



High-throughput and microwave investigation of rare earth phosphonatoethanesulfonates— $Ln(O_3P-C_2H_4-SO_3)$ ($Ln = Ho, Er, Tm, Yb, Lu, Y$)

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ABSTRACT

Following the strategy of using bifunctional phosphonic acids for the synthesis of new metal phosphonates, the flexible ligand 2-phosphonoethanesulfonic acid, $H_2O_3P-C_2H_4-SO_3H$ (H_3L), was used in a high-throughput (HT) and microwave investigation of rare earth phosphonatoethanesulfonates. The HT-investigation led to six isotypic compounds $Ln(O_3P-C_2H_4-SO_3)$ with $Ln = Ho$ (**1**), Er (**2**), Tm (**3**), Yb (**4**), Lu (**5**) and Y (**6**). The syntheses were scaled-up in glass reactor tubes in order to obtain larger amounts for a detailed characterization. Based on these results all compounds could be also synthesized by microwave-assisted heating and the influence of reaction time and stirring rate during the synthesis was established. For compound **2** the crystal structure was determined by single-crystal X-ray diffraction. The compounds contain isolated slightly distorted LnO_6 octahedra that are connected by the phosphonate and sulfonate groups into a three-dimensional framework. Thermogravimetric investigations demonstrate the high thermal stability of the compounds up to 460 °C.

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1. Introduction

Inorganic–organic hybrid materials based on metal carboxylates, sulfonates and phosphonates are intensively investigated due to their potential application, i.e. in the fields of gas separation, storage, as well as catalysis, or as sensor materials [1–4]. Especially porous hybrid compounds based on metal carboxylates [5–7] and phosphonates [8–11] have been in the focus of many studies 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 hybrid compounds. So far our focus has been on the use of phosphonocarboxylic [9], iminobis(methylphosphonic) ($(H_2O_3PCH_2)_2N-CH_2C_6H_4-COOH$) [12] as well as tetraphosphonic acids (1, 2, 4, 5 ($H_2O_3PCH_2)_4C_6H_4$) [13,14]. 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 recently been investigated. These few studies are limited to the use of linker molecules based on rigid phosphonoarylsulfonic acids [15–21]. To the best of our knowledge only three investigations by our group using the flexible linker 2-phosphonethanesulfonic acid has been reported in the literature [22–24]. Here we

report the high-throughput study of the system $LnX_3/H_3L/NaOH/H_2O$ ($LnX_3 = Ho(CH_3COO)_3, Er(NO_3)_3, Tm(NO_3)_3, YbCl_3, LuCl_3, Y(NO_3)_3$) in which a series of isotypic compounds $Ln(O_3P-C_2H_4-SO_3)$ with $Ln = Ho$ (**1**), Er (**2**), Tm (**3**), Yb (**4**), Lu (**5**), Y (**6**) were obtained. Suitable crystals of **2** could be isolated and the crystal structure was determined. Based on the results of the high-throughput study the syntheses were scaled-up successfully. Alternatively, all compounds can be synthesized by microwave heating. This study describes the influence of reaction time and stirring rate on the yield. IR spectroscopy and thermogravimetric (TG) analysis data are also presented.

2. Experimental section

2.1. Materials and methods

2-Phosphonoethanesulfonic acid (H_3L) was synthesized as previously reported [23]. All other reagents were of analytical grade (Aldrich and Fluka) and were used without further purification. High-throughput X-ray analysis was carried out in transmission geometry using a STOE high-throughput powder diffractometer equipped with a linear position sensitive detector (PSD) system [25]. The microwave reactions were performed using a Biotage Initiator-eight microwave synthesizer (max. 400 W). MIR spectra were recorded on an ATI Matheson Genesis spectrometer in the spectral range 4000–400 cm^{-1} using the KBr

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disk method. Thermogravimetric (TG) analyses were carried out in nitrogen (75 ml/min, 30–900 °C, 4 °C/min) using a NETSCH STA 409 CD Analyzer. CHNS 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.

