Inorganic Chemistry

Open-Framework Structures of Anhydrous Sr(CF₃COO)₂ and Ba(CF₃COO)₂

K. Tauni Dissanayake,[†] Laura M. Mendoza,[†] Philip D. Martin,[†] Leopoldo Suescun,[‡] and Federico A. Rabuffetti*,[†]

[†]Department of Chemistry, Wayne State University, Detroit, Michigan 48202, United States

[‡]Cryssmat-Lab/Cátedra de Física/DETEMA, Facultad de Química, Universidad de la República, Montevideo 11800, Uruguay

Supporting Information

ABSTRACT: Anhydrous Sr(CF₃COO)₂ and Ba(CF₃COO)₂ open-framework structures featuring three-dimensional connectivity of metal-oxygen polyhedra were crystallized from a mixture of water and CF₃COOH. Crystallization was induced via evaporation of the solvent mixture under a dry nitrogen flow. This approach differs from that routinely employed for crystallization of metal trifluoroacetates, which achieves solvent evaporation by heating under air and yields hydrated salts. Thermogravimetric and differential thermal analysis as well as single-crystal and synchrotron powder X-ray diffraction were employed to characterize the alkaline-earth trifluoroacetate products. Neither thermal analysis nor single-crystal X-ray diffraction detected the presence of crystallization water molecules, demonstrating these trifluoroacetates can be obtained in anhydrous form. Single-crystal X-ray diffraction studies showed



that $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ are isostructural and crystallize in the rhombohedral R3 space group. Both compounds belong to the class of organic-inorganic extended hybrids and exhibit an open-framework structural motif with threedimensional connectivity of the metal-oxygen polyhedra and one-dimensional channels along the c axis. The channels are decorated with the trifluoromethyl groups of the trifluoroacetate ligands, and their average (minimum) diameters are ~3.75 (2.60) and 3.45 (2.25) Å for Sr(CF₃COO)₂ and Ba(CF₃COO)₂, respectively. This size range is comparable to the kinetic diameter of small molecules such as hydrogen (2.3 Å). Chemical substitution of barium for strontium affects not only the diameter of the channels but also the spatial arrangement of the trifluoromethyl groups within the channels and the coordination environment of the metal atoms. The different coordination requirements of the strontium and barium atoms are accommodated through the displacement of one of the two chemically distinct trifluoroacetate ligands relative to the metal center.

INTRODUCTION

Alkaline-earth metal trifluoroacetates constitute an important class of precursors employed in solution-based routes to a wide range of functional materials, including high-temperature superconducting oxide thin films (e.g., $YBa_2Cu_3O_7$),^{1,7} upconversion nanocrystals (e.g., Er:Yb:SrF₂),³ and nanostructured fluoride ceramics (e.g., MgF_2 and CaF_2).^{4,5} Ba- $(CF_3COO)_2 \cdot xH_2O$ is the most extensively studied member of this family of materials because of its use in the preparation of YBa₂Cu₃O₇ thin films via chemical solution deposition of metal trifluoroacetates. This approach employs a stoichiometric mixture of the corresponding metal trifluoroacetates to prepare a coating solution that is subsequently deposited on a substrate and subjected to thermal treatment to induce decomposition of the metal-organic precursors. It has been extensively acknowledged that the purity of the coating solution, specifically its water content, directly affects the functionality of the superconducting oxide film.^{1,6-8} Thus, significant efforts have been devoted to the preparation of anhydrous coating solutions of metal trifluoroacetates.^{1,7,8} Chemisorption of atmospheric moisture during storage and handling and release of crystallization water during the dissolution of the metal

trifluoroacetates are the two main sources of contamination. The former can be avoided by storing and handling the coating solution in a moisture-free atmosphere; however, the crystallization of anhydrous trifluoroacetate precursors has proven to be elusive. As a result, synthetic methods targeting anhydrous coating solutions have focused on removing the crystallization water released upon dissolution of the trifluoroacetates, $^{1,9-11}$ rather than exploring new routes for crystallizing anhydrous trifluoroacetate precursors.

