

Anion Exchange in the Channels of a Robust Alkaline Earth Sulfonate Coordination Network

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Abstract: The barium sulfonate network presented herein, $\{[\text{Ba}_2(\text{L})\text{-(H}_2\text{O)}_5]\text{Cl}\}_\infty$ (**1**), represents the first metal sulfonate compound to possess a cationic framework. The network is layered with channels between pillaring ligands in which chloride ions reside. Compound **1** contracts slightly upon dehydration but retains its overall structural motif to 420 °C. Significantly, the chloride ions of the structure can be

exchanged in 80 % yield for fluoride ions in a facile manner. This exchange is quantified by elemental analyses, gravimetric determination, and ^{19}F NMR spectroscopy. Confirmation of retention

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of structure is provided by standardized powder X-ray diffraction experiments. This last point is notable as the F^- analogue of the structure is not attainable by a direct synthesis. These results illustrate one of the hallmark features of supramolecular chemistry, that a robust and functional framework can result through cooperative interactions between more weakly interacting units.

Introduction

The sulfonate group, RSO_3^- , bears a strong structural analogy to the phosphonate group, RPO_3^{2-} . Metal phosphonates represent a broadly studied class of solids.^[1] This owes to the fact that the PO_3 moiety of the phosphonate group bridges multiple metal centers to form highly regular and rigid inorganic layers. These layers serve to anchor and orient an extremely broad range of organic groups and generate solids with a diverse range of applications.^[2] In contrast, despite the structural analogy, sulfonates as building blocks for functional extended networks have only been examined to a small extent.^[3, 4] Undoubtedly, this fact stems from the notion that sulfonates are considered poor ligands as often evidenced by their inability to displace solvent molecules from the coordination spheres of many metal ions.^[3] Exceptions to this previous statement are silver sulfonates,^[4] which typically form very stable two-dimensional structures although, even within this family, the mode of coordination of the SO_3 group can vary.^[5]

Relying upon one of the fundamental premises of supramolecular chemistry,^[6] that cooperativity between weak interactions can provide enhanced bonding effects, our

contention has been that the use of the sulfonate group in the generation of extended structures will not compromise stability, but rather enhance structural diversity.^[7] To this end, we have recently reported two examples of barium sulfonate structures which illustrate this diversity. The first incorporated a “bent” pillar, 4,5-dihydroxybenzene-1,3-disulfonate, and selectively sorbed H_2S in its interlayer.^[8] We have also reported the structure of $[\text{Ba}(\text{2-pyridylethanesulfonate})_2 \cdot \text{EtOAc}]_\infty$, a one-dimensional structure which represented the first non-layered metal sulfonate complex.^[9] Herein, we report the single-crystal and powder X-ray diffraction (PXRD) analysis of a Ba^{2+} complex of a pseudo-trigonally symmetrical, trisulfonated ligand. The resulting structure is a pillared two-dimensional framework with channels filled with chloride anions. This compound represents the first characterized sulfonate network in which the framework itself is cationic. Significantly, the framework possesses anti-zeolitic qualities in that the chloride ions readily undergo facile exchange for fluoride ions. This phenomenon is studied by NMR spectroscopy, elemental analyses, and gravimetric analysis, while the network maintains its structural integrity, as shown by powder X-ray diffraction.

Results and Discussion

Choice of ligand and synthesis of compounds: The ligand designed for this study, the trianion of 1,3,5-tris(sulfomethyl)-benzene (**L**), possesses pseudo-trigonal symmetry. With

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simple monosulfonate groups, the orientation of sulfonate groups in a layered metal sulfonate, or for that matter, phosphonate groups in a layered metal phosphonate, allows for very efficient packing of the organic moieties in the interlayer and thus no void space. The mesitylene core was chosen with the expectation that, while the ligand may still form a two-dimensional solid, the organic groups would not pack efficiently in the interlayer region. The spherical shape of the sulfonate group enables the coordinating ability of L to extend into the third dimension (cf. a pyridine group or a carboxylic acid). Lower dimensional architectures are less robust, therefore, this added dimensionality is quite beneficial. This observation has been recently articulated for phosphonates by Sharma and Clearfield.^[10]