2.2. High-throughput investigation

The system $LnX_3/H_3L/NaOH/H_2O$ ($LnX_3 = Ho(CH_3COO)_3, Er(NO_3)_3, Tm(NO_3)_3, YbCl_3, LuCl_3, Y(NO_3)_3$) was investigated using high-throughput (HT) methods. The HT experiment was performed under hydrothermal conditions at 170 °C for 24 h in a custom made high-throughput reactor system containing 48 PTFE inserts each with a maximum volume of 300 μ L [25,26]. For all 48 reactions molar ratios of $Ln^{3+}:H_3L = 1:1$ were used. The NaOH content was varied in 8 steps from 0 to 7 mol equivalents based on the amount of H_3L . The reactions were performed starting from aqueous solutions of 0.25 M $Ho(CH_3COO)_3$, 1.0 M $Er(NO_3)_3$, 0.5 M $Tm(NO_3)_3$, 0.5 M $YbCl_3$, 0.5 M $LuCl_3$ and 1.0 M $Y(NO_3)_3$. Each reaction contained identical amounts of H_3L (0.025 mmol) and Ln^{3+} (0.025 mmol) ions. The evaluation of the HT experiments based on powder X-ray diffraction (XRD) is given in Fig. 1. Exact amounts of starting materials as well as the pH of reaction solutions are given in Table S1 in the supporting information.

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

Larger amounts of all title compounds were synthesized in glass reactors (DURAN® CULTURE TUBES 12 × 100 MM D50 GL 14 M.KAP, SCHOTT 261351155). For the synthesis of $Ln(O_3P-C_2H_4-SO_3)$ ($Ln = Er, Tm, Yb, Lu, Y$) 100 μ L (0.2 mmol) 2.0 M H_3L , 400 μ L (0.2 mmol) 0.5 M LnX_3 and 200 μ L (0.4 mmol) 2.0 M NaOH were combined. Water was added to a final volume of 1.10 ml. $Ho(CH_3COO)_3$ is less soluble than the other rare earth salts. Therefore 82.8 mg (\sim 0.2 mmol) of solid $Ho(CH_3COO)_3 \cdot xH_2O$ ($x \sim 4$) were used instead of a solution. According to the HT experiments for the synthesis of $Ho(O_3P-C_2H_4-SO_3)$ the addition of NaOH is not necessary. The mixtures were homogenized by shaking for 2 min and heated at 170 °C for 24 h. The precipitates were filtered, washed with water and identified as $Ln(O_3P-C_2H_4-SO_3)$; yields based on the amount of H_3L for $Ln = Ho$ (92%), Er (83%), Tm (76%), Yb (69%), Lu (35%), Y (76%). The identity of reaction products was validated by powder X-ray diffraction. Detailed amounts of starting materials are given in Table S2.

2.4. Microwave syntheses

All reactions were performed in Biotage microwave vials ($V_{max} = 2.0$) ml at 170 °C. The “normal” heating mode was used with high absorption level. Temperature, magnetron power and pressure were recorded during the whole reaction process (Fig. S1 in the supporting information). The reaction products consisting of small particles ($< 20 \mu$ m) were isolated by centrifugation and dried at 60 °C. All yields are based on the amount of H_3L . For each rare earth ion the identical reaction mixtures as described in Section 2.3 were used. The entire series of title compounds $Ln(O_3P-C_2H_4-SO_3)$ with $Ln = Ho, Er, Tm, Yb, Lu, Y$ has been successfully synthesized by microwave heating (2 h) with a stirring rate of 450 min^{-1} (yields: $Ln = Ho$ (56%), Er (30%), Tm (42%), Yb (39%), Lu (25%), Y (32%)). Elemental analyses: (1), $M = 352.02$ g/mol: found: C, 6.91; H, 1.19; S, 8.91. Calcd: C, 6.82; H, 1.15; S, 8.80. (2), $M = 354.35$ g/mol: found: C, 6.87; H, 1.20; S, 8.93. Calcd: C, 6.78; H, 1.14; S, 8.74. (3), $M = 356.02$ g/mol: found: C, 6.80; H, 1.19; S, 9.17. Calcd: C, 6.75; H, 1.13; S, 9.01. (4), $M = 360.13$ g/mol: found: C, 6.83; H, 1.21; S, 9.12. Calcd: C, 6.67;

