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Benzene Trisulfonic Acid (H_3BTS) as Analogue of Trimesic Acid for Building Open Frameworks: The First Rare Earth Examples $[La(BTS)(H_2O)_5]$ and $[RE(BTS)(H_2O)_4]$ (RE = Nd, Sm, Eu)

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Abstract. The reaction of benzene 1,3,5-trisulfonic acid (H_3BTS) with the hydroxides $RE(OH)_3$ (RE = La, Nd, Sm, Eu) in aqueous solution afforded the sulfonates $[La(BTS)(H_2O)_5]$ and $[RE(BTS)(H_2O)_4]$ (RE = Nd, Sm, Eu). Single crystal investigations were performed for the lanthanum and the europium compound, respectively. $[La(BTS)(H_2O)_5]$ is triclinic [$P\bar{1}$, $Z = 2$, $a = 783.18(6)$ pm, $b = 1056.94(8)$ pm, $c = 1082.38(8)$ pm, $\alpha = 114.860(2)°$, $\beta = 96.655(3)°$, $\gamma = 104.402(3)°$] whereas $[Eu(BTS)(H_2O)_4]$ exhibits monoclinic symmetry [$P2_1/n$, $Z = 4$, $a = 767.61(5)$ pm, $b = 1730.2(1)$ pm, $c = 1134.06(8)$ pm, $\beta = 108.375(8)°$]. Despite these crystallographic differences, the structural features of the lanthanum and europium compounds are very similar. They show the metal ions connected by BTS anions to layers that are further linked by hydrogen bonds. Interestingly, only two of the three sulfonate groups are connected to rare earth ions, whereas the third remains uncoordinated and acts as acceptor within the hydrogen bonds. According to powder XRD measurements the neodymium and samarium sulfonates are isotypic with the europium compound. The thermal analyses of the compounds show the dehydration in a temperature range between 100 and 300 °C, whereas the decomposition of the organic ligands takes place at temperatures as high as 550 °C. Thus the anhydrous sulfonates are much more stable than comparable salts of trimesic acid. The residues of the thermal decompositions were identified by XRD experiments.

Introduction

Metal-organic frameworks, so-called MOFs, have attracted significant interest because they do not only display a fascinating structural chemistry but bear also potential to act as materials in various applications.[1] One of these applications that were addressed to these compounds was their use as gas storage media, especially for hydrogen.[2] Usually carboxylic acids were used to build up open framework structures. The advantage of these acids is their commercial availability in a great variety at relatively low costs. However, the drawback of frameworks that are based on carboxylic acids is their thermal lability, i.e. they decompose quite easily upon heating. This is a great disadvantage with respect to gas storage applications because the absorption and desorption of gas usually causes or requires heating of the materials. One option to increase the thermal stability of metal-organic frameworks is to switch from carboxylate linkers to sulfonate linkers, which are known to be thermally more robust.[3] Unfortunately, the respective polysulfonic acids – in contrast to carboxylic acids – are hardly available. This is in particular true for the sulfo-analogues of terephthalic acid (**1**) and trimesic acid (**2**), which are widely used in MOF chemistry.[4,5] Therefore, we recently developed a convenient preparative route for the synthesis of benzene-1,4-disulfonic acid (**3**) (p-H_2BDS) and benzene-1,3,5-trisulfonic acid (**4**) (H_3BTS) starting from commercially available and cheap starting materials[6] (Figure 1). This route enables us to prepare the acids in a multigram scale, which makes them available for the performance of experiments to their implementation in MOF chemistry. Whereas our first attempts were devoted to copper compounds,[6] we here describe our recent results on rare earth elements. Building framework structures with these elements is of great interest because of their unique

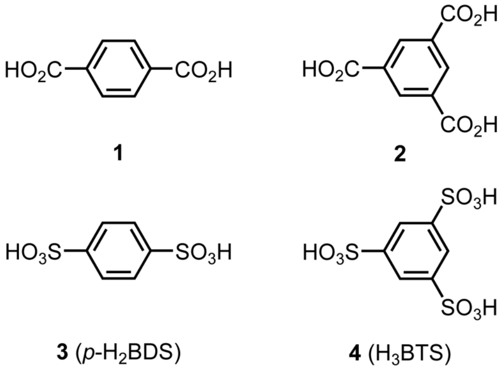

Figure 1. Carboxylic and sulfonic acids as linkers for metal-organic frameworks.