In addition, previous investigations of metal trifluoroacetates in the solid state have focused on understanding the physicochemical aspects of their thermal decomposition; investigation of their crystallochemical aspects has comparatively languished. Specifically in the case of alkaline-earth trifluoroacetates, only the crystal structure of $Ca(CF_3COO)_2$. H₂O has been reported;¹⁵ the crystal structures of Sr- $(CF_3COO)_2$ and $Ba(CF_3COO)_2$ remain unknown. This fundamental knowledge gap persists despite the fact that the relevance of the precursors' structure in their solution chemistry

Received: September 9, 2015



Figure 1. Thermogravimetric and differential thermal analysis of (a) Sr(CF₃COO)₂ and (b) Ba(CF₃COO)₂.

has been acknowledged.¹⁶ From this perspective, elucidation of the crystal structures of $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ is needed to establish structure–solution chemistry relationships that could guide synthetic approaches employed in a variety of areas; these include the preparation of coating solutions for the deposition of high-temperature superconducting oxide thin films, the synthesis of upconversion nanocrystals via thermal decomposition of trifluoroacetates in high-boiling point organic solvents, and the preparation of nanostructured fluoride ceramics via sol–gel routes.

In the course of our developments of anhydrous metalorganic precursors suitable for the synthesis of upconversion nanocrystals, we crystallized $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ powders from a mixture of water and CF₃COOH by inducing evaporation of the solvent mixture with a dry nitrogen flow. Our approach to crystallization of metal trifluoroacetates was drastically different from that first proposed by Roberts for the crystallization of rare-earth trifluoroacetates,¹⁸ which achieves solvent evaporation by heating under air. Interestingly, neither thermal analysis nor single-crystal X-ray diffraction (XRD) detected the presence of crystallization water molecules, indicating that $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ can be obtained in anhydrous form using the solvent evaporation method presented herein. Single-crystal XRD studies showed that $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ are isostructural and revealed an unexpected open-framework structural motif consisting of a network of metal-oxygen polyhedra with three-dimensional connectivity and one-dimensional channels along the c axis. The channels are decorated with trifluoromethyl groups of the trifluoroacetate ligands. Their average (minimum) diameters are ~3.75 (2.60) and 3.45 (2.25) Å for $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$, respectively. This size range is comparable to the kinetic diameter of small molecules such as hydrogen (2.3 Å). Chemical substitution of the alkalineearth metal affects not only the diameter of the channels but also the spatial arrangement of the trifluoromethyl groups within the channels. The significance of these findings is discussed from the perspective of employing $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ as precursors in solution-based approaches to functional solid-state materials and as functional materials themselves.

EXPERIMENTAL SECTION

Crystallization of Sr(CF_3COO)_2 and Ba(CF_3COO)_2. $SrCO_3$ (99.9%, Sigma-Aldrich), $BaCO_3$ (99.99%, Sigma-Aldrich), and anhydrous CF_3COOH (99%, Sigma-Aldrich) were used as received. Double-distilled water was employed as the solvent. A mixture of 5 mL of double-distilled water and 1 mL of CF_3COOH was prepared in a 50 mL two-neck round-bottom flask. Then, 2 mmol of the corresponding metal carbonate was added to this solution. Quantitative dissolution of

the metal carbonate occurred within 1-3 min and, as expected, was accompanied by vigorous gas evolution; a colorless, optically transparent solution was obtained. Crystallization of the desired metal trifluoroacetate was accomplished by solvent evaporation, which was induced by flowing dry nitrogen gas over the precursor solution. The reaction flask containing the precursor solution was connected to a nitrogen gas line through one of its necks; a glass adapter was placed on the other neck to allow venting of the nitrogen gas. Then, it was immersed in a sand bath at 65 °C, and the nitrogen gas flow was started. A needle-valve rotameter was employed to regulate the nitrogen flow rate. A constant flow rate of 200 mL min⁻¹ was employed for both $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$. The system was left undisturbed for 48 h at 65 °C under flowing nitrogen. After 48 h, white $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ powders were obtained at the bottom of the reaction flasks. Because of their deliquescent nature, these were stored in a glovebox (oxygen and water levels of <1 ppm) at room temperature for thermal and X-ray diffraction studies. Both trifluoroacetates were observed to deliquesce within minutes if exposed to ambient moisture.

