetraphosphonic acids (1,2,4,5 ($\text{H}_2\text{O}_3\text{PCH}_2$)₄ C_6H_4) [10]. Although a large number of metal phosphonates and metal sulfonates have been reported in the literature, compounds based on ligands containing simultaneously a phosphonic as well as a sulfonic acid group have only been recently investigated. These few studies are limited to the use of linker molecules based on rigid phosphonoarylsulfonic acids [11–15]. To the best of our knowledge only one investigation by our group using the flexible linker 2-phosphonethanesulfonic acid has been reported in the literature [16]. In course of our systematic investigation on the synthesis of inorganic–organic hybrid compounds based on $\text{H}_2\text{PO}_3-\text{C}_2\text{H}_4-\text{SO}_3\text{H}$ (H_3L) and di- as well as trivalent metal ions nine isotopic lanthanide phosphonatosulfonates $\text{Ln}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)(\text{H}_2\text{O})$ [16] with

*Corresponding author. Fax: +49 431 880 1775.

E-mail address: stock@ac.uni-kiel.de (N. Stock).

$Ln = La-Dy$ have been obtained. Here we report the synthesis and structural characterization of the ligand $H_2PO_3-C_2H_4-SO_3H$ and the high-throughput (HT) study of the system $BaCl_2/H_3L/NaOH/H_2O$ that led to the compound $BaH(O_3P-C_2H_4-SO_3)$. For additional information a thermogravimetric (TG)-analysis for compound **2** was carried out as well as IR spectroscopy for compounds **1** and **2**.

2. Experimental section

2.1. Synthesis of $H_2O_3P-C_2H_4-SO_3H$ (H_3L)

H_3L was synthesized based on the methods reported in the literature [17,18]. In the first step, diethyl-2-bromoethylphosphonate was synthesized. Therefore, 1, 2-dibromoethane (80.0 ml, 920 mmol) was added drop wise at $160^\circ C$ to triethylphosphite (26.7 ml, 153 mmol) over a period of 20 min. After the addition had been completed, the reaction mixture was heated for 3 h under reflux. Unreacted 1,2-dibromoethane was removed under reduced pressure and diethyl-2-bromoethylphosphonate was distilled off under vacuum (200 Pa) at $81-82^\circ C$. The colorless liquid (30.6 g) was identified as $Br-C_2H_4-PO_3Et_2$, IR (neat): 2981, 2930, 2908, 1478, 1443, 1393, 1368, 1288 cm^{-1} ; 1H NMR ($CDCl_3$): $\delta = 1.22$ (t, 6H, $^3J_{H,H} = 7.1$ Hz, $-CH_3$), 2.27 (m, 2H, $-CH_2-PO_3Et_2$), 3.42 (m, 2H, $-CH_2Br$), 4.01 (m, 4H, $-CH_2CH_3$) ppm; ^{13}C NMR: $\delta = 16.35$ (d, $^3J_{C,P} = 6$ Hz, $-CH_3$), 23.74 (s, $Br-CH_2$), 30.73 (d, $^1J_{C,P} = 134.7$ Hz, $-CH_2PO_3Et_2$), 61.95 (d, $^2J_{C,P} = 6$ Hz, $P-O-CH_2-$) ppm; ^{31}P NMR: $\delta = 26.25$ (s) ppm. For the sulfonation $Br-C_2H_4-PO_3Et_2$ was added to a boiling solution containing 20.7 g anhydrous sodium sulfite in 60 ml distilled water for 30 min. The sodium ions were exchanged in an ion exchange column with DOWEX[®] 50WX8-200 until the solution was free of Na^+ ions. The solution was concentrated by H_2O evaporation at reduced pressure to approximately 150 and 100 ml concentrated HCl were added and the solution was refluxed for 48 h. After the hydrolysis of the phosphonic acid ester the solvent was evaporated in a rotary evaporator to dryness and a white solid was obtained. The solid was dissolved in distilled water and evaporated several times until no HCl could be detected. The final product 21.3 g was identified as 2-phosphonoethanesulfonic acid, IR (neat): 3022, 2969, 2318, 1633, 1425 cm^{-1} ; 1H NMR (D_2O): $\delta = 2.00$ (m, 2H, CH_2), 2.88 (m, 2H, CH_2) ppm; ^{13}C NMR: $\delta = 22.44$ (d, $^1J_{C,P} = 136$ Hz, CH_2), 44.68 (d, $^2J_{C,P} = 3$ Hz, CH_2) ppm; ^{31}P NMR: $\delta = 27.64$ (s) ppm. The strongly hygroscopic acid was dried and stored under vacuum. For the following experiments aqueous solutions were prepared. The concentration and water content were determined by titration with NaOH ($H_2O_3P-C_2H_4-SO_3H \cdot xH_2O$, $x = 1.8$). The prepared H_3L -solutions were stored at $4^\circ C$ to prevent decomposition of the sulfonic acid group. Suitable single crystals for the crystal structure determination were isolated during the evaporating procedure.