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spectroscopic and magnetic properties. Our former work has shown that monosulfonates of these elements can be prepared and show a good thermal stability.[7] In this paper we present the first rare earth compounds of benzene-1,3,5-trisulfonic acid (**4**) and their thermal behavior.

Results and Discussion

Crystal Structure

The lanthanum compound crystallizes with five, the trisulfonates of the smaller *RE* ions Nd^{3+}, Sm^{3+} and Eu^{3+} with four molecules of crystal water per formula unit.[8] With respect to XRD measurements the tetrahydrates $[RE(BTS)(H_2O)_4]$ (*RE* = Nd, Sm und Eu) are isotypic and show monoclinic symmetry (space group $P2_1/n$) (Table 1). For the europium sulfonate a single crystal structure determination was performed, so that the structure description of the tetrahydrates will be given for this compound. The pentahydrate $[La(H_2O)_5(BTS)]$ is triclinic (see Table 2), but its structure is are very similar to those of the tetrahydrates. In both cases the rare earth ions are coordinated by four monodentate BTS^{3-} ions and the H_2O molecules. The coordination polyhedron is a distorted tricapped trigonal prism for La^{3+} whereas for the smaller Eu^{3+} ion is a distorted square *anti*-prism is found (Figure 2). The distances *RE*–O within the polyhedra range from 251 up to 265 pm for the lanthanum, and from 236 up to 245 pm for the europium compound, respectively (Table 3). No significant differences between the La–O distances originating from sulfonate groups or water molecules are observed. The BTS^{3-} ions of each polyhedron are linked to four further RE^{3+} ions leading to sheets according to the formulation $^{2}_{\infty}[RE(BTS)_{4/4}(H_2O)_{x/1}]$ (with $x = 5$

Table 1. X-ray powder diffraction results for the rare earth benzene trisulfonates.

compound	space group	*a* /pm	*b* /pm	*c* /pm	*α* /°	*β* /°	*γ* /°
$[La(H_2O]_5(BTS)]$	$P\bar{1}$	784.2(3)	1057.8(8)	1083.3(2)	114.91(7)	96.92(6)	105.02(7)
$[Nd(H_2O)_4(BTS)]$	$P2_1/n$	769.4(5)	1738.0(8)	1138.3(4)		108.38(5)	
$[Sm(H_2O)_4(BTS)]$	$P2_1/n$	766.9(4)	1729.8(5)	1134.8(4)		108.39(4)	
$[Eu(H_2O)_4(BTS)]$	$P2_1/n$	767.4(4)	1730.0(2)	1133.8(6)		108.36(6)	

Table 2. Crystallographic data and their determination.