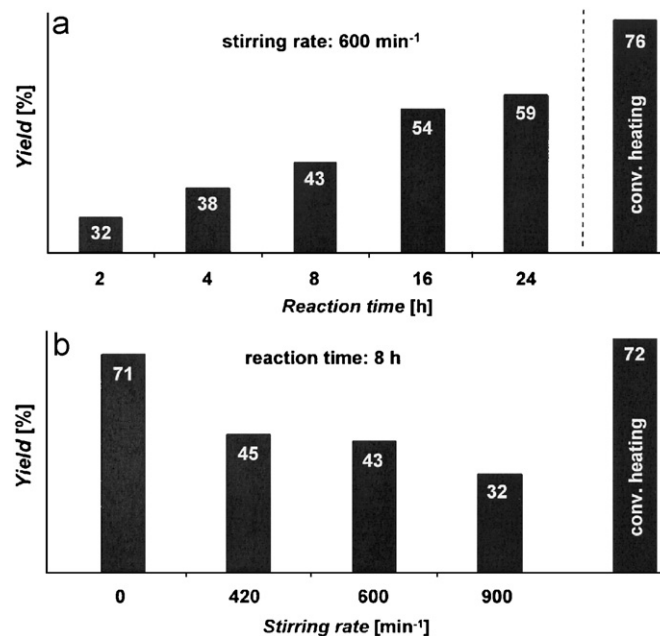


Fig. 2. Influence of reaction time (top) and stirring rate (bottom) at constant reaction temperature of 170 °C on the yield of $Y(O_3P-C_2H_4-SO_3)$ (6). (a) Indicates the conventional heating in glass tubes at 170 °C for 24 h and (b) for 8 h.

$Ln^{3+} : H_3L : NaOH$	1:1:0	1:1:1	1:1:2	1:1:3	1:1:4	1:1:5	1:1:6	1:1:7
$Ho(CH_3CO_2)_3$	●	●	⊗	⊗	⊗	⊗	●	●
$Er(NO_3)_3$	○	●	●	●	⊗	⊗	⊗	⊗
$Tm(NO_3)_3$	○	●	●	●	⊗	⊗	⊗	⊗
$YbCl_3$	○	●	●	●	⊗	⊗	⊗	⊗
$LuCl_3$	●	●	●	⊗	⊗	⊗	⊗	⊗
$Y(NO_3)_3$	○	○	●	●	○	○	⊗	●

● $Ln(O_3P-C_2H_4-SO_3)$ ● $Ln(OH)_3$
 ⊗ unidentified product ⊗ X-ray amorphous ○ no precipitate

Fig. 1. Crystallization diagram of the system $LnX_3/H_3L/NaOH/H_2O$ ($LnX_3 = Ho(CH_3COO)_3, Er(NO_3)_3, Tm(NO_3)_3, YbCl_3, LuCl_3, Y(NO_3)_3$). Results are based on powder XRD measurements.