The sodium salt of L was synthesized in two steps by the Wohl–Ziegler bromination of mesitylene followed by a Strecker-type sulfonation reaction with sodium sulfite.^[11] Complexation of Na₃L in aqueous solution with 1.5 equivalents of BaCl₂ resulted in the immediate precipitation of a microcrystalline white solid. The low solubility of this complex made the growth of single crystals quite challenging and, ultimately, hydrothermal conditions were employed. The precipitate was transferred to a Teflon-lined autoclave with a small amount of water and kept at 110 °C for eight days. A healthy crop of block-like crystals of $[\text{Ba}_2(\text{L})(\text{H}_2\text{O})_5]\text{Cl}$ (**1**), suitable for a single-crystal analysis were obtained and separated from the residual powder and solution. The structure of this material is identical to the original precipitate formed at ambient conditions, and the powder in the hydrothermal preparation, as confirmed by PXRD and elemental analysis. Allowing the hydrothermal preparation to proceed for a shorter duration simply results in a greater ratio of microcrystalline powder to single crystals. It is somewhat unexpected that this material, particularly the solid generated at ambient conditions, would incorporate both L and chloride anions given the high insolubility of other barium organosulfonate networks.^[8, 9] The observation of mixed anions is also rare in phosphonate chemistry. We are aware of only a few examples where this is the case and these actually incorporate cationic viologen pillars.^[2d, 12]

Structure of $[\text{Ba}_2(\text{L})(\text{H}_2\text{O})_5]\text{Cl}$ (1**):** The structure of **1** can be described as ruffled layers of SO₃-bridged Ba²⁺ ions “pillared” by the mesitylene core of L to generate channels occupied by chloride ions, as shown in Figure 1. The layers project perpendicular to the image. The interlayer distance is 10.695(2) Å corresponding to half the length of the *b* axis. Two sulfonate groups on one molecule of L interact with one layer while the remaining sulfonate group bridges to the adjacent layer. The next molecule of L, going along the *c* axis, is flipped with only one sulfonate group interacting with the first layer. The resulting network is cationic and channels, occupied by charge compensating chloride ions, align throughout the structure. The approximate dimensions of the channels are 9.09(1) × 7.91(1) Å as defined by the transannular Ba–Ba and H6–H6 centroid distances, respectively. These values convert to 5.09 × 6.71 Å when van der Waals radii are considered. The water oxygen atoms to Cl distances (O6–Cl = 3.259(2) Å, O7–Cl = 3.416(2) Å) indicate the hydrogen atoms of the

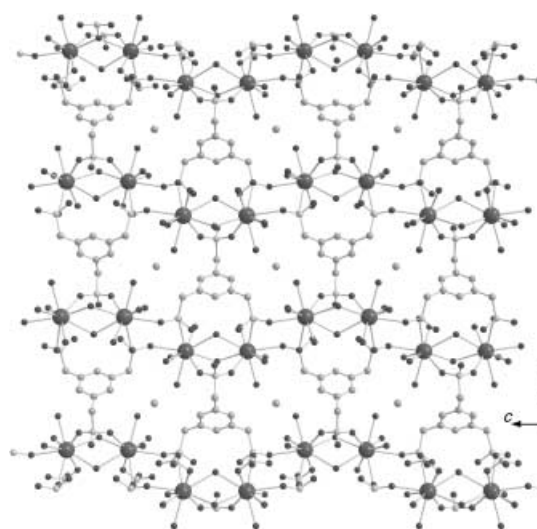


Figure 1. Structure of **1**, down the *a* axis showing the pillaring of layers by L. Ba atoms: large. Note the channels and the Cl[−] ions occupying them.