	$[La(H_2O)_5(BTS)]$	$[Eu(H_2O)_4(BTS)]$
lattice parameters	$a = 783.18(6)$ pm	$a = 767.61(5)$ pm
(single crystal data)	$b = 1056.94(8)$ pm	$b = 1730.2(1)$ pm
	$c = 1082.38(8)$ pm	$c = 1134.06(8)$ pm
	$\alpha = 114.860(2)°$	
	$\beta = 96.655(3)°$	$\beta = 108.375(8)°$
	$\gamma = 104.402(3)°$	
cell volume	762.2(1) $Å^3$	1429.4(1) $Å^3$
no. of formula units	2	4
crystal system	triclinic	monoclinic
space group	$P\bar{1}$ (Nr. 2)	$P2_1/n$
measuring device	BRUKER APEX II CCD	STOE IPDS I
radiation	Mo-K_α (graphite monochrom., $\lambda = 71.07$ pm)	Mo-K_α (graphite monochrom., $\lambda = 71.07$ pm)
temperature	153 K	153 K
theta range	$4.2° < 2\theta < 72.6°$	$6.1° < 2\theta < 56.6°$
index range	$-12 \leq h \leq 13$	$-9 \leq h \leq 9$
	$-17 \leq k \leq 17$	$-22 \leq k \leq 22$
	$-18 \leq l \leq 17$	$-15 \leq l \leq 15$
rotation angle; φ increment		$0° < \varphi < 270°$; 1.2°
no. of exposures		225
exposure time		1.5 min
detector distance		60 mm
data corrections	Polarization and Lorentz factors	Polarization and Lorentz factors
absorption correction	numerical	numerical
μ	32.8 cm^{-1}	48.96 cm^{-1}
measured reflections	14503	18988
unique reflections	4655	3350
with $I_o > 2\sigma(I)$	4403	2789
no. of variables	269	209
R_{int}	0.0226	0.0430
structure determinations	SHELXS-97 and SHELXL-97	SHELXS-97 and SHELXL-97
scattering factors	Intern. Tables Vol. C	Intern. Tables Vol. C
goodness of fit	1.135	0.912
$R1$; $wR2$ ($I_o > 2\sigma(I)$)	0.0252; 0.0642	0.0176; 0.0377
$R1$; $wR2$ (all data)	0.0269; 0.0649	0.0240; 0.0385
min./max. electron density / $e{\cdot}Å^{-3}$	–0.733/1.383	–1.53/1.03

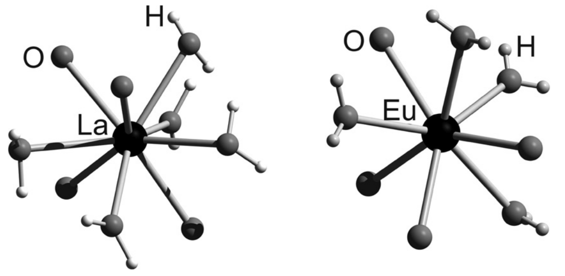

Figure 2. Coordination of the La^{3+} ions (left hand) and Eu^{3+} ions (right hand) in the crystal structures of $[La(BTS)(H_2O)_5]$ and $[Eu(BTS)(H_2O)_4]$, respectively.

for *RE* = La and $x = 4$ for *RE* = Eu). The linking pattern of BTS^{3-} anions and RE^{3+} cations is shown in the Figure 3 and Figure 5, respectively. One of the sulfonate groups of the anion (S3 in the left part in Figure 3) remains uncoordinated. This "free" sulfo group might cause potential activity of such materials as Brønsted acidic catalysts. Each of the other two sulfonate groups of the anion is coordinated by two oxygen atoms to two different RE^{3+} ions. This is in contrast to the findings for the structure of $[Cu_3(BTS)_2(H_2O)_{12}]\cdot4H_2O$ with only one coordinating oxygen atom per sulfonate group.[6] The right hand part of Figure 3 gives a larger section of this structure on the example of the lanthanum compound. The very special linking pattern of the BTS^{3-} anions and La^{3+} cations generates two different types of cavities or – in a three dimensional view – channels along the *a* axis. Eight-membered rings are formed by linking of two La^{3+} ions by two sulfonate groups of two different BTS^{3-} ions. Only water molecules are present in these small channels. The distances between adjacent La^{3+} ions are about 602 pm, between sulfur atoms about 462 pm. The second type of channels is surrounded by a larger ring of two La^{3+} ions and two BTS^{3-} ions. Distances between La^{3+} atoms are now about 706 pm. The distance of the carbon atoms between the sulfonate groups define a channel diameter of 890 pm. By stacking the ${}^{2}_{\infty}[La(BTS)_{4/4}(H_2O)_{5/1}]$ layers along the [100] direction (Figure 4) the benzene rings are lying upon each other with a little displacement, but are turned by 60° with respect to each other. As a result, the non-coordinating sulfonate groups are pointing into the larger channels, which are moreover occupied by water molecules. The layers are connected by hydrogen bonding, indicated as hatched lines in Figure 4. These bonds involve the H_2O molecules as donors and the sulfonate groups as acceptors. Furthermore, hydrogen bonding is observed within the layers, with water molecules acting as both acceptors and donors, and sulfonate groups as acceptors. With respect to the observed distances between donor and acceptor oxygen atom, the hydrogen bonds are medium strong (272–284 pm) with two exceptions of 307 and 318 pm that hint at only weak interactions (Table 4).[9] A similar stacking is observed for the europium sulfonate with stacking of layers of the composition ${}^{2}_{\infty}[Eu(BTS)_{4/4}(H_2O)_{4/1}]$ (Figure 6). Again, linkage is achieved by hydrogen bonds. These are slightly different compared to those discussed above due to the presence of only four water molecules. The respective values are also given in Table 4.

