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Synthesis of bimetallic trifluoroacetates through a crystallochemical investigation of their monometallic counterparts: the case of (A, A') $(CF_3COO)_2 \cdot nH_2O$ (A, A' = Mg, Ca, Sr, Ba, Mn)†

B. Dulani Dhanapala,^a Natalie A. Mannino,^a Laura M. Mendoza,^a K. Tauni Dissanayake,^a Philip D. Martin,^a Leopoldo Suescun^b and Federico A. Rabuffetti*^a

Owing to their potential as single-source precursors for compositionally complex materials, there is growing interest in the rational design of multimetallic compounds containing fluorinated ligands. In this work, we show that chemical and structural principles for a materials-by-design approach to bimetallic trifluoroacetates can be established through a systematic investigation of the crystal-chemistry of their monometallic counterparts. $A(CF_3COO)_2 \cdot nH_2O$ (A = Mg, Ca, Sr, Ba, Mn) monometallic trifluoroacetates were employed to demonstrate the feasibility of this approach. The crystal-chemistry of monometallic trifluoroacetates was mapped using variable-temperature single-crystal X-ray diffraction, powder X-ray diffraction, and thermal analysis. The evolution with temperature of the previously unknown crystal structure of Mg(CF₃COO)₂·4H₂O was found to be identical to that of Mn(CF₃COO)₂·4H₂O. More important, the flexibility of $Mn_x(CF_3COO)_{2x}$ ·4H₂O (x = 1, 3) to adopt two structures, one isostructural to Mg(CF₃COO)₂·4H₂O, the other isostructural to Ca₃(CF₃COO)₆·4H₂O, enabled the synthesis of Mg-Mn and Ca-Mn bimetallic trifluoroacetates. Mg0 45Mn0 55(CF3COO)2·4H2O was found to be isostructural to Mg(CF₃COO)₂·4H₂O and exhibited isolated metal-oxygen octahedra with Mg²⁺ and Mn²⁺ nearly equally distributed over the metal sites (Mq/Mn: 45/55). Ca172Mn128(CF3COO)6.4H2O was isostructural to $Ca_3(CF_3COO)_6$ ·4H₂O and displayed trimers of metal-oxygen corner-sharing octahedra; Ca²⁺ and Mn²⁺ were unequally distributed over the central (Ca/Mn: 96/4) and terminal (Ca/Mn: 38/62) octahedral sites.

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1. Introduction

Metal–organic compounds containing fluorinated ligands constitute an important class of precursors employed in the preparation of functional materials and nanomaterials.¹ Since the work of Roberts,² trifluoroacetic acid (CF₃COOH, tfaH) has been extensively used as a ligand to synthesize monometallic fluorinated precursors of alkali, alkaline-earth, transition, and rare-earth metals. Recently, there has been growing interest in the preparation of multimetallic fluorinated compounds in view of their potential as single-source precursors for compositionally complex functional materials. Mishra *et al.* reported the synthesis of a series of bimetallic compounds featuring Na and Y as metals and tfaH, tetrahydrofuran, and di-, tri-, and tetraglyme as ligands.³ These compounds were found to serve as single-source precursors for NaYF₄ upconverting nanocrystals. Likewise, Tereshchenko *et al.* reported the synthesis of a series of bimetallic trifluoroacetates featuring an alkali and divalent nickel or cobalt as metals.^{4,5} These compounds featured triangular trinuclear complex anions, which are potentially interesting in view of their magnetic properties.⁶

Despite their potential as precursors for functional materials, the rational assembly of multimetallic compounds containing trifluoroacetate ligands (tfa) remains challenging. With the aim of addressing this challenge, we hypothesized that a systematic investigation of the crystal-chemistry of monometallic trifluoroacetates yields chemical and structural principles that enable a materials-by-design approach to multimetallic compounds. A(tfa)₂·nH₂O (A = Mg, Ca, Sr, Ba, Mn^{II}) trifluoroacetates were employed as the materials platform to