Thermal Analysis. Thermogravimetric analysis (TGA) of the powders was conducted using a Pyris 1 TGA analyzer (Perkin-Elmer). Samples (\sim 5–10 mg) were heated at 35 °C for 30 min under flowing nitrogen (20 mL min⁻¹) and then heated to 600 °C at a rate of 10 °C min⁻¹ under an identical atmosphere. Differential thermal analysis (DTA) was conducted using an SDT2960 TGA-DTA analyzer (TA Instruments) under identical conditions. Samples were exposed to the atmosphere for <30 s prior to thermal analysis.

Single-Crystal X-ray Diffraction. Colorless single crystals of $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ were recovered from the polycrystalline powders and used for structural determination. Both crystals were columnar with approximate dimensions of 0.2 mm \times 0.2 mm \times 0.3 mm. These were mounted in Paratone N oil on a Bruker X8 Apex single-crystal diffractometer, and X-ray intensities were measured at -173 °C using Mo K α radiation ($\lambda = 0.71073$ Å). Frames were integrated using Bruker SAINT software. Experimental data were corrected for Lorentz, polarization, and absorption effects; for the latter, the multiscan method was employed. Structures were determined using direct methods and Fourier synthesis as embedded in the SHELXL-2014/7 software.¹⁹ Resulting crystal structures were visualized using the VESTA software.²⁰ Crystal data of Sr(CF₃COO)₂ and Ba(CF₃COO)₂ were deposited in the Cambridge Crystallographic Data Centre as entries 1421987 and 1421988, respectively. Structural models derived from single-crystal X-ray diffraction studies were employed to estimate the average and minimum diameters of the onedimensional channels, as will be shown below.

Synchrotron Powder X-ray Diffraction. Synchrotron XRD patterns of the polycrystalline $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ powders were collected in the 2θ range of $1-40^\circ$ at the 11-BM line of the Advanced Photon Source of Argonne National Laboratory (Argonne, IL). Samples were packed in double-nesting Kapton tubes, and both ends of the tubes were sealed with clay. Packing was conducted inside the glovebox to minimize degradation of the samples. Diffraction patterns were collected in transmission mode. An incident photon energy of 29.936 keV ($\lambda = 0.4141650$ Å) was employed. The



Figure 2. Crystal structures of (a-d) Sr(CF₃COO)₂ and (e-h) Ba(CF₃COO)₂. Atoms are colored green (Sr and Ba), brown (C), red (O), and light blue (F). For each structure, the following are shown: (a and e) ball-and-stick representation, (b and f) polyhedral representation showing onedimensional channels parallel to the *c* axis, along with the diameter of the circular projection of the centroids of the fluorine atoms on the (001) plane (C–C, C–F, and C–O bonds have been omitted for the sake of clarity), (c and g) coordination environment of the alkaline-earth metal, including the two distinct trifluoroacetate ligands, and (d and h) spatial arrangement of the two distinct trifluoromethyl groups in the onedimensional channels. The F(4) atom has been included in the coordination sphere of barium (g), but not in that of strontium (c); see the text for details.

step size and scan speed were 0.001° and 0.01° s⁻¹, respectively. Diffraction patterns were recorded at 25 °C.

RESULTS AND DISCUSSION

Thermograms of $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ are shown in panels a and b of Figure 1, respectively. $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ exhibit total weight losses of 62.2 and 51.3 wt %, respectively, upon being heated to 600 °C under dry nitrogen. Both experimental results are in excellent agreement with the theoretical weight losses expected upon decomposition of the trifluoroacetates to the corresponding SrF_2 (60.0 wt %) and BaF_2 (51.8 wt %) phases. Powder XRD patterns of the decomposition products confirmed both trifluoroacetates decompose to the corresponding fluorite phase (Figure S1). A single weight loss in the 295–385 and 300–390 °C ranges is observed for $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$, respectively. Inspection of the first derivative of the thermograms (Figure S2), however, indicates that multiple processes occur within this temperature range, in agreement with previous inves-