Table 3. Selected bond lengths /pm and angles /° in the crystal structures of $[La(BTS)(H_2O)_5]$ and $[Eu(BTS)(H_2O)_4]$.

La1	–O1		256.7(2)	Eu1	–O1		245.2(2)
	–O2		253.9(2)		–O2		235.6(2)
	–O3		252.7(2)		–O3		239.9(2)
	–O4		264.6(2)		–O4		242.4(2)
	–O5		252.1(2)				
	–O11		252.3(2)		–O12		242.6(2)
	–O12		253.3(2)		–O13		237.6(2)
	–O21		257.1(2)		–O22		238.9(2)
	–O22		251.4(2)		–O23		240.5(2)
O1	–H11		71(7)	O1	–H11		81(7)
	–H12		97(7)		–H12		83(6)
O2	–H21		96(7)	O2	–H21		71(7)
	–H22		96(9)		–H22		68(8)
O3	–H31		85(4)	O3	–H31		79(7)
	–H32		77(5)		–H32		77(7)
O4	–H41		79(4)	O4	–H41		81(6)
	–H42		96(9)		–H42		78(7)
O5	–H51		95(6)				
	–H52		81(6)				
S1	–O11		146.2(2)	S1	–O11		144.2(2)
	–O12		145.3(2)		–O12		145.9(2)
	–O13		145.7(2)		–O13		146.2(2)
	–C1		177.7(2)		–C1		177.3(2)
S2	–O21		145.8(2)	S2	–O21		144.5(2)
	–O22		146.1(2)		–O22		146.7(2)
	–O23		146.0(2)		–O23		146.5(2)
	–C3		176.8(2)		–C5		177.0(2)
S3	–O31		146.3(2)	S3	–O31		145.0(2)
	–O32		146.4(2)		–O32		146.7(2)
	–O33		145.1(2)		–O33		145.0(2)
	–C5		177.4(3)		–C5		178.0(2)
O11	–S1–	O12	112.0(1)	O11	–S1–	O12	114.4(1)
O11	–S1–	O13	111.3(1)	O11	–S1–	O13	111.8(1)
O12	–S1–	O13	113.5(1)	O12	–S1–	O13	111.6(1)
O11	–S1–	C1	106.4(1)	O11	–S1–	C1	107.4(1)
O12	–S1–	C1	106.1(1)	O12	–S1–	C1	106.1(1)
O13	–S1–	C1	107.0(1)	O13	–S1–	C1	104.7(1)
O21	–S2–	O22	112.5(1)	O21	–S2–	O22	112.4(1)
O21	–S2–	O23	112.4(1)	O21	–S2–	O23	113.0(1)
O22	–S2–	O23	112.2(1)	O22	–S2–	O23	111.8(1)
O21	–S2–	C3	106.3(1)	O21	–S2–	C5	107.6(1)
O22	–S2–	C3	106.1(1)	O22	–S2–	C5	105.9(1)
O23	–S2–	C3	106.8(1)	O23	–S2–	C5	105.5(1)
O31	–S3–	O32	110.8(1)	O31	–S3–	O32	111.8(1)
O31	–S3–	O33	113.7(2)	O31	–S3–	O33	114.4(2)
O32	–S3–	O33	112.8(2)	O32	–S3–	O33	112.2(2)
O31	–S3–	C5	106.8(1)	O31	–S3–	C3	105.6(1)
O32	–S3–	C5	106.5(1)	O32	–S3–	C3	105.9(1)
O33	–S3–	C5	105.7(1)	O33	–S3–	C3	106.0(1)