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^aDepartment of Chemistry, Wayne State University, Detroit, MI 48202, USA. E-mail: far@chem.wayne.edu

^bCryssmat-Lab/Cátedra de Física/DETEMA, Facultad de Química, Universidad de la República, Montevideo 11800, Uruguay

[†] Electronic supplementary information (ESI) available: (1) Additional crystallographic information of Mg(tfa)₂·4H₂O, Mn₃(tfa)₆·4H₂O, Mg_{0.45}Mn_{0.55}(tfa)₂·4H₂O, and Ca_{1.72}Mn_{1.28}(tfa)₆·4H₂O, including CIF files; (2) Rietveld analysis of Mn_x(tfa)_{2x}·4H₂O; (3) crystallochemical features of alkaline-earth trifluoroacetates; and (4) thermograms and differential thermograms of Mg(tfa)₂·4H₂O and Mn_x(tfa)_{2x}·4H₂O. See DOI: 10.1039/c6dt04152c

test this hypothesis. Alkaline-earth trifluoroacetates have been used as precursors to functional materials such as superconducting YBa₂Cu₃O₇ thin films,^{7,8} Er:Yb:SrF₂ upconversion nanocrystals,9 and MgF2 and CaF2 fluoride composites and ceramics.10-12 Yet, an investigation of the structures and crystal-chemistry of alkaline-earth trifluoroacetates crystallized directly from a mixture of tfaH and water has not been performed. Boyle et al. reported a study of the crystal-chemistry and structures of alkaline-earth trifluoroacetates, but these were recrystallized from basic solvents such as pyridine and tetrahydrofuran.¹³ A similar situation is observed in the family of trifluoroacetates containing first-row transition metals such as divalent manganese. Several researchers have synthesized and structurally characterized manganese(II) complexes containing trifluoroacetate ligands. However, in all cases, these contained ligands other than tfa and H₂O (e.g., pyridine,¹⁴ benzonitrile¹⁴ tetrahydrofuran,¹⁵ bipyridine,¹⁶ acetic acid¹⁷). Manganese(II) trifluoroacetate was first crystallized directly from a mixture of tfaH and H₂O by Baillie et al. in 1968.¹⁸ Interestingly, its crystal structure was not elucidated until 2000, when Olejnik and Lis reported the solution of the hightemperature (>215 K) phase of Mn(tfa)₂·4H₂O;¹⁹ the structure of the low-temperature counterpart was not reported and, to the best of our knowledge, its solution was not further pursued. Finally, no attempts at performing a systematic comparison between the crystal-chemistry of different families of monometallic trifluoroacetates (e.g., alkali and alkaline-earth vs. transition metals, transition metals vs. rare-earths, etc.) have been reported.

Herein, we report a systematic investigation of the crystalchemistry of $A(tfa)_2 \cdot nH_2O$ (A = Mg, Ca, Sr, Ba, Mn) and the synthesis and structural solution of bimetallic trifluoroacetates containing Mg-Mn and Ca-Mn as metal centers. Variabletemperature single-crystal X-ray diffraction, powder X-ray diffraction, and thermal analysis were employed to map the chemical and structural relationships within the $A(tfa)_2 \cdot nH_2O$ (A = Mg, Ca, Sr, Ba, Mn) family of monometallic trifluoroacetates. Emphasis was placed on (i) identifying common crystallochemical patterns encountered in alkaline-earth and manganese trifluoroacetates, and (ii) utilizing those patterns to synthesize bimetallic trifluoroacetates containing alkaline-earth and divalent manganese cations as metal centers. Critical to accomplishing these goals were the solutions of the structures of Mg(tfa)₂·4H₂O and of Mn₃(tfa)₆·4H₂O, as well as understanding their evolution in the 100-300 K temperature range.