tigations of the thermal decomposition of metal trifluoroacetates.^{12,13,16,17} This is further confirmed by inspecting the DTA curves, in which two peaks are observed for $Sr(CF_3COO)_2$ (305 and 379 °C) and Ba(CF₃COO)₂ (366 and 377 °C). The presence of exothermic peaks $[379 \ ^{\circ}C \text{ for } Sr(CF_3COO)_2 \text{ and}$ 366 and 377 °C for Ba(CF₃COO)₂] confirms that crystallization of the corresponding fluoride occurs during this weight loss. It is worth noting the presence of an endothermic peak at 305 °C in the DTA curve of $Sr(CF_3COO)_2$. The process giving rise to this peak precedes the crystallization of the SrF₂ phase and is not observed in the DTA curve of the barium counterpart, suggesting the decomposition of $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ occurs through different pathways. Although an investigation of these pathways is beyond the scope of this work, it is important to note that the temperature at which the endothermic process occurs prior to the crystallization of SrF2 is too high to be attributed to the desorption and vaporization of solvent molecules (i.e., H₂O and CF₃COOH) coordinated to the metal atoms or bonded to the

Artic

	$Sr(CF_3COO)_2$	$Ba(CF_3COO)_2$		
formula weight (g)	313.66 364.71			
temperature (°C)	-173(2)			
wavelength (Å)	0.71073			
crystal system	trigonal	trigonal		
space group	R3	$R\overline{3}$		
lattice parameters	a = b = 21.9891(7) Å	a = b = 21.2541(18) Å		
	c = 9.4696(9) Å	c = 10.4984(10) Å		
	$\alpha = \beta = 90^{\circ}$	$\alpha = \beta = 90^{\circ}$		
	$\gamma = 120^{\circ}$	$\gamma = 120^{\circ}$		
volume (Å ³)	3965.3(5)	4107.1(8)		
Ζ	18	18		
calculated density (g cm ⁻³)	2.364	2.645		
$\mu \ (\mathrm{mm}^{-1})$	6.212	4.442		
F(000)	2664	2988		
θ range (deg)	1.85–45.35 (0.50 Å resolution)	1.92–26.36 (0.80 Å resolution)		
index ranges	$-43 \le h \le 42$	$-26 \le h \le 26$		
	$-44 \le k \le 41$	$-25 \le k \le 21$		
	$-18 \le l \le 18$	$-13 \le l \le 13$		
no. of reflections collected	79321	21122		
no. of independent reflections	7364 ($R_{\rm int} = 5.05\%$)	1871 ($R_{\rm int} = 4.44\%$)		
independent reflection coverage (%)	99.5	100.0		
refinement method	full-matrix least squares on F^2			
function minimized	$\sum w(F_o^2 - F_c^2)^2$			
weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0270P)^2 + 0.3321P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^{2}(F_{o}^{2}) + (0.0157P)^{2} + 35.938P], \text{ where} $ $P = (F_{o}^{2} + 2F_{c}^{2})/3$		
data, restraints, parameters	7364, 0, 136	1871, 0, 136		
$\Delta/\sigma_{ m max}$	0.003	0.001		
largest difference peak and hole (e $Å^{-3}$)	0.833 and -0.702	1.484 and -0.680		
root-mean-square deviation (e $Å^{-3}$)	0.132	0.143		
R	2.86% [5648 data with $I > 2\sigma(I)$]	2.31% [1545 data with $I > 2\sigma(I)$]		
	5.31% (all data)	3.85% (all data)		
R _w	5.13% [5648 data with $I > 2\sigma(I)$]	4.45% [1545 data with $I > 2\sigma(I)$]		
	5.54% (all data)	5.10% (all data)		
goodness of fit on F^2	1.020	1.097		

trifluoromethyl groups via hydrogen bonding. Indeed, extensive investigation of the thermal decomposition of alkaline-earth and rare-earth metal trifluoroacetates has shown that desorption of crystallization water molecules takes place below 160 °C.^{5,12,13,15} Further, no simultaneous weight losses and sharp endothermic peaks that could indicate the presence of crystallization solvent molecules are observed in the lowtemperature range (100–160 °C) of the TGA and DTA curves of $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$. This is in agreement with results of single-crystal XRD studies, which demonstrate the absence of crystallization solvent molecules in the structures of both $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ (vide infra). We attribute the anhydrous character of these compounds to the crystallization approach employed in this work, that is, to the use of a dry nitrogen flow to induce evaporation of the solvent. Evaporating the solvent under atmospheric conditions, instead, yields the hydrated products.^{13,14} The relevance of this finding lies on the demonstration that Sr(CF3COO)2 and Ba- $(CF_3COO)_2$ can be crystallized in anhydrous form provided that an adequate crystallization method is employed.