2.2. High-throughput investigation

The system $BaCl_2/H_3L/NaOH/H_2O$ was investigated using HT methods. The reactions were performed under hydrothermal conditions at $150^\circ C$ for 48 h in a custom made HT reactor system containing 48 PTFE inserts each with a maximum volume of $300\ \mu l$ [19,20]. In the HT set up seven molar ratios $Ba^{2+} : H_3L$ (1:1, 1:2, 1:3, 1:4, 2:1, 3:1 and 4:1) were used and the NaOH content was increased in different steps from 0 to 10 mol equivalents based on the amount of H_3L . The results of the HT experiment, based on powder X-ray diffraction (XRD) pattern, are given in Fig. 1. Exact amounts of starting materials are given in Table S1 in the supporting information. Single crystals for XRD were isolated from the reaction vessel with the molar ratio $Ba^{2+} : H_3L : NaOH$ (1:1:3).

2.3. Synthesis scale up of $BaH(O_3P-C_2H_4-SO_3)$

Larger amounts of microcrystalline product were synthesized in an open flask at $100^\circ C$. 3.2 g $H_2O_3P-C_2H_4-SO_3H \cdot xH_2O$ with $x = 1.8$ were dissolved in 200 ml boiling water and $Ba(OH)_2$ was added to adjust the pH to 6. During the addition of $Ba(OH)_2$ a white precipitate was observed. The solid (3.8 g) was filtered and washed with water and ethanol (yield: 69% based on H_3L). The powder XRD pattern compares well with the one simulated from the single-crystal structure determination (Fig. S1, Supporting Information). Elemental analysis $BaH(O_3P-C_2H_4-SO_3)$, $M = 325.44\text{ g/mol}$: found: C, 7.30; H, 1.17; S, 9.99. Calc. C, 7.37; H, 1.24; S, 9.84.

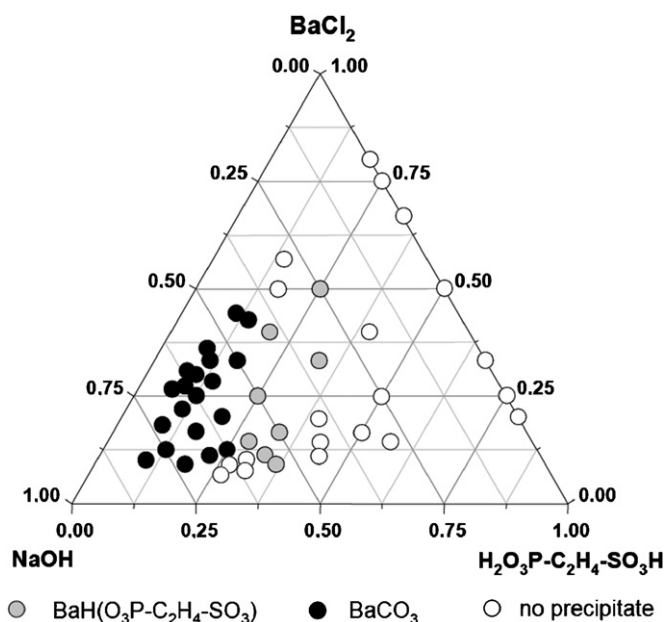


Fig. 1. Crystallization diagram of the system $BaCl_2/H_2O_3P-C_2H_4-SO_3H/NaOH/H_2O$. Results are based on powder XRD measurements. Small amounts of $BaCO_3$ are due to the affinity of NaOH towards CO_2 from air during dispensing and traces of carbonate in the NaOH employed in the synthesis.

2.4. Materials and methods

The phosphonoethanesulfonic acid was synthesized as described in 2.1. All other reagents were of analytical grade (Aldrich and Fluka) and were used without further purification. HT X-ray analysis was carried out in transmission geometry using a STOE HT powder diffractometer equipped with a linear position sensitive detector (PSD) system [20]. MIR spectra were recorded on an ATI Matheson Genesis in the spectral range 4000–400 cm^{-1} using the KBr disk method. TG analyses were carried out in nitrogen (75 ml/min, 30–800 °C, 4 °C/min) using a NETSCH STA 409 CD analyzer. ^1H , ^{31}P and ^{13}C solution NMR spectra were recorded on a Bruker Avance 400 pulse Fourier transform spectrometer at 300 MHz using CDCl_3 and D_2O as solvents. Elemental analyses were performed on an Eurovektor EuroEA elemental analyzer. The semi-quantitative elemental analyses were performed using a Phillips ESEM XL 30 hot cathode scanning electron microscope equipped with an energy dispersive X-ray (EDX) EDAX analyzer for elemental analysis.