2. Experimental

2.1. Crystallization of Mg(tfa)₂·4H₂O

 $MgCO_3$ (99.9%, Sigma Aldrich) and anhydrous tfaH (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 tfaH was prepared in a 50 mL two-neck round-bottom flask. Then, 2 mmol of $MgCO_3$ (168.63 mg) were added to this solution. A colorless, optically transparent

solution was obtained upon quantitative dissolution of the metal carbonate. Crystallization of $Mg(tfa)_2 \cdot 4H_2O$ was accomplished by solvent evaporation at room temperature, which was induced by flowing dry nitrogen gas over the precursor solution.²⁰ This approach to crystallization of metal trifluoro-acetates differs from that first proposed by Roberts, which achieves solvent evaporation by heating under air.² A needle-valve rotameter was employed to regulate the nitrogen flow rate. The flow rate was maintained constant at 35 mL min⁻¹ for 24 h. Next, it was increased to 200 mL min⁻¹ and maintained constant for 4 days. A colorless polycrystalline solid was obtained at the bottom of the reaction flask. Single crystals of $Mg(tfa)_2 \cdot 4H_2O$ were recovered from the powder for structural determination.

2.2. Crystallization of Mn₃(tfa)₆·4H₂O

 $MnCO_3$ (99.9%, Sigma Aldrich) was used as received. A mixture of 3 mL of double-distilled water and 3 mL of tfaH was prepared in a 50 mL two-neck round-bottom flask. Then, 1 mmol of $MnCO_3$ (115.20 mg) was added to this solution. A brown, optically transparent solution was obtained. Crystallization of $Mn_3(tfa)_6\cdot 4H_2O$ was accomplished by a solvent evaporation approach identical to that employed for the magnesium compound. The only difference was that the nitrogen flow rate was maintained constant at 70 mL min⁻¹ for 12 days. Single crystals of $Mn_3(tfa)_6\cdot 4H_2O$ suitable for structural determination were then recovered.

2.3. Crystallization of Mg–Mn and Ca–Mn bimetallic trifluoroacetates

A mixture consisting of 1 mmol of $MgCO_3$ (CaCO₃) and 1 mmol of $MnCO_3$ was used in the synthesis of Mg–Mn (Ca–Mn) bimetallic trifluoroacetate. Crystallization was accomplished by a solvent evaporation approach identical to that described above. The only difference was that the nitrogen flow rate was maintained constant at 70 mL min⁻¹ for 9 days. Gelatin-like products were obtained, from which a few single crystals suitable for structural determination were carefully isolated.

2.4. Single-crystal X-ray diffraction

2.4.1. Mg(tfa)₂·4H₂O. Single-crystal X-ray structure determinations were carried out at 100, 143, 160, 200, and 300 K. Colourless crystals of Mg(tfa)₂·4H₂O appeared as parallelepipeds. A crystal with approximate dimensions $0.10 \times 0.20 \times 0.20$ mm, that turned out to be a two-component twin, was selected for structure determination at 100 K. The geometric relation between the two domains suggested this crystal had a higher symmetry at room temperature, leading us to perform a more complete structural analysis. A crystal with approximate dimensions $0.13 \times 0.15 \times 0.42$ mm was then selected for structure determination at 300 K, as well as for study of the reversible phase transition to the low-temperature polymorph. Crystals were mounted in Paratone N oil or epoxy in a Bruker X8 Apex single crystal diffractometer. X-ray intensities were measured at the desired temperature using Mo K α radiation ($\lambda = 0.71073$ Å).