water molecules are likely to be hydrogen bonded, although these H atoms were not located in the crystal structure. The asymmetric unit for **1** consists of one Ba²⁺ ion, half a molecule of L, 2.5 water molecules, all of which are coordinating to barium, and half a chloride ion. The Ba²⁺ center is nine-coordinate with an irregular geometry. Its coordination sphere is comprised of five sulfonate oxygen atoms, from five different sulfonate groups, and four water molecules. There is a mirror plane through the ligand which bisects the central benzene ring perpendicularly along a line to S2. The ligand exists in a *cis–cis–trans* conformation with respect to the orientation of the methylsulfonate groups and the central ring, meaning two sulfonate groups lie to one side of the benzene ring, while the third is on the opposite side. This conformation, along with the complete ligation of L, are shown in the ORTEP representation in Figure 2. Overall, L bridges ten Ba²⁺ centers. The two symmetry-related sulfonate groups, centered on S1, each bridge three barium ions, each

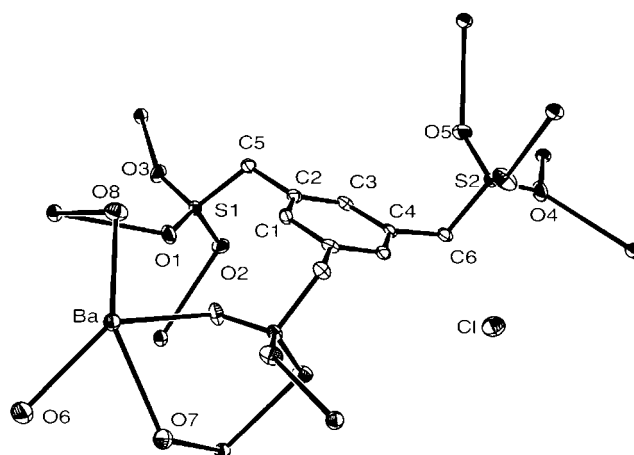


Figure 2. ORTEP representation of $[\text{Ba}_2(\text{L})(\text{H}_2\text{O})_5]\text{Cl}$ (**1**). A complete molecule of L is represented, coordinating to ten symmetry equivalent Ba²⁺ centers, to illustrate the coordination modes of the various sulfonate groups and water molecules (O6–O8) as well as the *cis–cis–trans* conformation of L. Ellipsoids of 50% probability are depicted.

oxygen atom forming a single bond to a different Ba^{2+} center ($\text{Ba}-\text{O}1 = 2.762(2) \text{ \AA}$, $\text{Ba}-\text{O}2 = 2.857(2) \text{ \AA}$, $\text{Ba}-\text{O}3 = 2.843(2) \text{ \AA}$). The sulfonate group centered on S2 bridges four Ba^{2+} ions. Each O5 forms a single bond to one barium ion ($\text{Ba}-\text{O}5 = 2.768(2) \text{ \AA}$), while O4 bridges two Ba^{2+} centers ($\text{Ba}-\text{O}4 = 2.844(2) \text{ \AA}$). There are three types of water molecules in the structure which all coordinate to Ba^{2+} ions. One type of water molecule is half-occupied and sits on a center of symmetry. Its oxygen atom, O6, forms a single bond to the Ba^{2+} center ($\text{Ba}-\text{O}6 = 2.770(2) \text{ \AA}$). The remaining two types of water molecules, both fully occupied, each bridge two Ba^{2+} centers ($\text{Ba}-\text{O}7 = 2.905(2) \text{ \AA}$, $\text{Ba}-\text{O}7a = 2.934(2) \text{ \AA}$, $\text{Ba}-\text{O}8 = 2.905(2) \text{ \AA}$). This results in the observed ratio of five water molecules per molecule of **1**.

Thermal analyses: Compound **1** is quite a robust network. DSC/TGA shows the loss of water molecules in two steps. A mass loss was observed from 50°C to 120°C corresponding to the loss of three water molecules (7.13 % calcd, 7.07 % obsd). Heating beyond 120°C , a more gradual mass loss occurs to 225°C corresponding to the loss of two more water molecules (4.75 % calcd, 4.64 % obsd). The sample is then stable until decomposition at 420°C . A PXRD run at 150°C and 250°C showed that both these dehydrated samples contract slightly upon dehydration, as shown in Figure 3. The splitting of the