H, 1.12; S 8.90. (5), $M = 362.06$ g/mol: found: C, 6.75; H, 1.17; S, 8.84. Calcd: C, 6.63; H, 1.11; S, 8.86. (6), $M = 275.99$ g/mol: found: C, 8.71; H, 1.46; S, 11.62. Calcd: C, 8.67; H, 1.41; S, 11.59. To investigate the influence of reaction time and stirring rate on the yield, further experiments were performed for the yttrium compound (Fig. 2). The influence of the reaction time on the yields was investigated by five syntheses 2 h (32%), 4 h (38%), 8 h (43%), 16 h (54%) and 24 h (59%) with a stirring rate of 600 min^{-1} . The effect of the stirring rate on the yield was investigated in four steps with a constant reaction time of 8 h (stirring rate and yields: 0 min^{-1} (71%), 420 min^{-1} (45%), 600 min^{-1} (43%) and 900 min^{-1} (32%)). For a better comparison with the conventional reaction in a glass tube the synthesis of the yttrium compound was performed without stirring for 8 h at 170°C (yield: 72%).

3. Crystallography

3.1. X-ray structure analysis

Although many experiments were performed to grow single crystals of the title compounds only for compound 2 crystals suitable for single-crystal X-ray diffraction were obtained. Crystals of $\text{Er}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)$ (2) were carefully selected from the HT experiment using a polarizing microscope. Single-crystal X-ray diffraction was performed on an Enraf Nonius Kappa-CCD diffractometer equipped with a rotating anode (Mo $K\alpha$ radiation, $\lambda = 71.073$ pm). For data reduction and absorption correction the program XRED was used [27]. The crystal structure was solved by direct methods and refined using the program package SHELXTL [28]. All tested crystals were racemically twinned. Therefore a refinement with the TWIN and BASF commands in SHELXTL was necessary. The crystal structure could only be refined in the chiral space group Pn (no. 7). PLATON [29] suggests a change to space group $P2_1/c$ (no. 14). However, a refinement in this space group was not possible. The structure is pseudo-centro-symmetric and therefore the atoms C1, C2 and O6 were refined using isotropic displacement parameters. All hydrogen atoms of the $-\text{CH}_2-$

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

Compound	2
Empirical formula	$\text{ErC}_2\text{H}_4\text{O}_6\text{PS}$
Formula weight	354.35
Crystal system	Monoclinic
Space group	Pn
a (pm)	547.02(11)
b (pm)	862.67(17)
c (pm)	773.68(15)
α (deg)	90
β (deg)	97.408(3)
γ (deg)	90
V ($\times 10^6 \text{ pm}^3$)	362.05(12)
Z	2
T (K)	293(2)
ρ_{calc} (g cm^{-3})	3.250
μ (mm^{-1})	12.08
$F(000)$	326
Abs. corr.	Spherical
$T_{\text{min.}}/T_{\text{max.}}$	0.6889/1.0000
Total data collect.	6725
Unique/obs. data ($I > 2\sigma(I)$)	1559/1523
$R(\text{int})$	0.0420
$R1, wR2$ ($I > 2\sigma(I)$)	0.0273, 0.0708
$R1, wR2$ (all data)	0.0287, 0.0719
Goodness of fit	1.047
No. of variables	86
Δe min/max ($\text{e}\text{\AA}^{-3}$)	-1.712/0.893

Table 2
Selected bond lengths (pm) for $\text{Er}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)$ (2)

Er1–O1	215.4(9)	P1–O1	148.5(7)
Er1–O2	215.9(8)	P1–O2	149.6(8)
Er1–O3	221.3(7)	P1–O3	150.2(7)
Er1–O4	233.6(8)	S1–O4	146.1(7)
Er1–O5	223.7(7)	S1–O5	146.5(8)
Er1–O6	226.7(10)	S1–O6	146.2(9)
S1–C2	177.4(13)	C1–C2	152.7(12)
P1–C1	176.9(16)		

groups were placed onto calculated positions. Experimental data and results of the structure determination are given in Table 1. Selected bond lengths are summarized in Table 2.

3.2. Powder XRD pattern indexing and refinement

While for compound 2 a suitable crystal for X-ray structure analysis was obtained, compounds 1, 3, 4 and 5 were only isolated as microcrystalline products and characterized thoroughly by powder X-ray diffraction (XRD) (Fig. S2) and elemental analysis. The powder XRD patterns were indexed and the lattice parameters refined with the STOE WinXPOW program. The indexing was carried out using the Loefer's algorithm (DICVOL) [30]. The refined cell parameters are summarized in Table 3.