Frames were integrated using the Bruker SAINT software. Experimental data were corrected for Lorentz, polarization, and absorption effects; for the latter, the multiscan method was employed using Bruker TWINABS software. The structure was solved using a dual space approach as implemented in SHELXT²¹ and difference Fourier maps as embedded in the SHELXL-2014/7 software²² running under ShelXle²³ and visualized using the VESTA software.²⁴ Hydrogen atom positions were determined for the 100 and 300 K structures employing difference Fourier maps; these were later used as a starting point for structural solution at other temperatures (143, 160, and 200 K). Hydrogen positions were refined with the following constraints: (1) an O-H bond distance of 0.840(0.001) Å; (2) a H···H distance of 1.360(0.002) Å, corresponding to a 104.5° angle; and (3) $U_{iso} =$ $1.5U_{eq}$ of the parent oxygen atom. The final refined positions of hydrogen atoms defined a reasonable hydrogen-bond network. An unconstrained approach yielded unreasonable bond distances and angles. Table 1 summarizes crystal data, data collection, and structure refinement details for the five datasets collected at 100, 143, 160, 200, and 300 K. For the diffraction data collected at 160 K, structure refinement was attempted using both triclinic and monoclinic symmetries; structure refinement details are given for both models and discussed below. Crystal data of $Mg(tfa)_2 \cdot 4H_2O$ were deposited in the Cambridge Crystallographic Data Centre with numbers 1443800 (100 K), 1505493 (300 K), 1505494 (200 K), 1505495 (160 K, monoclinic), 1505496 (160 K, triclinic), and 1505497 (143 K). Additional structural details are given in the ESI (Tables S1–S18 and Fig. S1–S6†).

2.4.2. $Mn_3(tfa)_6 \cdot 4H_2O$. Single-crystal X-ray structure determination was carried out at 100 K. Colourless crystals of $Mn_3(tfa)_6 \cdot 4H_2O$ appeared as parallelepipeds. A crystal with approximate dimensions $0.13 \times 0.29 \times 0.49$ mm, that turned out to be a multicomponent twin, was selected and processed as a four-component twin; components below 5 wt% were disregarded. The structure was solved by intrinsic phasing methods. Data collection and structure refinement procedures were similar to those employed for the magnesium compounds. Table 2 summarizes crystal data, data collection, and structure refinement details. Crystal data of $Mn_3(tfa)_6 \cdot 4H_2O$ were deposited in the Cambridge Crystallographic Data Centre with number 1505498. Additional structural details are given in the ESI (Tables S19–S21 and Fig. S7†).