3. Crystallography

Suitable single crystals of compounds **1** and **2** were carefully selected using a polarizing microscope. Single-crystal XRD for compound **1** was performed on an Enraf Nonius Kappa-CCD diffractometer equipped with a rotating anode (Mo $K\alpha$ radiation, $\lambda = 71.073$ pm). The data collections for compound **2** were performed on a STOE AED II diffractometer (298 K) and for low-temperature data collection (170 K) on a STOE IPDS diffractometer. Both instruments are equipped with a fine-focus sealed tube (Mo $K\alpha$ radiation, $\lambda = 71.073$ pm). For data reduction and absorption correction the program XRED was used [21]. The single-crystal structures were solved by direct methods and refined using the program package SHELXTL [22]. All hydrogen atoms of the $-\text{CH}_2-$ groups were placed onto calculated positions. The hydrogen atoms of the protonated phosphonate- and sulfonate group in compound **1** as well as the phosphonate group in compound **2** could not be located in the difference Fourier map. Experimental data and results of **1** and **2** are given in Table 1. Selected bond lengths and bond angles of both compounds are summarized in Table 2.

4. Results and discussion

4.1. High-throughput investigation

Our HT methodology allows a fast and systematic investigation of a large part of the parameter space while employing identical reaction conditions such as time, temperature, heating rate, etc. for all 48 reaction vessels [19,20]. The evaluation of the system $\text{BaCl}_2/\text{H}_3\text{L}/\text{NaOH}/\text{H}_2\text{O}$ is based on the powder XRD measurements and is summarized in Fig. 1. Seven different molar ratios

Table 1

Summary of crystal data, intensity measurement, and structure refinement parameters for $\text{H}_2\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3\text{H}$ (H_3L) (**1**) and $\text{BaH}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)$ (**2**)

Compound	1	2
Crystal system	Trigonal	Orthorhombic
Space group	$P3_2$	$Ibam$
<i>a</i> (pm)	814.58(1)	953.39(19)
<i>b</i> (pm)	814.58(1)	855.55(17)
<i>c</i> (pm)	861.20(2)	867.82(17)
α (deg)	90	90
β (deg)	90	90
γ (deg)	120	90
Volume (10^6 pm 3)	494.88(1)	707.9(2)
Temperature (K)	298	298
<i>Z</i>	3	4
Formula mass (g/mol)	190.11	325.43
ρ (g/cm 3)	1.914	3.044
<i>F</i> (000)	294	604
μ (mm $^{-1}$)	0.706	6.110
Absorption correction	Numerical	Numerical
$T_{\text{min.}}/T_{\text{max}}$	0.8282/0.9283	0.3846/0.4806
θ range (deg)	3.73–27.46	3.20–30.02
Range in <i>hkl</i>	$-10 \leq h \leq 10$, $-10 \leq k \leq 10$, $-11 \leq l \leq 10$	$-13 \leq h \leq 13$, $-12 \leq k \leq 12$, $-12 \leq l \leq 3$
Total data collect.	8926	2747
Unique/obs. data ($I > 2\sigma(I)$)	1508/1467	550/481
Extinction coeff.	0.187(10)	None
<i>R</i> (int)	0.0437	0.0322
<i>R</i> ₁ , <i>wR</i> ₂ ($I > 2\sigma(I)$)	0.0254, 0.0758	0.0162, 0.0417
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0262, 0.0765	0.0216, 0.0429
Goodness of fit	1.067	1.065
No. of variables	104	35
Δe Min/max (e Å $^{-3}$)	−0.374/0.329	−0.741/0.577

Table 2

Selected bond lengths (pm) and angles (deg) for $\text{H}_2\text{PO}_3-\text{C}_2\text{H}_4-\text{SO}_3\text{H}$ (**1**) and $\text{BaH}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)$ (**2**)

Bond distances (1)		Bond angles (1)	
P1–O1	152.7(2)	O–P–C	104.5(3)–110.1(3)
P1–O2	152.3(2)	O–P–O	109.0(3)–114.2(3)
P1–O3	151.7(4)	O–S–C	106.4(2)–108.6(3)
S1–O4	146.9(2)	O–S–O	111.6(1)–111.6(1)
S1–O5	146.5(2)	P1–C1–C2	112.4(1)
S1–O6	148.5(4)	S1–C2–C1	111.7(1)
Bond distances (2)		Bond angles (2)	
Ba1–O1	277.0(2)	O2–P1/S1–O1	112.0(1)
Ba1–O2	281.7(2)	O2–P1/S1–C1	107.4(1)
P1/S1–O1	150.8(2)	O1–P1/S1–C1	107.2(1)
P1/S1–O2	149.8(2)		

$\text{M}:\text{H}_3\text{L} = 1:1, 1:2, 1:3, 1:4, 2:1, 3:1$ and $4:1$ were investigated in one experiment in parallel and the amount of NaOH was increased in different steps from 0 to 10 mol equivalents. Under acidic conditions ($\text{pH} < 4$) no precipitate is obtained. $\text{BaH}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)$ is formed at molar ratios of $\text{H}_3\text{L}:\text{NaOH} = 0.5-1$ and low molar ratios $\text{Ba}^{2+}:\text{H}_3\text{L} = 1$ or 2 . Highly alkaline conditions led to small amounts of BaCO_3 due to the affinity of NaOH toward