The crystal structures of $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ determined by single-crystal XRD are shown in Figure 2. Crystal and structural determination data are listed in Table 1. Fractional atomic coordinates, anisotropic atomic thermal displacement parameters, and thermal ellipsoid plots are given in Tables S1–S4 and Figure S3. $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ are isostructural and crystallize in the rhombohedral $R\overline{3}$ space group, with the unit cell containing 18 formula units. The unit cell of $Sr(CF_3COO)_2$ is slightly larger along the a and b axes than that of its barium counterpart (~21.99 vs 21.25 Å), whereas that of $Ba(CF_3COO)_2$ is larger along the c axis (\sim 10.45 vs 9.47 Å). Overall, the unit cell volume expands by ~3.5% upon substitution of barium for strontium. The most remarkable feature of these hybrid structures is their open-framework nature due to presence of infinite channels that run parallel to the c axis (Figure 2a,e). Using a polyhedral representation, these channels can be visualized as the assembly of a corona of metal-oxygen polyhedra and the trifluoromethyl groups of the trifluoroacetate ligands, which are directed inward (Figure 2d,f). It is likely that the electrostatic repulsion between the negatively charged trifluoromethyl groups plays an important role in the formation of these channels. It should be mentioned that coordination polyhedra are used here just to facilitate visualization of the crystal structure; the highly distorted coordination environments of the metal atoms prevents them from being described in terms of distortions of regular polyhedra (vide infra). The average diameter of the channels can be estimated using the diameter of a cylinder with a volume equal to that of the void space in the channel; void spaces of 105(12) and 98(9) Å³ were

computed for $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$, respectively, using the PLATON software.²¹ This translates into average diameters of ~3.75 Å for Sr(CF₃COO)₂ and ~3.45 Å for $Ba(CF_3COO)_2$; both values are comparable to the kinetic diameter of small molecules such as carbon dioxide (3.4 Å) and methane (3.8 Å).²² The projection of the centroids of the fluorine atoms of the trifluoromethyl groups on the (001) plane yields circles of diameter ~5.54 and 5.19 Å for $Sr(CF_3COO)_2$ and Ba(CF₃COO)₂, respectively (Figure 2b,f). If we account for the van der Waals radius of the fluorine atom (1.47 Å), these values translate into minimum diameters of ~2.60 and 2.25 Å for $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$, respectively. Both values are comparable to the kinetic diameter of the hydrogen molecule (2.3 Å).²² Both structures belong to the organic–inorganic hybrid framework class of materials reviewed by Rao et al.²³ in 2004 and Cheetham et al.²⁴ in 2006. Specifically, they are reminiscent of the nickel succinate reported by Forster and Cheetham in 2002²⁵ and of the cadmium malonate reported by Vaidhyanathan et al. in 2003.²⁶ Despite featuring dicarboxylates as ligands, those hybrid frameworks feature three remarkable similarities with the $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ structures reported herein: (1) a honeycomb arrangement of the metal-oxygen polyhedra and one-dimensional channels when viewed down the *c* axis, (2) three-dimensional connectivity of the metal-oxygen polyhedra, and (3) the substituents of the organic ligand (i.e., methylene groups) lining the channels. Some of these features are also observed in the structure of the manganese glutarate framework reported by Vaidhyanathan et al.²⁶ and in that of the nickel glutarate framework reported by Guillou et al.²⁷ In terms of the size of the channels, Forster and Cheetham reported an 8.0 (4.0) Å atom-to-atom distance for the widest (narrowest) cavities present in nickel succinate.²⁵ This size range is comparable to that observed for the average and minimum diameters of the channels present in $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$. We decided to investigate whether further chemical control of the size (and eventually shape) of the channels could be achieved by substituting calcium for strontium, but no open-framework structure was observed for $Ca(CF_3COO)_2$ crystallized under similar conditions; a layered structure similar to that reported by Khristov et al. was observed instead (see the Supporting Information).¹⁵