Chemical formula	Mg(tfa) ₂ ·4H ₂ O					
Formula weight (g)	322.41	322.41	322.41	322.41	322.41	322.41
Temperature (K)	100	143	160	160	200	300
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space-group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	C2/c	C2/c	C2/c
a, b, c (Å)	8.0985(9), 9.0458(11), 9.3604(11)	8.1395(4), 9.0727(5), 9.3369(5)	8.142(2), 9.099(3), 9.250(3)	13.243(2), 12.8685(19), 8.1543(13)	13.2595(9), 12.7856(9), 8.1950(7)	13.2064(6), 12.6063(6), 8.3132(4)
α, β, γ (°)	88.324(6), 65.021(5), 71.131(6)	88.102(3), 65.910(2), 70.795(2)	87.850(16), 67.112(14), 69.439(14)	90, 120.701(7), 90	90, 120.562(6), 90	90, 118.849(2), 90
Volume (Å ³)	583.55(12)	590.32(5)	587.2(3)	1194.9(3)	1196.30(17)	1212.24(10)
Z, Z'	2, 1	2, 1	2,1	4, 0.5	4, 0.5	4, 0.5
$\mu (mm^{-1})$	0.27	0.27	0.27	0.26	0.26	0.26
Crystal size (mm)	0.20 imes 0.20 imes	0.42 imes 0.15 imes	0.42 imes 0.15 imes	0.42 imes 0.15 imes	0.42 imes 0.15 imes	0.42 imes 0.15 imes
•	0.10	0.13	0.13	0.13	0.13	0.13
T_{\min}, T_{\max}	0.691, 0.745	0.885, 0.967	0.885, 0.967	0.885, 0.967	0.885, 0.967	0.885, 0.967
θ range (°)	2.4-25.3	2.4 - 28.4	2.4 - 28.4	2.4 - 28.3	2.4-28.3	2.4 - 28.3
$(\sin \theta / \lambda)_{\max} (\text{\AA}^{-1})$	0.600	0.669	0.669	0.666	0.668	0.667
Index ranges	$-9 \le h \le 9$	$-10 \le h \le 10$	$-10 \le h \le 10$	$-17 \le h \le 17$	$-17 \le h \le 17$	$-17 \le h \le 17$
	$-10 \le k \le 10$	$-12 \le k \le 12$	$-11 \le k \le 11$	$-16 \le k \le 17$	$-17 \le k \le 17$	$-16 \le k \le 16$
	$-11 \leq l \leq 11$	$-12 \le l \le 12$	$-12 \le l \le 12$	$-10 \le l \le 18$	$-10 \le l \le 10$	$-11 \leq l \leq 11$
Measured, independent, and observed $[I > 2\sigma(I)]$ reflections	34 199, 34 199, 29 303	9250, 9250, 7136	5346, 5346, 3230	16 302, 1402, 841	31 440, 1480, 1159	31 593, 1511, 1313
Refinement method	Full-matrix least square	es on F^2				
Weighting scheme	w = $1/[\sigma^2(F_0^2) + (0.0299P)^2 + 0.1114P]$ where $P = (F_0^2 + 2F_c^2)/3$	w = $1/[\sigma^2(F_o^2) + (0.1059P)^2 + 0.2653P]$ where P = $(F_o^2 + 2F_c^2)/3$	w = $1/[\sigma^2(F_o^2) + (0.2P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^{2}(F_{o}^{2}) + (0.0897P)^{2} + 22.3022P] \text{ where } P = (F_{o}^{2} + 2F_{c}^{2})/3$	w = $1/[\sigma^2(F_o^2) + (0.1187P)^2 + 0.7162P]$ where P = $(F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^{2}(F_{o}^{2}) + (0.0433P)^{2} + 0.3461P] \text{ where}$ $P = (F_{o}^{2} + 2F_{c}^{2})/3$
Reflections, parameters, restraints	34 199, 197, 12	9250, 173, 0	5346, 173, 6	1402, 120, 72	1480, 148, 107	1511, 149, 100
H atom treatment	Only H-atom coordinates refined	H-atom parameters c	onstrained			
$\Delta_{\rm max}, \Delta_{\rm min} \ ({\rm e} \ {\rm \AA}^{-3})$	0.26, -0.27	0.73, -0.41	1.51, -1.21	0.54, -0.89	0.67, -0.53	0.27, -0.18
$R[F^2 > 2\sigma(F^2)]$	3.1%	6.0%	10.6%	11.0%	6.0%	2.7%
$wR(F^2)$	7.8%	17.7%	31.0%	31.8%	17.6%	7.8%
		1.05	1.07	1.07	1.00	1.05

Table 2 Crystal and structural determination data of Mn₃(tfa)₆·4H₂O

Chemical formula	Mn ₃ (tfa) ₆ ·4H ₂ O
Formula weight (g)	915.00
Temperature (K)	100
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space-group	$P2_1/n$
a, b, c (Å)	9.0195(5), 9.0431(5), 15.9167(9)
α, β, γ (°)	90, 90.694(3), 90
Volume (Å ³)	1298.14(13)
Z, Z'	2, 0.5
$\mu (mm^{-1})$	1.64
Crystal size (mm)	$0.49 \times 0.29 \times 0.13$
T _{min} , T _{max}	0.641, 0.794
θ range (°)	2.6-28.8
$(\sin\theta/\lambda)_{\rm max}$ (Å ⁻¹)	0.678
Index ranges	$-12 \le h \le 12$
C	$0 \le k \le 12$
	$0 \le l \le 21$
Measured, independent and	4315, 4315, 3639
observed $[I > 2\sigma(I)]$ reflections	
Refinement method	Full-matrix least squares on F^2
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.038P)^2 + 4.929P]$
0 0	where $P = (F_0^2 + 2F_c^2)/3$
Reflections, parameters,	4315, 368, 586
restraints	
H atom treatment	Only H-atom coordinates refined
$\Delta_{\rm max}, \Delta_{\rm min} (e {\rm \AA}^{-3})$	1.20, -0.76
$R[F^2 > 2\sigma(F^2)]$	5.2%
$wR(F^2)$	12.2%
S	1.05