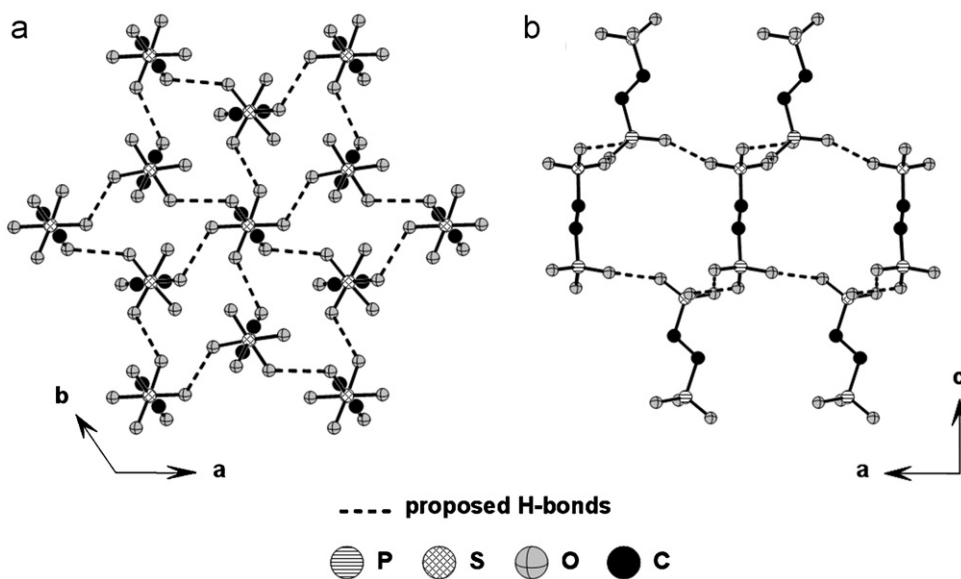


Fig. 2. Three-dimensional H-bonding network of $\text{H}_2\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3\text{H}$ molecules: (a) along the c -axis and (b) along the b -axis. Hydrogen bonds are presented by dashed lines. H-atoms connected to C-atoms have been omitted for sake of clarity.

CO_2 from air during dispensing and traces of carbonate in the NaOH employed in the synthesis ($K_{\text{sp}}(\text{BaCO}_3) = 5.1 \times 10^{-9}$ at 20°C [23]).

4.2. Crystal structures

4.2.1. Crystal structure of $\text{H}_2\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3\text{H}$ (H_3L)

The asymmetric unit of H_3L is shown in Fig. S2. Due to the similar scattering factor of phosphorus and sulfur a differentiation based on the structure refinement is not trivial. This can be unequivocally accomplished by comparing bond lengths with data given in the literature. While in the barium phosphonates $\text{Ba}(\text{HO}_3\text{PC}_6\text{H}_5)_2$ [24] and $[\text{Ba}_3(\text{O}_3\text{PCH}_2\text{NH}_2\text{CH}_2\text{PO}_3)_2(\text{H}_2\text{O})_4] \cdot 3\text{H}_2\text{O}$ [8] P–O bond lengths in the range of 149.8(4)–158(4) pm are observed, the corresponding S–O bond lengths in the barium sulfonates $[\text{Ba}((\text{O}_3\text{S})_2\text{C}_6\text{H}_2(\text{OH})_2)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ [25] and $\text{Ba}(\text{C}_{10}\text{H}_6\text{S}_2\text{O}_6)(\text{H}_2\text{O})_2$ [26] are significantly shorter 143.7(2)–147.2(3) pm. These values compare well with the bond lengths observed in our study, where P–O and S–O distances of 151.7(4)–152.7(2) and 146.5(2)–148.5(4) pm, respectively, are observed. For charge neutrality the acid molecules have to be fully protonated. The hydrogen atoms could not be located in the difference Fourier map. However, the observed interatomic distances O2–O4 (250.9(4) pm), O3–O5 (256.6(2) pm) and O1–O6 (255.4(2) pm) indicate strong hydrogen bonds. The proposed H-bonding scheme is given in Fig. S3 and shows that all oxygen atoms of the sulfonate — and the phosphonate group are involved in hydrogen bonding. Thus, a three-dimensional network is formed as shown in Fig. 2.