Thermal Decomposition

The thermal decomposition of $[La(BTS)(H_2O)_5]$ occurs in several stages (Figure 7, for data see Table 5). The dehydration takes place between 115 and 295 °C and can be divided in three well defined steps, correlating to the loss of three, one, and again one water molecule with respect to the observed mass loss. After dehydration the anhydrous compound remains stable up to 550 °C before the degradation of the sulfonate

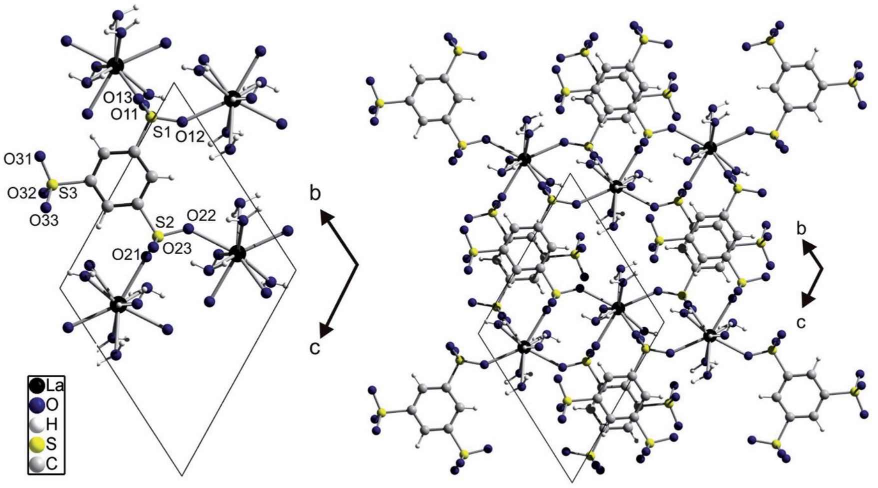

Figure 3. Coordination of the BTS^{3-} anions in the crystal structure of $[La(BTS)(H_2O)_5]$ (left hand) and their connection to sheets according to $^2_\infty[La(BTS)_{4/4}(H_2O)_{5/1}]$.

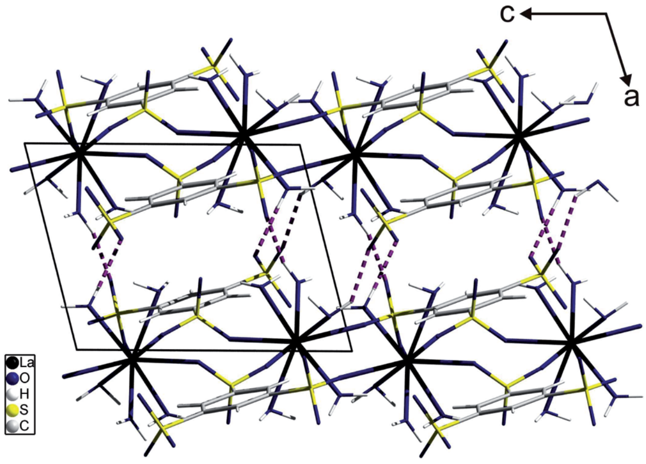

Figure 4. Linkage of the $^2_\infty[La(BTS)_{4/4}(H_2O)_{5/1}]$ sheets shown in Figure 3 by hydrogen bonds (dashed violet lines).