2.4.3. Mg–Mn and Ca–Mn bimetallic trifluoroacetates. Single-crystal X-ray structure determinations were carried out at 100 K. Crystals with approximate dimensions $0.36 \times 0.33 \times 0.14$ and $0.44 \times 0.36 \times 0.21$ mm were selected for

 $Mg_{0.45}Mn_{0.55}(tfa)_2 \cdot 4H_2O$ and $Ca_{1.72}Mn_{1.28}(tfa)_6 \cdot 4H_2O$, respectively. Both structures were solved using a dual space approach. Mg_{0.45}Mn_{0.55}(tfa)₂·4H₂O exhibited the same type of twinning observed in Mg(tfa)2·4H2O. The observed electronic density of the metal site was found to be larger (lower) than that expected for magnesium (manganese), suggesting a partial substitution of manganese with magnesium. Thus, metal site occupancy was refined for manganese and magnesium atoms with constrained coordinates and thermal parameters yielding a Mg/Mn occupancy ratio of 45/55, in good agreement with the nominal composition of the starting mixture. Likewise, mixed-metal site occupancies were observed in Ca1.72Mn1.28(tfa)6.4H2O. Metal site occupancies for the two crystallographically distinct sites in this structure were refined independently, using constrained atomic positions and anisotropic displacement parameters. Split atomic positions were also refined for crystallographically distinct trifluoroacetate ligands. Table 3 summarizes crystal data, data collection, and structure refinement details. Crystal data of Mg_{0.45}Mn_{0.55}(tfa)₂·4H₂O and Ca_{1.72}Mn_{1.28}(tfa)₆·4H₂O were deposited in the Cambridge Crystallographic Data Centre with numbers 1507757 and 1510812, respectively. Additional structural details are given in the ESI (Tables S22-S28 and Fig. S8 and S9†).

2.5. Room-temperature powder X-ray diffraction and Rietveld analysis of Mn_x(tfa)_{2x}·4H₂O

Polycrystalline $Mn_x(tfa)_{2x} \cdot 4H_2O$ (x = 1, 3) was characterized using a Bruker daVinci powder diffractometer operated at 40 kV and 40 mA. Cu K α radiation ($\lambda = 1.5418$ Å) was employed. Diffractograms were collected in 8–80° 2 θ range using a step

Table 3 Crystal and structural determination data of Mg-Mn and Ca-Mn trifluoroacetates