4.2.2. Crystal structure of $\text{BaH}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)$

The asymmetric unit of $\text{BaH}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)$ is shown in Fig. 3. The crystal structure was solved and refined in the

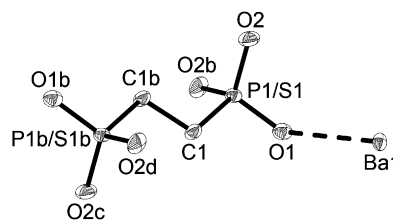


Fig. 3. Asymmetric unit of $\text{BaH}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)$. For clarity, symmetry equivalent atoms are shown. Phosphorus and sulfur could not be distinguished. Thermal ellipsoids are drawn at 50% probability.

space group $Ibam$ (No. 72). In this space group, the anion $\text{H}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)^{2-}$ lays on a center of inversion and therefore P and S occupy the same crystallographic position. Thus, an averaged structure of the anion can be expected. The P and S atoms were refined at identical sites with an occupation factor of 0.5 each. Therefore, the commands EXYZ and EADP in SHELXL-97 were used [22]. To verify the disorder of the $\text{H}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)^{2-}$ anion, several structure refinements in space groups with lower symmetry were performed in which the anion is located in a general position. The results show no significant differences in P–O and S–O bond lengths which excludes an ordered arrangement of the anion as observed in $\text{H}_2\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3\text{H}$ (1) and $\text{Ln}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)(\text{H}_2\text{O})$ [16]. Furthermore, a single-crystal XRD experiment at 170 K was performed. The data show no additional reflections due to the presence of a superlattice or the change of space group symmetry. For charge neutrality the anion has to be singly protonated. This is supported by the interatomic distances O2–O2 (270.1(2) pm) that indicate the presence of a hydrogen bond (Fig. 4). The Ba^{2+} ions are surrounded by eight oxygen atoms ($4 \times \text{O1}$ and $4 \times \text{O2}$). Each Ba^{2+} ion is connected to eight

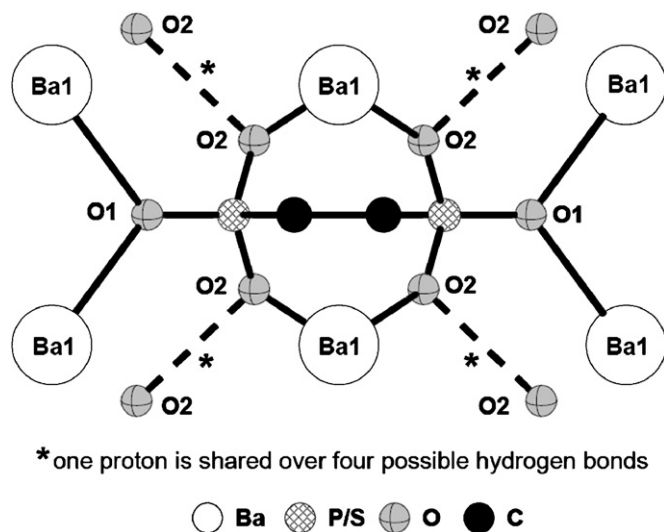


Fig. 4. Coordination sphere of the anion $[H(O_3P-C_2H_4-SO_3)]^{2-}$ in compound **2**. H-atoms connected to C-atoms have been omitted for sake of clarity.

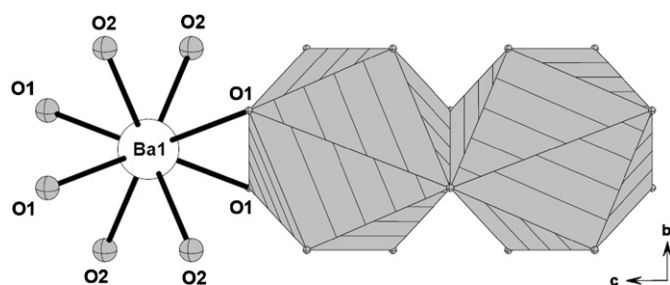


Fig. 5. Edge sharing BaO_8 polyhedra form chains along the c -axis in $BaH(O_3P-C_2H_4-SO_3)$ (**2**). The BaO_8 polyhedra are shaded in grey.

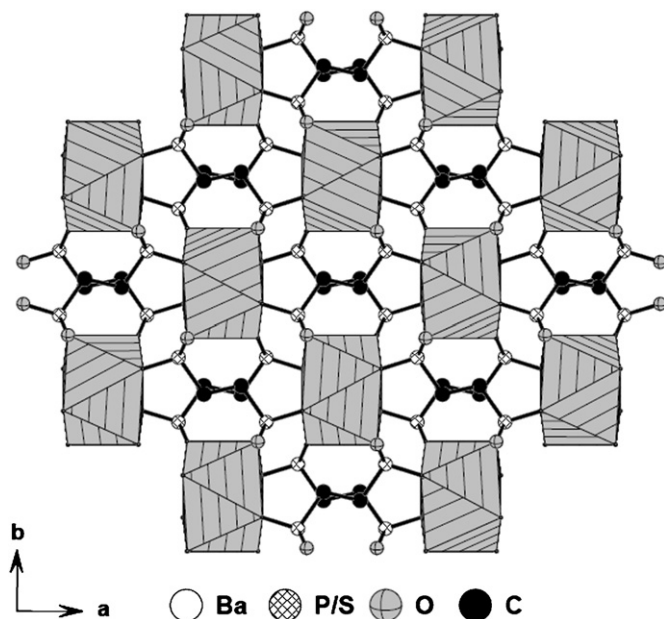


Fig. 6. The chains of edge sharing BaO_8 polyhedra (shaded in grey) along the c -axis in $BaH(O_3P-C_2H_4-SO_3)$ (**2**) are connected to a three-dimensional framework by the $-CH_2CH_2-$ linker of the ligand.