takes place. XRD investigations of the residue show the presence of La_2O_2S and La_2S_3. The oxide sulfide as a decomposition product is not unexpected as it has also been observed for the decomposition of the sulfonate $La(CH_3SO_3)_3{\cdot}2H_2O$ at similar temperatures.[7]

The dehydration process of $[Eu(BTS)(H_2O)_4]$ is similar to that of the lanthanum compound. The water molecules are released in three separate steps and the anhydrous compound is obtained at about 300 °C (Figure 8, Table 5). According to the mass loss observed the first step is correlated to the loss of two water molecules whereas each of the following steps can be attributed to the loss of one H_2O molecule. For the europium compound the anhydrous material decomposes also at about 550 °C proving the thermal stability of the sulfonate anion. In contrast to the lanthanum compound different decomposition products are observed in the powder diffraction pattern of the residue. It could be unambiguously interpreted assuming a mixture of Eu_2O_2S[10] and the sulfide EuS.[11] The lattice

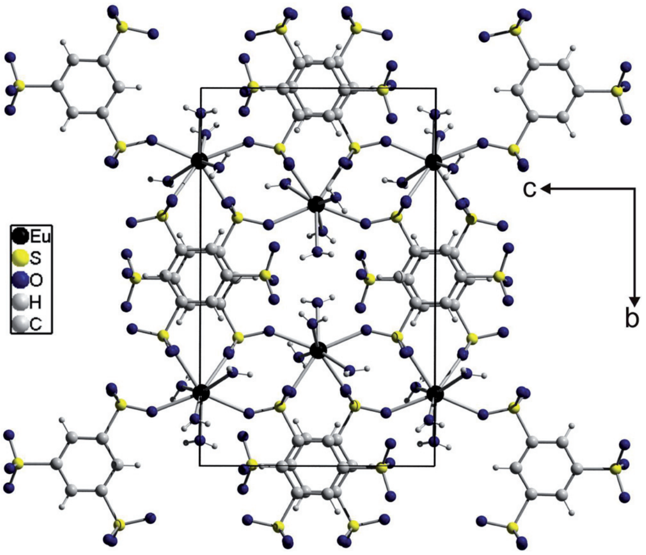

Figure 5. Sheets according to $^2_\infty[Eu(BTS)_{4/4}(H_2O)_{4/1}]$ in the crystal structure of $[Eu(BTS)(H_2O)_4]$. Note, that the linkage of the anions is the same as in $[La(BTS)(H_2O)_5]$ (cf. Figure 3).

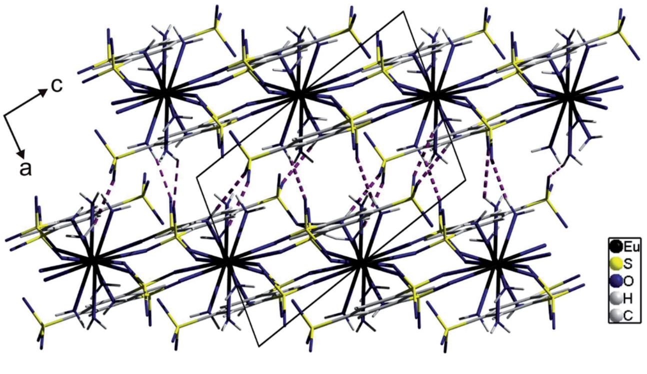

Figure 6. Linkage of the $^2_\infty[Eu(BTS)_{4/4}(H_2O)_{4/1}]$ sheets shown in Figure 5 by hydrogen bonds (dashed violet lines).