The coordination environment of the alkaline-earth metal is heavily distorted in both $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ (Figure 2c,g). In the case of $Sr(CF_3COO)_2$, the trifluoroacetate ligand is coordinated to the metal atoms via the oxygen atoms of the carboxylate group. Two coordination modes can be distinguished. In the first mode, the carboxylate acts a bidentate bridging ligand: three strontium atoms coordinate to one carboxylate group, with oxygen atoms O(1) and O(2) shared by two metal atoms. In the second mode, only the O(3) atom of the carboxylate group bridges two strontium atoms, whereas O(4) coordinates to a single metal atom. In the case of $Ba(CF_3COO)_{2}$, two chemically distinct trifluoroacetate ligands are present, as well, but both of their carboxylate groups coordinate to the metal atom in a bidentate bridging mode. The presence of two chemically distinct trifluoroacetate ligands in both $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ affects not only the coordination environment of the metal atom but also the spatial arrangement of the trifluoromethyl groups exposed in the onedimensional channels (Figure 2g,h). Selected metal-oxygen and metal-fluoride distances are listed in Table 2 to further illustrate the difference in the coordination environments of the

Table 2. Selected Metal–Oxygen and Metal–Fluoride Distances

	distance (Å)		distance (Å)
Sr-O(1)	2.4979(6)	Ba-O(1)	2.654(3)
Sr-O(1)'	2.7095(7)	Ba-O(1)'	2.813(3)
Sr-O(2)	2.5110(7)	Ba-O(2)	2.707(3)
Sr-O(2)'	2.7119(7)	Ba-O(2)'	2.968(3)
Sr-O(3)	2.5785(7)	Ba-O(3)	2.686(3)
Sr-O(3)'	2.5866(7)	Ba-O(3)'	2.863(3)
Sr-O(4)	2.4623(7)	Ba-O(4)	2.676(3)
		Ba-O(4)'	3.050(3)
Sr-F(4)	2.8619(6)	Ba-F(4)	3.056(2)

alkaline-earth metal atoms. The coordination environment of strontium features strontium-oxygen distances in the 2.46-2.71 Å range, and the metal atom is depicted as heptacoordinated. A Sr...F(4) short distance of 2.86 Å is also observed; as a result, non-negligible bonding interactions between the two atoms may be present.²⁸ Barium-oxygen distances in the 2.65-3.05 Å range and a barium-fluoride distance of 3.06 Å are observed in the coordination environment of barium; in this case, the metal atom is depicted as nonacoordinated. Short Ba…F contacts within the 2.85-3.30 Å range have been reported previously in organometallic compounds containing large alkaline-earth metal atoms and fluorinated ligands.^{29,30} Altogether, these results show that chemical substitution of the barium for strontium induces changes in the coordination environment of the metal atom, and that these changes are accommodated through the displacement of one of the two chemically distinct trifluoroacetate ligands relative to the metal center.

The phase purity of the polycrystalline $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ powders was probed using synchrotron powder XRD. The corresponding experimental diffraction patterns are shown in Figure 3. $Sr(CF_3COO)_2$ powder exhibits just a trace amount of secondary phases. Indeed, with the exception of two low-intensity diffraction maxima appearing at $2\theta \sim 2.51$ and 6.28° , all the peaks in the pattern of $Sr(CF_3COO)_2$ can be indexed to the alkaline-earth trifluoroacetate. In the case of



Figure 3. Experimental powder XRD patterns of $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$. Tick marks depict the position of the diffraction maxima calculated using the structural models derived from single-crystal studies. Diffraction maxima resulting from secondary phases are shown in the insets using asterisks. Rietveld analysis was possible only for $Sr(CF_3COO)_2$ (see the text and Figure S4 for details).

 $Ba(CF_3COO)_2$, the presence of secondary phases is more noticeable; the alkaline-earth trifluoroacetate remains, however, the major phase. Attempts to quantitatively analyze the powder patterns of Sr(CF₃COO)₂ and Ba(CF₃COO)₂ using Rietveld refinements were only partially successful because of the damage suffered by both samples upon exposure to the X-ray beam (i.e., peak broadening and shift). In the case of $Sr(CF_3COO)_2$, an adequate fit to the experimental pattern could be obtained using the structural model derived from single-crystal studies (Figure S4). In contrast, adequate modeling of the shape of the diffraction maxima of $Ba(CF_3COO)_2$ was not possible. From a qualitative standpoint, however, results from powder XRD studies demonstrate that polycrystalline $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ with openframework structures can be obtained with adequate phase purity using the crystallization approach presented in this work.