$H(O_3P-C_2H_4-SO_3)^{2-}$ ions through eight P/S–O–Ba bonds. The oxygen atoms act as bridging (O1) as well as end on monodentate (O2) ligands. Thus, edge sharing BaO_8 polyhedra are observed, that form chains along the c -axis (Fig. 5). These chains are connected to a three-dimensional framework by the $-CH_2-CH_2-$ linker of the ligand (Fig. 6).

The structural chemistry of metal phosphonosulfonates is strongly determined by the flexibility of the ligand and the presence of additional co-ligands during the synthesis. While the use of phosphonosulfonic acids with rigid organic linker molecules, i.e. phosphonoarylsulfonic acids, together with phen or bipy ligand lead to tetra- or hexanuclear metal-phosphonoarylsulfonate clusters ($M = Zn^{2+}$ [13], Ln^{3+} [12]) the flexible phosphonoethanesulfonic acid has exclusively yielded compounds with extended M–O–M structures up to now. The formation of such extended M–O–M structures was also observed with flexible as well as rigid phosphonic acids in barium phosphonates. Thus, the barium hydrogenphosphonates, $Ba(HO_3PC_6H_5)_2$ [24], $Ba(HO_3PC_6H_4PO_3H)$ [27] and $Ba(HO_3PC_6H_4C_6H_4PO_3H)$ [27], contain layers of eight-coordinate Ba^{2+} ions and phosphonate groups. These compounds are structurally related and exhibit the same Ba–O–P topology. Whereas, in the monophosphonate a layered structure is formed, the two bisphosphonates crystallize in a pillared structure. The barium phosphonates containing flexible linker molecules, $[Ba_3(O_3PCH_2NH_2CH_2PO_3)_2(H_2O)_4] \cdot 3H_2O$ [8], $Ba[HN(CH_2PO_3H)_3] \cdot H_2O$ [28] and $[(H_2O)_2Ba\{Cl_2C(PO_3Et)_2\}_2Ba(H_2O)_2]_n$ [29] show a larger structural variability. For example, in $[Ba_3(O_3PCH_2NH_2CH_2PO_3)_2(H_2O)_4] \cdot 3H_2O$ [8] a porous three-dimensional M–O–M framework is observed with the phosphonic acid molecules lining the inner wall of the pores. This M–O–M dimensionality is reduced in the other two structures by using the amino-tris(methylenephosphonic) acid $N(CH_2PO_3H)_3$ [28] or blocking one of the phosphonate oxygen atoms through the use of a phosphonic acid ester [29].

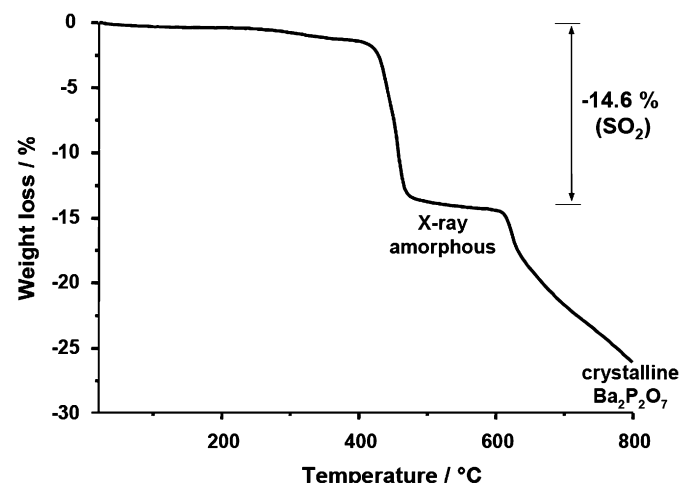


Fig. 7. Thermogravimetric investigation of $BaH(O_3P-C_2H_4-SO_3)$ (**2**).

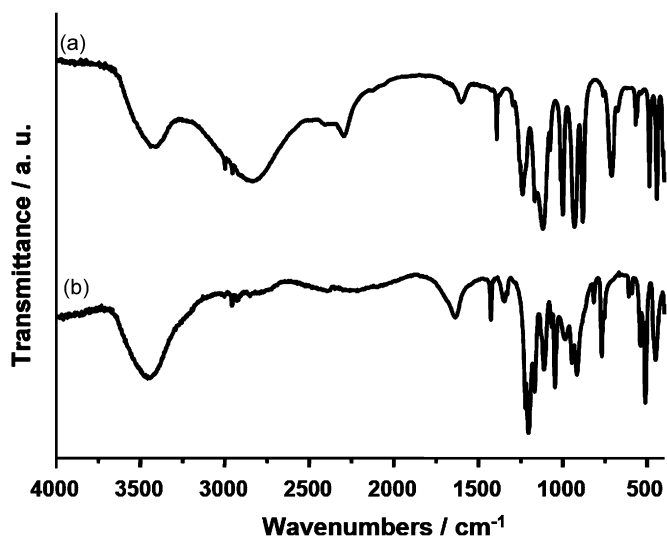


Fig. 8. IR spectra: (a) $\text{H}_2\text{O}_3\text{P-C}_2\text{H}_4\text{-SO}_3\text{H}\cdot x\text{H}_2\text{O}$ with $x = 1.8$ (**1**) and (b) $\text{BaH}(\text{O}_3\text{P-C}_2\text{H}_4\text{-SO}_3)$ (**2**).