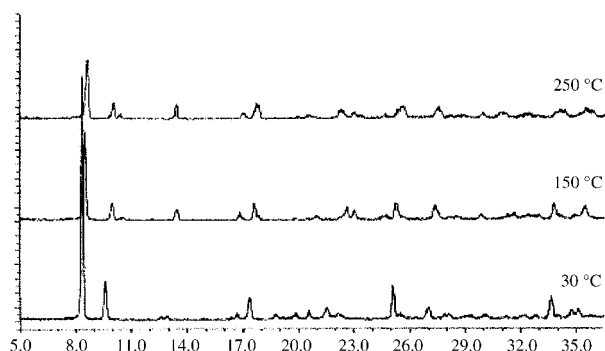


Figure 3. PXRD of **1** at 25°C (bottom), 150°C (middle), and 250°C (top), showing a slight structural contraction with dehydration, but that the framework still remains intact. DSC shows no other changes to 420°C .

signal at $2\theta = 12.5^\circ$ is due to the fact that the VT-PXRD is run under vacuum and desolvation is already beginning during the run even at ambient temperature. From room temperature to 250°C , the interlayer spacing shifts to 10.278 \AA , corresponding to a 3.9% contraction. Undoubtedly there will be some slight shifting of the sulfonate moieties to maximize interactions with each Ba^{2+} center, however, the overall structural motif observed in compound **1** persists. DSC data then indicate that the network is stable until decomposition at $\approx 420^\circ\text{C}$.

Ion-exchange studies: A very significant feature of the framework of **1** is that the chloride ions can be readily exchanged for fluoride ions while maintaining structural integrity. In the presence of only one equivalent of fluoride ion, a 75–85 % exchange of the chloride ions is observed. This was confirmed by gravimetric analysis, PXRD, ^{19}F NMR

spectroscopy, and C, H, Cl, and F elemental analyses. A sample of **1** was suspended in MeCN, a solvent in which the framework is completely insoluble, and the exchange performed with one equivalent of $(\text{Bu})_4\text{NF}$. The solution from the exchange experiment was analyzed for chloride ions gravimetrically by AgCl precipitation. The gravimetric analysis indicated a 75 % exchange of F^- for Cl^- after three hours. Monitoring the ^{19}F NMR spectrum of the exchanging solution over the same time frame shows the expected decrease in the signal corresponding to free F^- as it is incorporated in the solid. After three hours, the decrease in the solution F^- resonance was quantified as 85 % as referenced to an internal hexafluorobenzene standard. The exchange was further corroborated by the elemental analysis data, based on C, H, Cl, and F, allowing for the same degree of hydration as **1**, with values of $\approx 80\%$ exchange.^[13] Significantly, PXRD data showed that the structure of the exchanged solid was identical to that of **1**, as shown in Figure 4a and b. A possibility which

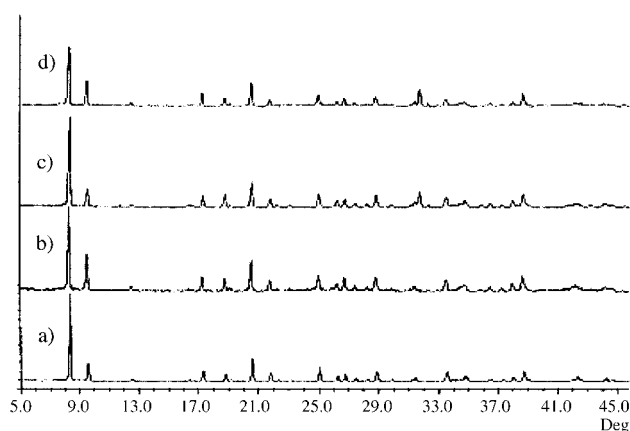


Figure 4. PXRD data of: a) unexchanged **1**; b) **1** exchanged with F^- ; c) unexchanged **1** spiked including a 10 % NaCl standard visible at $2\theta = 32^\circ$; d) **1** exchanged with F^- including a 10 % NaCl standard visible at $2\theta = 32^\circ$.

merits consideration at this point is that the exchanged product is actually amorphous and that the observed PXRD pattern of the exchanged solid is due solely to the $\approx 20\%$ of unexchanged material. In order to rule this possibility out, the PXRD samples of both unexchanged and exchanged solids were run containing 10 % NaCl as an internal standard. The consistent intensity of this peak ($2\theta = 32^\circ$), as shown in Figure 4c and d, confirms that the exchanged material is not amorphous. Therefore the observed PXRD is arising from the entire sample and the exchanged product is isostructural to **1**. Another possibility which can be discounted is that the solution F^- ions recombine with Ba^{2+} ions on the solid surface to form BaF_2 . If this were the case, there would also be evidence of this in the PXRD pattern.