CONCLUSIONS

In summary, crystallization of the anhydrous $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ open-framework structures was accomplished by inducing evaporation of the H₂O/CF₃COOH solvent mixture with a dry nitrogen flow. This approach to crystallization of metal trifluoroacetates departs from that first proposed by Roberts for the crystallization of rare-earth trifluoroacetates¹⁸ and was routinely employed to crystallize a variety of metal trifluoroacetate salts. Powder XRD demonstrated both trifluoroacetate powders could be obtained with adequate phase purity; only trace and minor amounts of secondary phases were observed in $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$, respectively. The anhydrous nature of the trifluoroacetates was confirmed by thermal analysis and singlecrystal XRD, which did not detect the presence of crystallization solvent molecules. Sr(CF₃COO)₂ and Ba- $(CF_3COO)_2$ are isostructural and belong to the organicinorganic extended hybrids class of materials. They exhibit an open-framework structural motif with three-dimensional connectivity of the metal-oxygen polyhedra and one-dimensional channels along the c axis. The channels are decorated with the trifluoromethyl groups of the trifluoroacetate ligands, and their average (minimum) diameters were estimated to be ~ 3.75 (2.60) and 3.45 (2.25) Å for Sr(CF₃COO)₂ and $Ba(CF_3COO)_2$, respectively. This size range is comparable to the kinetic diameter of molecules such as hydrogen (2.3 Å). From this perspective, we believe that an investigation of the ability of these structures to accommodate guest molecules would be worthwhile. Chemical substitution of barium for strontium affected not only the diameter of the channels but also the spatial arrangement of the trifluoromethyl groups within the channels and the coordination environment of the metal atom. The different coordination requirements of the strontium and barium atoms were found to be accommodated through the displacement of one of the two chemically distinct trifluoroacetate ligands relative to the metal center.

From a synthetic standpoint, this work demonstrates the feasibility of synthesizing anhydrous $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ if the proper crystallization approach is employed. This finding is relevant from a functional materials standpoint because anhydrous trifluoroacetate precursors are highly desirable in solution-based approaches to electronic and optical materials. Furthermore, elucidation of the crystal structures of $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$ provides a structural basis for better understanding the solution chemistry of these precursors and for attempting an expansion of their

scope of application to areas such as the adsorption of small gases.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02081.

Powder XRD patterns of the thermal decomposition products of $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$, differential thermograms (first-derivative) of $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$, additional crystallographic information about $Sr(CF_3COO)_2$ and $Ba(CF_3COO)_2$, Rietveld analysis of $Sr(CF_3COO)_2$, and thermal analysis and single-crystal XRD study of $Ca(CF_3COO)_2$ (PDF) Crystallographic information file (CIF) Crystallographic information file (CIF) Crystallographic information file (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: far@chem.wayne.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge the financial support of the Department of Chemistry at Wayne State University. They also thank the Lumigen Instrument Center at Wayne State University for the use of the Bruker X8 Apex single-crystal X-ray diffractometer and Drs. Stephanie L. Brock and Charles H. Winter for the use of the TGA and DTA analyzers. Use of the Advanced Photon Source at Argonne National Laboratory was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract DE-AC02-06CH11357.

REFERENCES

- (1) Araki, T. Bull. Chem. Soc. Jpn. 2004, 77, 1051-1061.
- (2) Araki, T.; Hayashi, M.; Fuke, H. IEEE Trans. Appl. Supercond. 2013, 23, 6603105.
- (3) Du, Y.-P.; Sun, X.; Zhang, Y.-W.; Yan, Z.-G.; Sun, L.-D.; Yan, C.-H. Cryst. Growth Des. 2009, 9, 2013–2019.

(4) Fujihara, S.; Kadota, Y.; Kimura, T. J. Sol-Gel Sci. Technol. 2002, 24, 147–154.

(5) Fujihara, S.; Tada, M.; Kimura, T. J. Sol-Gel Sci. Technol. 2000, 19, 311-314.

(6) McIntyre, P. C.; Cima, M. J.; Smith, J. A.; Hallock, R. B.; Siegal, M. P.; Phillips, J. M. J. Appl. Phys. **1992**, 71, 1868–1877.