Table 4. Hydrogen bonding in the structure of [La(BTS)(H_2O)$_5$] and [Eu(BTS)(H_2O)$_4$].

D–H	*d*(D–H) /pm	*d*(H···A) /pm	<DHA /°	*d*(D···A) /pm	A
[La(BTS)(H_2O)$_5$]					
O1–H11	71	265	132.9	318	O13
O1–H12	97	179	163.8	273	O13
O2–H21	96	195	142.6	277	O33
O2–H22	96	202	143.3	284	O3
O3–H31	85	223	126.3	281	O1
O3–H31	85	258	118.1	307	O13
O3–H32	77	198	159.7	272	O23
O4–H41	79	207	156.4	280	O23
O4–H42	96	212	130.2	284	O13
O4–H42	96	226	111.6	276	O5
O5–H51	95	184	157.4	274	O32
O5–H52	81	204	176.7	284	O31
[Eu(BTS)(H_2O)$_4$]					
O1–H11	81	201	158.4	277	O21
O1–H12	83	195	162.9	275	O11
O2–H21	71	200	177.1	271	O33
O2–H22	68	206	171.8	274	O32
O3–H31	79	205	161.9	281	O32
O3–H31	77	199	164.6	274	O31
O4–H41	81	216	158.5	293	O31
O4–H42	78	225	141.9	290	O11
O4–H42	78	233	133.2	292	O21

Table 5. Data for the thermal decomposition of [La(BTS)(H_2O)$_5$] and [Eu(BTS)(H_2O)$_4$].

Compound	Stage	T_{onset} /°C	T_{end} /°C	T_{max} /°C	Mass loss obs.	Mass loss calcd.
[La(BTS)(H_2O)$_5$]	1. loss of three equiv. of H_2O	86	139	115	8.6 %	9.9 %
	2. loss of one equiv. of H_2O	158	198	175	3.9 %	3.3 %
	3. loss of one equiv. of H_2O	256	312	295	3.6 %	3.3 %
	4. decomposition to La_2O_2S and La_2S_3	548	570	560	63.5 %	62.4 %
[Eu(BTS)(H_2O)$_4$]	1. loss of two equiv. of H_2O	110	175	160	6.8 %	6.7 %
	2. loss of one equiv. of H_2O	175	240	205	3.7 %	3.3 %
	3. loss of one equiv. of H_2O	240	320	280	3.7 %	3.3 %
	4. decomposition to Eu_2S_2O and EuS	574	591	586	50.2 %	47.3 %

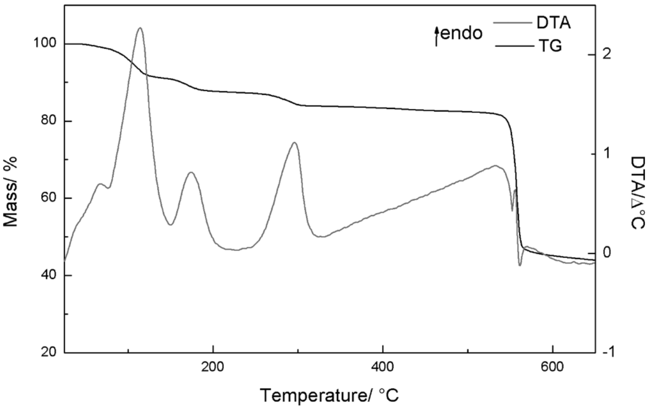

Figure 7. Thermal analysis of [La(BTS)(H_2O)$_5$].