The mechanism of the F^- for Cl^- exchange is proposed as simply two-way passage of ions through the channels. As mentioned previously, taking van der Waals radii into account, the dimensions of the channels are $5.09 \times 6.71 \text{ \AA}$. This value assumes a situation for exchange in which the water molecules on the Ba centers lining the channel are mobile. Monitoring the ^1H NMR spectrum of a solution of a sample of

1 in CD_3CN revealed that $\approx 20\%$ of the water directed into the channel made its way to the external solution within three hours, the timeframe of the exchange experiment. The significance of this result is that the aquo ligands are labile and can move within the channel. The van der Waals radii for Cl^- and F^- are 1.75 \AA and 1.47 \AA , respectively. Therefore, the minimum channel breadth required for two-way passage of the exchanging ions is 6.44 \AA . Comparing this value with the channel dimensions would seem to indicate that the channel is not sufficiently wide for the ions to pass. However, as illustrated in Figure 5, the passage of F^- and Cl^- need not

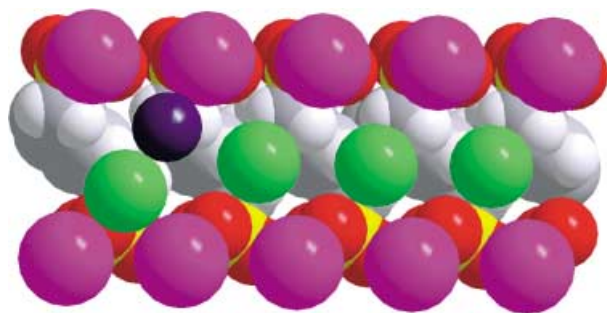


Figure 5. Space-filling representation, at van der Waals distances, of **1**, showing a cross-section of a single channel. The figure depicts the two-way passage of Cl^- and F^- ions within the confines of each channel. As the coordinated water molecules are labile, they are not included in the representation. Ba: pink, Cl^- : green, F^- : black, S: yellow, O: red, C: grey, H: white. The positions of the atoms lining the channel and the three chloride ions on the right are from the single crystal X-ray data. The positions of the chloride ion on the left and the fluoride ion have been artificially placed to depict a plausible exchange.

occur on a line between the two nearest transannular barium centers. A much more plausible route to ion exchange would have the two ions passing along a line between one Ba center and another Ba center laterally displaced down the channel. This is a distance of 10.37 \AA , which converts to 6.37 \AA with van der Waals considerations. Comparing this value with the effective channel dimensions shows that an additional 0.07 \AA would still be required for the ion exchange to occur as postulated. The additional length can be more than provided for by the anions residing in the small pockets or dips that exist between adjacent Ba^{2+} ions. Surprisingly, whereas the isostructural bromide analogue of **1** is readily attained from an analogous preparation with BaBr_2 ,^[14] the fluoride analogue of **1** cannot be synthesized beginning with BaF_2 . In the presence of Na_3L in aqueous solution, pure BaF_2 precipitates at both ambient and hydrothermal conditions leaving Na_3L in solution. This result corroborates the DSC/TGA findings and is a further indication of the robustness of the cationic framework in **1**.