4. Results and discussion

4.1. High-throughput and microwave syntheses

The high-throughput 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. By using this method a fast screening of the reaction system $\text{LnX}_3/\text{H}_3\text{L}/\text{NaOH}/\text{H}_2\text{O}$ ($\text{LnX}_3 = \text{Ho}(\text{CH}_3\text{COO})_3$, $\text{Er}(\text{NO}_3)_3$, $\text{Tm}(\text{NO}_3)_3$, YbCl_3 , LuCl_3 , $\text{Y}(\text{NO}_3)_3$) was possible and a series of isotopic rare earth compounds was obtained. The results of the HT-investigation based on powder XRD data are given in Fig. 1. Acidic starting conditions (pH = 1.5–5) lead to the formation of the title compounds $\text{Ln}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)$. Higher pH values lead to $\text{Ln}(\text{OH})_3$ or to unidentified products depending on the rare earth salt employed (Fig. 1). The unidentified products are either of low crystallinity or contain no sulfur or phosphorus (EDX-analyses). Thus, no further characterization was carried out. The change of the counter ions of the rare earth salts has only a minor influence on the product formation. Starting from the acetate salt a shift ($\Delta\text{pH} = 1-1.5$) to higher pH values of the reaction solution was observed in respect to the chloride and nitrate salts. Thus the formation of $\text{Ho}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)$ starting from $\text{Ho}(\text{CH}_3\text{OO})_3$ was observed using a lower NaOH content (0 and 1 mol equivalent). Based on the established formation conditions from the HT-investigation, the synthesis scale-up was achieved (for Er-, Tm-, Yb-, Lu- and Y-compound $\text{Ln}^{3+}:\text{H}_3\text{L}:\text{NaOH} = 1:1:2$, and for Ho-compound 1:1:0).

Microwave heating is often chosen to speed up the synthesis of compounds. This is due to the effective and uniform heating of the reaction mixture. Furthermore, modern instruments allow a good control of parameters such as temperature, pressure, and stirring rate during the synthesis. Recently, microwave heating has been applied to the synthesis of inorganic-organic hybrid compounds [31–33]. Our microwave system allows a fast heating of the reaction mixture in 2 min to 170°C as well as fast cooling to room temperature in less than 4 min. We have investigated the influence of microwave heating, i.e. (a) the transferability of the synthesis

Table 3
Results of the indexed XRD powder patterns for **1**, **3**, **4**, **5** and **6**.

Compound	1	3	4	5	6
Empirical formula	HoC ₂ H ₄ O ₆ PS	TmC ₂ H ₄ O ₆ PS	YbC ₂ H ₄ O ₆ PS	LuC ₂ H ₄ O ₆ PS	YC ₂ H ₄ O ₆ PS
Formula weight	352.02	356.02	360.13	362.06	275.99
<i>a</i> (pm)	549.5(2)	546.6(1)	544.9(1)	543.4(1)	549.1(1)
<i>b</i> (pm)	866.5(2)	861.2(2)	858.1(3)	856.9(2)	864.6(2)
<i>c</i> (pm)	777.8(2)	773.6(2)	771.1(2)	769.2(2)	776.6(1)
β (deg)	97.23(2)	97.36(2)	97.30(2)	97.07(1)	97.23(1)
<i>V</i> ($\times 10^6$ pm ³)	367.4(2)	361.1(2)	358.1(3)	355.5(2)	365.7(2)
Figure of merit	<i>F</i> (30) = 43.8 (0.014, 48)	<i>F</i> (30) = 52.2 (0.012, 46)	<i>F</i> (30) = 38.2 (0.015, 54)	<i>F</i> (30) = 49.4 (0.012, 50)	<i>F</i> (30) = 70.4 (0.009, 45)