4.3. Thermal study

In order to learn more about the thermal stability of compound **2** a TG investigation (Fig. 7) was performed. Up to 400°C no significant weight loss is observed. From 400 to 520°C a weight loss of 14.6% is observed, which cannot be easily explained. Therefore, in a second TG experiment the measurement was stopped at 520°C and a XRD amorphous powder was obtained. The EDX elemental analysis shows the absence of sulfur. Thus, we assume that the decomposition of the sulfonate — group takes place and SO_2 (calcd. 14.8%) is released. Upon further heating a continuous weight loss due to decomposition of the organic part is observed. At the final temperature of 800°C the powder XRD pattern shows formation of crystalline $\text{Ba}_2\text{P}_2\text{O}_7$.

4.4. IR spectroscopy study

The hygroscopic powder of $\text{H}_2\text{O}_3\text{P-C}_2\text{H}_4\text{-SO}_3\text{H}$ (**1**) could only be investigated in a hydrated form $\text{H}_2\text{O}_3\text{P-C}_2\text{H}_4\text{-SO}_3\text{H}\cdot x\text{H}_2\text{O}$ with $x = 1.8$ (calculated by titration with NaOH). The IR spectra of $\text{H}_2\text{O}_3\text{P-C}_2\text{H}_4\text{-SO}_3\text{H}\cdot x\text{H}_2\text{O}$ ($x = 1.8$) (**1**) and $\text{BaH}(\text{O}_3\text{P-C}_2\text{H}_4\text{-SO}_3)$ (**2**) are shown in Fig. 8. They exhibit typical bands in the region between 1300 and 950cm^{-1} that are due to the stretching vibrations of the CPO_3^- and the CSO_3^- -group; however, the individual bands cannot be assigned unambiguously. Bands in the region from 2960 to 2919cm^{-1} are due to C–H stretching vibrations. The corresponding CH_2 deformation vibration appears at 1422cm^{-1} . Furthermore, the spectrum of H_3L (**1**) shows several broad bands in the range from 3200 to 2100cm^{-1} that are typical for the presence of P–O–H...O and S–O–H...O hydrogen bonds [30].

5. Conclusion

The flexible bi-functional 2-phosphonoethanesulfonic acid is a versatile ligand for the synthesis of crystalline inorganic–organic hybrid compounds. The synthesized compounds $\text{BaH}(\text{O}_3\text{P-C}_2\text{H}_4\text{-SO}_3)$ and $\text{Ln}(\text{O}_3\text{P-C}_2\text{H}_4\text{-SO}_3)(\text{H}_2\text{O})$ with $\text{Ln} = \text{La-Dy}$ [16] are both built up from M–O–M chains of MO_8 polyhedra of different connectivity. While in $\text{BaH}(\text{O}_3\text{P-C}_2\text{H}_4\text{-SO}_3)$ disorder of the anion is observed (S/P–O = $149.8(2)$ – $150.8(2)$ pm) in the series $\text{Ln}(\text{O}_3\text{P-C}_2\text{H}_4\text{-SO}_3)(\text{H}_2\text{O})$ with $\text{Ln} = \text{La-Dy}$ the $-\text{CSO}_3^-$ and $-\text{CPO}_3^-$ groups can be clearly distinguished (S–O = $145.5(4)$ – $147.2(4)$ pm; P–O = $149.1(4)$ – $154.0(4)$ pm). We are currently investigating the use of other metal ions that may lead to compounds with interesting optical and magnetic properties [31]. Thus, based on additional HT-experiments crystalline rare earth (series Ho–Lu, Y) and transition metal phosphonatoethanesulfonates were investigated and characterized. These compounds exhibit isolated M–O polyhedra, M–O–M cluster as well as M–O–M chains and layers. These results will be reported soon.

Acknowledgments

The authors thank Dr. Peter Mayer and Priv.-Doz. Dr. Christian Näther for the acquisition of the single-crystal data of $\text{H}_2\text{O}_3\text{P-C}_2\text{H}_4\text{-SO}_3\text{H}$ (**1**) and $\text{BaH}(\text{O}_3\text{P-C}_2\text{H}_4\text{-SO}_3)$ (**2**), respectively. This work is supported by the DFG-Project STO 643/2-2.

Appendix A. Supporting Information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2007.12.003.