Cation exchange represents one of the principal uses of zeolites, for example, as water softening agents.^[15] Framework **1** represents an anti-zeolitic structure in that it possesses channels capable of exchanging anions. The demonstration of ion exchange in extended coordination solids is rare. Yaghi et al. have reported two examples of 4,4'-bipyridine coordination frameworks which show ion exchange properties. $[\text{Ag}(4,4'\text{-bpy})](\text{NO}_3)$ exchanges anions to PF_6 in 95% yield

after six hours based upon microanalysis and IR data, but changes structure in doing so.^[16] In this example, the authors reported only a slight excess of the new anion was required. $[\text{Ni}(4,4'\text{-bpy})](\text{ClO}_4) \cdot 1.5(4,4'\text{-bpy})$ undergoes an unquantified perchlorate to hexafluorophosphate exchange after stirring in 0.2 M NaPF_6 (aq) for 15 minutes.^[17] We have demonstrated a 40% ion exchange, based on solid-state ^{13}C NMR spectroscopy, of OTs for BF_4 in a two-dimensional silver(I) array using a dithia ligand after treating the network three times for 30 minutes with 0.1 M NaOTs (aq).^[18] Recently, Sun et al. reported that $[\text{Cd}(1,3\text{-bis}(\text{imidazol-1-ylmethyl})\text{-5-methylbenzene})_2(\text{MeOH})_2](\text{ClO}_4)_2$ showed a 50% exchange of BF_4 for ClO_4 , based upon microanalysis, upon stirring with a ≈ 25 -fold excess of NaBF_4 for one day.^[19] Jung et al. have also recently reported a silver(I) 3,3'-thiobispyridine framework that converts between a two-dimensional framework and a helical structure with anion dependence.^[20] Finally, Min and Suh have shown reversible exchange of both nitrate and perchlorate for triflate in a family of silver polynitrile networks.^[21] These exchanges occur in a roughly three-fold excess of the new anion in periods ranging from 10 minutes to 24 hours. From the previous examples, the observations which can be made are that, in most cases, anion exchange within coordination frameworks is not facile but can be brought about over time and in considerable excess of the new anion. More often than not, the exchange causes some form of structural rearrangement to occur although this is not necessarily detrimental. In each of the preceding examples, the exchanged product is attainable by a direct synthesis.

Conclusion

The first cationic metal sulfonate framework has been reported. It is a Ba sulfonate coordination network which exchanges F^- for Cl^- in $\approx 80\%$ yield in three hours in the presence of a stoichiometric amount (one equivalent) of the new anion. Furthermore, the network maintains its structure in the exchanged state, a highly significant feature given that the F^- analogue is not attainable from a direct synthetic route. The fact that, despite employing weaker metal sulfonate interactions, framework **1** is able to sustain ion exchange is very significant. In a broad sense, these results serve to underscore the basic principles of supramolecular chemistry and the importance of cooperative bonding effects.^[6]

Experimental Section

General procedures and instrumentation: Powder X-ray diffraction data were acquired on a Scintag X2 Powder X-ray diffractometer equipped with a Micristar variable temperature controller. TGA/DSC analyses of **1** was performed on a Netzsch 449C Simultaneous Thermal Analyzer under a N_2 atmosphere at a scan rate of 5°C min^{-1} . All chemicals were purchased from Aldrich Chemical Company and used as received. Ligand **L** was synthesized as reported previously.^[11]

Synthesis of $\{[\text{Ba}_2(\text{L})(\text{H}_2\text{O})_5]\text{Cl}\}_\infty$ (1**):** A colorless solution of the ligand was prepared by dissolving Na_3L (0.356 g , 0.834 mmol) in H_2O (15 mL). White crystalline $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (0.408 g , 1.670 mmol) was added to this solution at room temperature with vigorous stirring. The addition of the metal salt resulted in the immediate precipitation of a white solid from solution. The

complexation was stirred for a total of 18 h before the white precipitate was isolated by suction filtration and allowed to dry for an additional 2 h before being weighed. Yield: 0.564 g (0.745 mmol, 89 %); IR (KBr): 3612.1 (br), 3492.0 (br), 3420.9 (br), 1634.6 (m), 1612.8 (m), 1459.8 (w), 1416.1 (w), 1268.6 (m), 1241.3 (s), 1192.1 (vs), 1159.3 (vs), 1137.5 (s), 1044.6 (vs), 766.0 (m), 716.8 (m), 662.2 (m), 602.1 (w), 569.4 (m), 531.1 cm^{-1} (m); DSC/TGA: 40 °C–130 °C (209.5 J g^{-1} , endo.) – 7.10 % obsd and – 7.13 % calcd for loss of 3 H_2O , 140 °C–240 °C (73.2 J g^{-1} , endo.) – 4.65 % obsd and – 4.68 % calcd for loss of 2 H_2O , 420 °C decomposition of L. Elemental analysis calcd (%) for **1**: C 14.30, H 2.53; found: C 15.08, H 1.96.