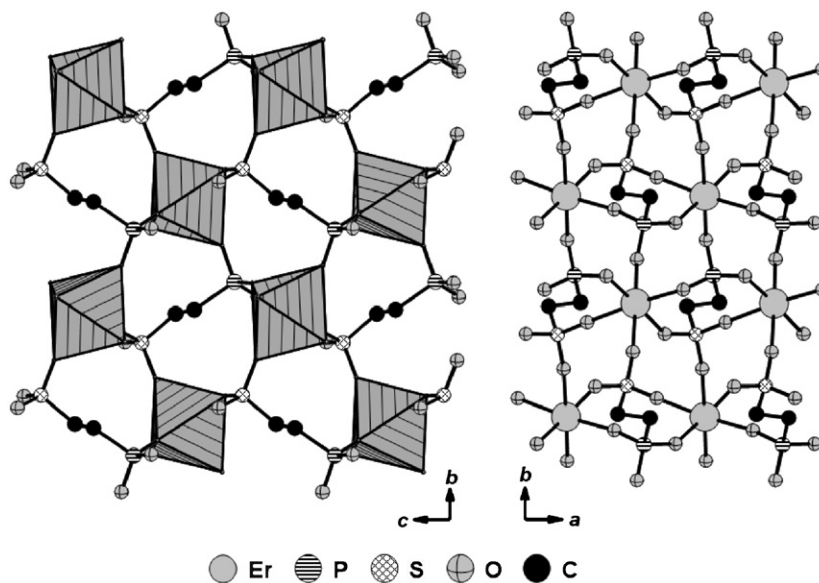


Fig. 3. Three-dimensional structure of $Ln(O_3P-C_2H_4-SO_3)$ with $Ln = Ho, Er, Tm, Yb, Lu$ and Y . The isolated LnO_6 polyhedra are shaded in gray. H-atoms have been omitted for the sake of clarity.

procedures form conventional heating, (b) the influence of reaction time and (c) the influence of the stirring rate during the reaction.

The first experiments using identical reaction conditions as applied in the conventional reactions yielded the entire series $Ln(O_3P-C_2H_4-SO_3)$ ($Ln = Ho-Lu, Y$) as phase pure compounds. To investigate the influence of stirring rate and reaction time the yttrium compound was studied in detail. The results are given in Fig. 2. Without stirring the microwave reaction as well as the conventionally heated synthesis mixture lead in 8 h to a yield of 71% and 72%, respectively. Thus under identical reaction conditions, microwave heating has in our case no influence on the yield. Under stirring at identical reaction times a decrease of the yields is observed down to 32% at 900 min^{-1} . Under a constant stirring rate of 600 min^{-1} the increase of the reaction time leads to an increase of the yield. These results cannot be easily explained, but could be due to kinetic phenomena. On the other hand short reaction times or high stirring rates could lead to smaller particles (nanoparticles) that are not isolated in the work-up procedure. This could explain the influence of the reaction time at constant stirring rate. Ostwald-ripening leads to larger particles that are isolated by centrifugation.

4.2. X-ray diffraction and structure

Since the title compounds are isotypic the crystal structure of $Er(O_3P-C_2H_4-SO_3)$ (**2**) is representative. 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 rare earth phosphonates containing Er^{3+} [34–36], Y^{3+} [35] and Ho^{3+} [35] P–O bond lengths in the range 148.6(4)–157.2(8) are observed, the corresponding S–O bond lengths in similar rare earth sulfonates containing Yb^{3+} [37–39] and Ho^{3+} [40] are significantly shorter 144.2(5)–147.7(5) pm. These values compare well with the bond lengths observed in our study where P–O and S–O distances of 148.5(7)–150.2(7) pm and 146.1(7)–146.5(8) pm, respectively, are observed. The dense three-dimensional structure is composed of Er^{3+} and 2-phosphonatoethanesulfonate $(O_3P-C_2H_4-SO_3)^{3-}$ ions. The erbium ions are surrounded by six oxygen atoms from six $(O_3P-C_2H_4-SO_3)^{3-}$ ions through three P–O–Er and three S–O–Er bonds. All oxygen atoms coordinate end on, thus isolated slightly distorted ErO_6 octahedra are observed. The octahedra are linked by the ligand into a three-dimensional structure as shown in Fig. 3.