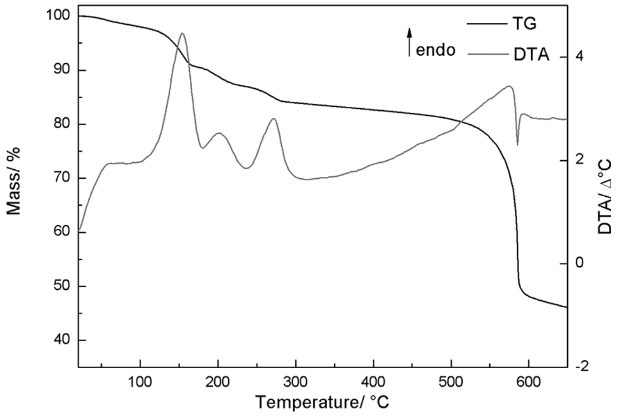

Figure 8. Thermal analysis of [Eu(BTS)(H_2O)$_4$].

parameter refinement for these phases gave: Eu_2O_2S, $P\bar{3}m1$, a = 387.1(3) pm, c = 668.9(6) pm; EuS, $Fm\bar{3}m$, a = 597.2(2) pm. According to the mass loss observed both compounds are obtained in an almost 1:1 ratio.

Conclusions

The convenient synthesis of benzene-1,3,5-trisulfonic acid (H_3BTS) as an analogue of trimesic acid in a multigram scale is the crucial step for the implementation of this acid in building metal-organic frameworks. In this paper we have demonstrated this on the example of the first lanthanide trisulfonates [La(BTS)(H_2O)$_5$] and [*RE*(BTS)(H_2O)$_4$] (*RE* = Nd, Sm, Eu), which show layer type structures with one of the sulfonate groups remaining uncoordinated. Thermoanalytical investigations show that after dehydration these compounds are stable up to nearly 550 °C. This is a significantly higher decomposition temperature compared to the related carboxylates and proves that sulfonic acids are good candidates to build thermally robust frameworks.

Experimental Section

Preparation of [La(BTS)(H_2O)$_5$] and [RE(BTS)(H_2O)$_4$] (RE = Nd, Sm, Eu)

For the synthesis of each compound a solution of H_3BTS (0.1 g) in water (10 mL) was used. At a temperature of 50 °C, the rare earth hydroxides *RE*(OH)$_3$ (*RE* = La, Nd, Sm, Eu) were slowly added to these solutions until neutrality was achieved. After cooling, the solutions were kept under ambient conditions and block-shaped single crystals separated from the solutions after a few days. They showed the colors of the respective rare earth ions (lanthanum: colorless, neodymium: violet, samarium: yellow, europium: light yellow) and were collected by filtration. With respect to their powder XRD patterns the products are single phased.

X-ray Crystallography

For the structure determinations, single crystals of [La(BTS)(H_2O)$_5$] and [Eu(BTS)(H_2O)$_4$], respectively, were glued onto glass fibers and intensity data were collected with an image plate diffractometer (STOE IPDS I) for the europium compound and a CCD diffractometer (BRUKER APEX II) for the lanthanum compound. The structure solution and refinement was successful in space group $P\bar{1}$ (La) and $P2_1/n$ (Eu) using the programs SHELXS97 and SHELXL97, respectively.[12, 13] A numerical absorption correction was applied to the data with the help of the programs X-RED and X-SHAPE.[14, 15] Details of the data collection and the crystallographic parameters are summarized in Table 2. For all compounds X-ray powder diffraction measurement were performed on fine powdered samples of the substances using a flat sample holder. Reflections were detected in the range from 5° to 90° with the diffractometer STADI P (STOE) using Cu-K_α radiation (λ = 154.18 pm). Lattice parameter refinement was performed with the help of the diffractometer software.[16] The same technique and the same powder diffractometer were used for the characterization of the residues of the thermal decomposition.

Thermal Analysis

For the investigation of the thermal behavior the respective compound (about 10 mg) was placed into a corundum container that was heated (10 K·min^{-1}) up to 800 °C under flowing argon using the thermo analyzer METTLER TOLEDO SDTA 851e. The data were processed with the software of the analyzer.[17]

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