The growth of single crystals suitable for an X-ray crystallographic analysis proved quite challenging as a result of the low solubility of **1** in aqueous media at room temperature. Ultimately, hydrothermal conditions had to be employed in order to grow X-ray quality single crystals. The isolated powder from the room temperature reaction can be employed in the hydrothermal growth of crystals; however, more typically the synthesis was conducted from the start under hydrothermal conditions. In a representative reaction, Na_3L (0.208 g, 0.487 mmol) and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (0.238 g, 0.973 mmol) were placed in a Teflon-lined autoclave along with H_2O (13 mL). The hydrothermal apparatus was then assembled and placed in an oven at 175 °C. After 12 days the autoclave was removed from the oven and allowed to slowly cool back down to room temperature. The needle-like crystals which had formed on the bottom of the Teflon cup along with a small amount of microcrystalline powder were isolated from the aqueous solution by suction filtration and dried for 1 h before being weighed. Yield: 0.279 g (0.368 mmol, 76 %); elemental analysis calcd (%) for **1**: C 14.30, H 2.53; found: C 14.34, H 2.55. The IR spectrum and DSC/TGA data were found to be identical to that of the room temperature product and as such will not be listed here. In addition, the PXRD of the room temperature product and the microcrystalline powder from the hydrothermal preparation were identical to that of structurally characterized **1**. If the reaction time of the hydrothermal synthesis is reduced, simply a greater ratio of microcrystalline powder to crystals is observed.

General X-ray crystallography: Crystals were selected under an optical microscope, coated in oil and frozen onto a glass fiber. Data for **1**, were collected on a Bruker SMART APEX CCD diffractometer (MoK_α radiation, $\lambda = 0.71073 \text{ \AA}$) using the ω scan mode ($3^\circ < 2\theta < 57.3^\circ$). The structure was solved by direct methods and refined by full-matrix least squares, based on F^2 , by using SHELXL-97.^[22] Barium and sulfur atoms were located first and the remaining atoms found by difference Fourier maps. All non-hydrogen atoms were refined anisotropically. Relevant crystallographic data and selected bond lengths and angles are shown in Tables 1 and 2, respectively. CCDC-167132 contains the supplementary

Table 1. Crystal data and refinement summaries for structure **1**.

formula	$\text{C}_9 \text{H}_{19} \text{Cl O}_{14} \text{S}_3 \text{Ba}_2$
M_r	757.55
crystal system	Orthorhombic
space group	Pbcm
a [Å]	4.9865(4)
b [Å]	21.389(2)
c [Å]	18.934(1)
α [°]	90
β [°]	90
γ [°]	90
V [Å ³]	2019.4(3)
Z	4
ρ_{calcd} [g cm^{-3}]	2.492
μ [mm^{-1}]	4.386
crystal dimensions [mm ³]	$0.61 \times 0.14 \times 0.09$
θ range for data collection	2.15 to 26.40°
reflections [$I > 2\sigma(I)$]	2013
unique reflections	2139
measured reflections	10032
R_i [$I > 2\sigma(I)$] ^[a]	0.0273
R_w [$I > 2\sigma(I)$] ^[b]	0.0712
goodness of fit	1.183
residual electron density [e \AA^{-3}]	– 1.438/0.711

[a] $R_i = (\Sigma(F_o - F_c)/\Sigma(F_o))$. [b] $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{0.5}$.