As expected, the lanthanide contraction leads to a linear decrease of the lattice parameters in the isotypic series, whereas the monoclinic angle remains almost constant (Fig. 4). The reduction of the cell parameters is also well observed in the powder X-ray diffractions, in which the reflections positions shift to higher 2-theta values with smaller lattice parameters (Fig. S2).

The structural chemistry of metal phosphonatosulfonates is strongly determined by the flexibility of the ligand and the presence of additional co-ligands during the synthesis. The use of

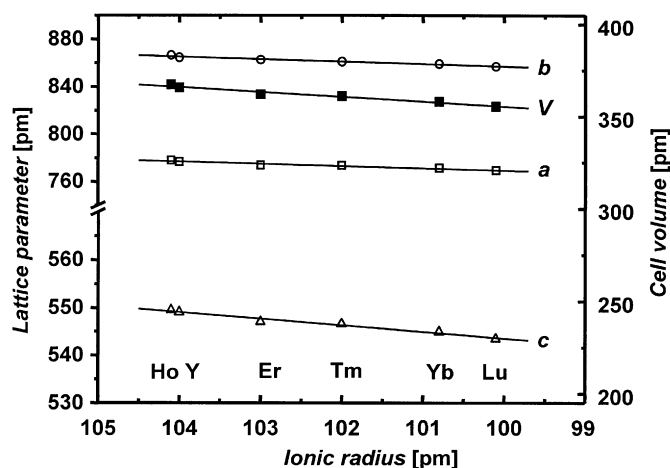


Fig. 4. Correlation between lattice parameters/cell volume and ionic radii as observed for $\text{Ln}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)$.

phosphonosulfonic acids with rigid organic linker molecules, i.e. phosphonoarylsulfonic acids, together with phen or bipy ligands lead to di-, tetra- or hexanuclear metal-phosphonoarylsulfonate clusters ($M = \text{Ln}^{3+}$ [16], Zn^{2+} [17], Mn^{2+} [20], Cd^{2+} [21]). The flexible phosphonoethanesulfonic acid has yielded compounds with a large variety of M–O–M structures such as extended layers in $\text{Cu}_{2.5}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)(\text{OH})$ [24], infinite chains in $\text{Cu}_2[(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)(\text{OH})(\text{H}_2\text{O})](\text{H}_2\text{O})$ [24], $\text{Ln}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)(\text{H}_2\text{O})$ [22], $\text{BaH}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)$ [23] and trimeric cluster in $\text{Cu}_{1.5}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)(\text{H}_2\text{O})$ [24]. In this study metal phosphonatosulfonates containing isolated slightly distorted LnO_6 octahedra are reported, which can be categorized by the recently proposed classification as a 3-D coordination polymer (1^0O^3) [2]. To the best of our knowledge only one analogue rare earth ethyl-diphosphate structure $\text{LnH}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{PO}_3)$ [41] with the entire rare earth metal series is reported in the literature. The structure is composed of eight coordinated lanthanide ions, which are connected by a $\mu\text{-O}$ to form M–O–M chains. These M–O–M chains are interconnected by the phosphonate group and form inorganic $\text{Ln}-\text{O}-\text{P}$ layers which are further interconnected by the alkyl chains to a three-dimensional framework. The proton for charge neutrality was not located. Similar structures were obtained by reducing and increasing the length of the alkyl chain to one or three $-\text{CH}_2-$ groups, respectively [41]. Thus, the inter-layer distance can be tuned by the length of the alkyl chain. The previously reported structure of the rare earth phosphonatosulfonate $\text{Ln}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)(\text{H}_2\text{O})$ [22] with larger eight coordinated ions $\text{Ln} = \text{La}-\text{Dy}$ show also these similar pillared structure. However, this structure contains an uncoordinated oxygen atom from the sulfonate group, which is involved in hydrogen bonds. A decrease of the rare earth ion size investigated in this work (series: Ho–Lu, Y) lead to a reduction of the coordination number to six and isolated slightly distorted MO_6 octahedra are formed in $\text{Ln}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)$. Thus, the series of rare earth phosphonatoethanesulfonates (La–Dy and Ho–Lu, Y) are split into two different structural regions depending on the ionic radii and consequently the coordination number.