Detailed reaction parameters of the HT investigation. This material is available free of charge via the Internet at <http://www.pubs.acs.org>. CCDC 664308 and 664309 for **1** and **2**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax, +44 1223 336033; e-mail, deposit@ccdc.cam.ac.uk).

References

- [1] C. Sanchez, B. Julian, P. Belleville, M. Popall, J. Mater. Chem. 15 (2005) 3559.
- [2] A. Clearfield, Metal Phosphonate Chemistry in Progress in Inorganic Chemistry, vol. 47, Wiley, New York, 1998, p.371.
- [3] A.K. Cheetham, G. Férey, T. Loiseau, Angew. Chem. Int. Ed. 38 (1999) 3268.
- [4] H. Li, M. Eddaoudi, M. O’Keeffe, O.M. Yaghi, Nature 402 (1999) 276.
- [5] M. Latroche, S. Suble, C. Serre, C. Mellot-Drazniéks, P.L. Llewellyn, J. Lee, J. Chang, S.H. Jhung, G. Férey, Angew. Chem. Int. Ed. 45 (2006) 8227.
- [6] E. Biemmi, T. Bein, N. Stock, Solid State Sci. 8 (2006) 363.

- [7] C. Serre, J.A. Groves, P. Lightfoot, A.M.Z. Slawin, P.A. Wright, N. Stock, T. Bein, M. Haouas, F. Taulelle, G. Férey, *Chem. Mater.* 18 (2006) 1451.
- [8] S. Bauer, H. Müller, T. Bein, N. Stock, *Inorg. Chem.* 44 (2005) 9464.
- [9] S. Bauer, T. Bein, N. Stock, *J. Solid State Chem.* 179 (2006) 145.
- [10] N. Stock, N. Guillou, J. Senker, G. Férey, T. Bein, *Z. Anorg. Allg. Chem.* 631 (2005) 575.
- [11] A.F. Benedetto, P.J. Squattrito, F. Adani, E. Montoneri, *Inorg. Chim. Acta* 260 (1997) 207.
- [12] Z.Y. Du, H.B. Xu, J.G. Mao, *Inorg. Chem.* 45 (2006) 9780.
- [13] Z.Y. Du, H.B. Xu, J.G. Mao, *Inorg. Chem.* 45 (2006) 6424.
- [14] F. Adani, M. Casciola, D.J. Jones, L. Massinelli, E. Montoneri, J. Rozière, R. Vivani, *J. Mater. Chem.* 8 (1998) 961.
- [15] G.B. Deacon, R. Harika, P.C. Junk, B.W. Skelton, A.H. White, *New J. Chem.* 31 (2007) 634.
- [16] A. Sonnauer, C. Näther, H.A. Höpfe, J. Senker, N. Stock, *Inorg. Chem.* 46 (2007) 9968.
- [17] A.H. Ford-Moore, J. Howarth Williams, *J. Chem. Soc.* (1947) 1465.
- [18] E. Montoneri, G. Ricca, *Phosphor, Sulfur Silicon* 55 (1991) 111.
- [19] N. Stock, T. Bein, *Solid State Sci.* 5 (2003) 1207.
- [20] N. Stock, T. Bein, *Angew. Chem.* 116 (2004) 767; N. Stock, T. Bein, *Angew. Chem. Int. Ed.* 43 (2004) 749.
- [21] XRED version 119, X-Shape Version 1.06, Stoe & Cie GmbH, Darmstadt, Germany, 1999.
- [22] G.M. Sheldrick, *SHELXTL-PLUS Crystallographic System*, Siemens, Analytical X-Ray Instruments Inc., Madison, WI, 1992.
- [23] *CRC Handbook of Chemistry and Physics*, 83rd ed., CRC Press, Boca Raton, FL, 2002.
- [24] D.M. Poojary, B. Zhang, A. Cabeza, M.A.G. Aranda, S. Bruque, A. Clearfield, *J. Mater. Chem.* 6 (1996) 639.
- [25] A.P. Côté, G.K.H. Shimizu, *Chem. Commun.* (2001) 251.
- [26] J. Cai, C. Chen, C. Liao, X. Feng, X. Chen, *Acta Crystallogr. B* 57 (2001) 520.
- [27] D.M. Poojary, B. Zhang, A. Clearfield, *Anal. Quim. Int. Ed.* 94 (1998) 401.
- [28] K.D. Dermandis, S.D. Katarachia, R.G. Raptis, H. Zhao, P. Baran, *Cryst. Growth Des.* 6 (2006) 836.
- [29] M. Kontturi, E. Vuokila-Laine, S. Peräniemi, T.T. Pakkanen, J.J. Vepsäläinen, M. Ahlgren, *J. Chem. Soc. Dalton Trans.* (2002) 1969.
- [30] G. Socrates, *Infrared and Raman Characteristic Group Frequencies*, vol. 3, Wiley, New York, 2001, p. 220.
- [31] A.K. Cheetham, C.N.R. Rao, *Science* 318 (2007) 58.