Table 2. Selected bond lengths and angles for **1**.^[a]

Bond	Length [Å]	Bond	Length [Å]
Ba–O1	2.762(2)	Ba–O6	2.770(2)
Ba–O2	2.857(2)	Ba–O7	2.905(2)
Ba–O3	2.843(2)	Ba–O7#4	2.934(2)
Ba–O4	2.844(2)	Ba–O8	2.905(2)
Ba–O5	2.768(2)	S1–O1	1.465(2)
S1–O2	1.461(2)	S1–O3	1.457(2)
S2–O4	1.469(3)	S2–O5	1.453(2)
Bond	Angle [°]	Bond	Angle [°]
O1–Ba–O5#1	140.06(7)	O1–Ba–O6	131.56(7)
O5#1–Ba–O6	66.37(7)	O1–Ba–O3#2	96.44(6)
O5#1–Ba–O3#2	122.86(7)	O6–Ba–O3#2	83.37(8)
O1–Ba–O4#3	74.22(8)	O5#1–Ba–O4#3	73.03(8)
O6–Ba–O4#3	84.23(8)	O3#2–Ba–O4#3	152.76(7)
O1–Ba–O2#4	71.30(6)	O5#1–Ba–O2#4	110.79(7)
O6–Ba–O2#4	149.73(7)	O3#2–Ba–O2#4	73.26(7)
O4#3–Ba–O2#4	124.85(7)	O1–Ba–O7	69.78(6)
O5#1–Ba–O7	131.90(7)	O6–Ba–O7	67.36(7)
O3#2–Ba–O7	62.77(6)	O4#3–Ba–O7	90.06(7)
O2#4–Ba–O7	115.64(6)	O1–Ba–O8	70.51(8)
O5#1–Ba–O8	73.88(8)	O6–Ba–O8	133.28(8)
O3#2–Ba–O8	140.87(7)	O4#3–Ba–O8	60.86(7)
O2#4–Ba–O8	67.63(7)	O7–Ba–O8	135.78(7)
O1–Ba–O7#4	149.02(6)	O5#1–Ba–O7#4	59.98(7)
O6–Ba–O7#4	73.77(7)	O3#2–Ba–O7#4	65.65(6)
O4#3–Ba–O7#4	132.80(8)	O2#4–Ba–O7#4	79.12(6)
O7–Ba–O7#4	117.31(8)	O8–Ba–O7#4	106.73(7)

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x$, $y - 1/2$, z ; #2: $-x$, $-y + 1$, $-z$; #3: $-x + 1$, $y - 1/2$, $-z + 1/2$; #4: $x - 1$, y , z ; #5: x , y , $-z + 1/2$; #6: $x + 1$, y , z ; #7: $-x + 1$, $y + 1/2$, $-z + 1/2$; #8: $-x + 1$, $y + 1/2$, z ; #9: $-x$, $y + 1/2$, z .

crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/contents/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Exchange experiment: $n\text{Bu}_4\text{NF} \cdot \text{H}_2\text{O}$ (0.262 g, 1.00 mmol) was added to a dry MeCN suspension (5 mL) of **1** (0.760 g, 1.00 mmol) and stirred for 4 h. Initial solubility tests had been performed to insure the insolubility of **1** in MeCN. The exchanged white solid was isolated by suction filtration and washed twice with cold H_2O ($2 \times 10 \text{ mL}$). Elemental analysis found: C 14.43, H 2.87, Cl < 0.3, F 1.93. These elemental results correspond to 75–80 % exchange of F^- for Cl^- depending on the element used for the calculation. An aliquot of the MeCN filtrate (4.00 mL), containing a mixture of $n\text{Bu}_4\text{NCl}$ and $n\text{Bu}_4\text{NF}$, was removed for AgCl gravimetric analysis. The solution was taken to dryness leaving a clear glassy solid, which was further dried in vacuo for 12 h. The solid was then redissolved in H_2O (10 mL) to give a clear solution to which was added an excess of an aqueous solution of AgNO_3 (5 mL) (1.336 g, 7.865 mmol). A white AgCl precipitate formed immediately and was isolated by suction filtration on a dried, preweighed fine frit, washed twice with cold H_2O ($2 \times 10 \text{ mL}$), with cold MeOH ($1 \times 10 \text{ mL}$), and with diethyl ether ($2 \times 10 \text{ mL}$). The frit and sample were dried at 225 °C for 10 h and then reweighed; $\Delta\text{mass} = 0.086 \text{ g}$ (74.7 % exchange).

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