(7) Araki, T.; Hirabayashi, I. Supercond. Sci. Technol. 2003, 16, R71–R94.

(8) Roma, N.; Ricart, S.; Moreto, J. M.; Morlens, S.; Castano, O.; Pomar, A.; Puig, T.; Obradors, X. J. Phys.: Conf. Ser. 2006, 43, 178– 181.

(9) Wojtczak, W. A.; Hampden-Smith, M. J.; Duesler, E. N. Inorg. Chem. 1998, 37, 1781–1790.

(10) Mishra, S.; Hubert-Pfalzgraf, L. G.; Daniele, S.; Rolland, M.; Jeanneau, E.; Jouguet, B. *Inorg. Chem. Commun.* **2009**, *12*, 97–100.

(11) Erbe, M.; Hanisch, J.; Freudenberg, T.; Kirchner, A.; Monch, I.; Kaskel, S.; Schultz, L.; Holzapfel, B. *J. Mater. Chem. A* **2014**, *2*, 4932–4944.

(12) Eloussifi, H.; Farjas, J.; Roura, P.; Camps, J.; Dammak, M.; Ricart, S.; Puig, T.; Obradors, X. J. Therm. Anal. Calorim. 2012, 108, 589–596.

(13) Farjas, J.; Camps, J.; Roura, P.; Ricart, S.; Puig, T.; Obradors, X. *Thermochim. Acta* **2012**, *544*, 77–83.

(14) Glazunova, T. Yu.; Boltalin, A. I.; Fedorov, P. P. Russ. J. Inorg. Chem. 2006, 51, 983–987.

(15) Khristov, M.; Peshev, P.; Angelova, O.; Petrova, R.; Macicek, J. *Monatsh. Chem.* **1998**, *129*, 1093–1102.

(16) Llordes, A.; Zalamova, K.; Ricart, S.; Palau, A.; Pomar, A.; Puig, T.; Hardy, A.; Van Bael, M. K.; Obradors, X. *Chem. Mater.* **2010**, *22*, 1686–1694.

(17) Gazquez, J.; Sandiumenge, F.; Coll, M.; Pomar, A.; Mestres, N.; Puig, T.; Obradors, X.; Kihn, Y.; Casanove, M. J.; Ballesteros, C. *Chem. Mater.* **2006**, *18*, 6211–6219.

(18) Roberts, J. E. J. Am. Chem. Soc. 1961, 83, 1087-1088.

(19) Sheldrick, G. M. SHELXL 2014: Program for Crystal Structure Solution; University of Göttingen: Göttingen, Germany, 2014.

(20) Momma, K.; Izumi, F. J. Appl. Crystallogr. 2011, 44, 1272–1276.
(21) Spek, A. L. Acta Crystallogr., Sect. D: Biol. Crystallogr. 2009, 65, 148–155.

(22) Breck, D. W. Zeolite Molecular Sieves: Structure, Chemistry, and Use; John Wiley and Sons, Inc.: New York, 1974.

(23) Rao, C. N. R.; Natarajan, S.; Vaidhyanathan, R. Angew. Chem., Int. Ed. 2004, 43, 1466–1496.

(24) Cheetham, A. K.; Rao, C. N. R.; Feller, R. K. Chem. Commun. 2006, 4780-4705.

(25) Forster, P. M.; Cheetham, A. K. Angew. Chem., Int. Ed. 2002, 41, 457–459.

(26) Vaidhyanathan, R.; Natarajan, S.; Rao, C. N. R. Dalton Trans. 2003, 1459-1464.

(27) Guillou, N.; Livage, C.; Drillon, M.; Ferey, G. Angew. Chem., Int. Ed. 2003, 42, 5314–5317.

(28) Sarazin, Y.; Liu, B.; Roisnel, Th.; Maron, L.; Carpentier, J.-F. J. Am. Chem. Soc. 2011, 133, 9069–9087.

(29) Labrize, F.; Hubert-Pfalzgraf, L. G.; Daran, J.-C.; Halut, S. J. Chem. Soc., Chem. Commun. 1993, 1556–1558.

(30) Chi, Y.; Ranjan, S.; Chou, T.-S.; Liu, C.-S.; Peng, S.-M.; Lee, G.-H. J. Chem. Soc., Dalton Trans. 2001, 2462–2466.