4.3. Spectroscopic and thermal studies

The title compounds were studied by IR spectroscopy (Fig. S3). All compounds exhibit typical bands in the region between 1250 and 950 cm^{-1} that are due to the stretching vibrations of the CPO_3 and the CSO_3 groups; however, the individual bands cannot be

assigned unambiguously. Bands in the region from 2960 to 2920 cm^{-1} are due to C–H stretching vibrations. The corresponding CH_2 deformation vibrations appear in the region between 1405 and 1420 cm^{-1} . The broad weak band in the region $3700\text{--}3300\text{ cm}^{-1}$ is due to traces of water in KBr.

Since all title compounds are isotypic only for compounds **2** and **6** TG measurements were performed (Fig. S4). The water-free compounds show a high thermal stability up to 460°C without significant weight loss. At higher temperatures a weight loss between 460 and 600°C is observed (21.1% (**2**), 19.9% (**6**)). This weight loss could be due to the decomposition of the sulfonate group, presumably under release of SO_2 or SO_3 (calcd. **2**: SO_2 18.1% SO_3 22.6%; calcd. **6**: SO_2 17.7, SO_3 22.1%). Above this temperature a continuous weight loss up to 900°C was observed. This could be due to the decomposition of the remaining organic part (total weight loss: 24.9% (**2**), 22.4% (**6**)).

5. Conclusion

Employing our high-throughput methodology we have investigated the system $\text{LnX}_3/\text{H}_3\text{L}/\text{NaOH}/\text{H}_2\text{O}$ ($\text{LnX}_3 = \text{Ho}(\text{CH}_3\text{COO})_3$, $\text{Er}(\text{NO}_3)_3$, $\text{Tm}(\text{NO}_3)_3$, YbCl_3 , LuCl_3 , $\text{Y}(\text{NO}_3)_3$) under hydrothermal conditions at 170°C . Under acidic reaction conditions six new isotopic compounds $\text{Ln}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)$ ($\text{Ln} = \text{Ho}-\text{Lu}$, Y) were obtained. The used counter ions of the rare earth salts have no significant influence on the product formation; however the pH of the reaction solution is changed. The syntheses were scaled-up for the entire series and all compounds were also obtained employing microwave heating. The microwave synthesis of $\text{Y}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)$ was investigated in more detail. While stirring during the synthesis lead to smaller yields, the increase of reaction time at constant stirring rate lead to an increase of the yield. The overall yield using conventional or microwave heating (170°C) for 8 h is identical. The structure of the isotopic series $\text{Ln}(\text{O}_3\text{P}-\text{C}_2\text{H}_4-\text{SO}_3)$ contains isolated slightly distorted LnO_6 octahedra, which are linked by the organic part of the linker molecule to a dense three-dimensional structure. The flexible bifunctional 2-phosphonoethanesulfonic acid has been shown to be a versatile ligand for the synthesis of crystalline inorganic–organic hybrid compounds with a great structural diversity. To investigate the influence of an extension of the alkyl chain of the final structure, 4-phosphonbutanesulfonic ($\text{H}_2\text{O}_3\text{P}-\text{C}_4\text{H}_8-\text{SO}_3\text{H}$) acid was recently synthesized. HT investigations and crystal structures based on the extended ligand will be reported soon.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2008.08.006.

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