Chemical formula	$Mg_{0.45}Mn_{0.55}(tfa)_2 \cdot 4H_2O$	Ca _{1.72} Mn _{1.28} (tfa) ₆ ·4H ₂ O
Formula weight (g)	339.19	889.46
Temperature (K)	100	
Wavelength (Å)	0.71073	
Crystal system	Triclinic	Monoclinic
Space-group	$P\bar{1}$	$P2_1/n$
a, b, c (Å)	8.1926(6), 9.0995(7), 9.4154(7)	9.0523(5), 9.1619(5), 16.3326(10)
α, β, γ (°)	88.761(4), 63.982(3), 71.251(4)	90, 92.621(3), 90
Volume (Å ³)	591.40(8)	1353.15(13)
Z	2	2
$\mu ({\rm mm^{-1}})$	0.79	1.13
Crystal size (mm)	0.36 imes 0.33 imes 0.14	0.44 imes 0.36 imes 0.21
T _{min} , T _{max}	0.829, 0.889	0.661, 0.801
θ range (°)	2.4-30.7	2.5-34.8
$(\sin\theta/\lambda)_{\rm max}$ (Å ⁻¹)	0.717	0.804
Index ranges	$-10 \le h \le 11$	$-14 \le h \le 14$
C C	$-12 \le k \le 13$	$0 \le k \le 14$
	$0 \le l \le 13$	$0 \le l \le 25$
Measured, independent and observed	6410, 6410, 5166	8732, 8732, 6192
$[I > 2\sigma(I)]$ reflections		
Refinement method	Full-matrix least squares on F^2	
Weighting scheme	$w = 1/[\sigma^2(F_0^2) + (0.0257P)^2 + 0.1582P]$	$w = 1/[\sigma^2(F_0^2) + (0.0553P)^2 + 0.3102P]$
0	where $P = (F_0^2 + 2F_c^2)/3$	where $P = (F_0^2 + 2F_c^2)/3$
Reflections, parameters, restraints	6410, 198, 12	8732, 397, 288
H atom treatment	Only H-atom coordinates refined	
$\Delta_{\rm max}, \Delta_{\rm min} (e {\rm \AA}^{-3})$	0.44, -0.30	0.82, -0.82
$R[F^2 > 2\sigma(F^2)]$	3.0%	4.0%
$wR(F^2)$	6.6%	11.3%
S	1.03	1.07

size of 0.016° and a step time of 3 s. Details of the Rietveld analysis^{25,26} of the powder diffraction pattern are given in the ESI (Fig. S10†).

3. Results and discussion

3.1. Low-temperature phase of Mg(tfa)₂·4H₂O (100 K)

The crystal structure of the low-temperature phase of $Mg(tfa)_2 \cdot 4H_2O$ is shown in Fig. 1a–e. $Mg(tfa)_2 \cdot 4H_2O$ crystallizes in the triclinic $P\bar{1}$ space-group with Z = 2. The compound has a monomeric structure in which the Mg^{2+} cation is octahedrally coordinated by oxygen atoms: four of these atoms belong to water molecules in a square-planar configuration, while the

other two (*trans* positioned) belong to the carboxylate groups of the trifluoroacetate anions, which act as monodentate ligands (Fig. 1a). The Mg–O bond lengths are in the 2.0259(18)–2.0995(16) Å range. The O–Mg–O bond angles of 176.19(8)–177.43(7)° (*trans*) and 87.67(7)–94.15(7)° (*cis*) correspond to a nearly regular octahedron. Both trifluoroacetate ligands are oriented with the –CF₃ groups in opposite corners of the magnesium–oxygen octahedral monomer; C–C bonds are almost parallel to the O1'–Mg–O1 line connecting the oxygen atoms of the two carboxylate groups. The remaining two oxygen atoms O2' and O2 are both hydrogen-bonded to the O1W water molecule. As a result, both carboxylates are nearly coplanar, with a dihedral angle of 21.67(11)° between C1'–O1'–O2'–Mg and C1–O1–O2–Mg planes. Magnesium–



Fig. 1 Crystal structure of $Mg(tfa)_2 \cdot 4H_2O$ at 100 K. Mg: orange, C: dark grey, O: red, F: green, H: purple. (a) First coordination sphere of the Mg^{2+} cation. Intramonomer hydrogen-bonds are depicted with black dashed lines. (b) Hydrogen-bond network connecting a magnesium–oxygen monomer with four neighboring monomers. Hydrogen bonds are depicted with black dashed lines. $-CF_3$ groups are omitted for clarity. (c) Polyhedral representation of the structure in the [010] direction, where zig-zag chains running parallel to the *a* axis are observed. (d) Hydrogen bonds between zig-zag chains. Intrachain and interchain interactions are depicted with long- and short-dashed lines, respectively. $-CF_3$ groups are omitted for clarity. (e) Polyhedral representation of the structure in the [100] direction, where one-dimensional channels running along the *a* axis are observed. The channels are lined with $-CF_3$ groups.

Table 4 Donor (D)–acceptor (A) hydrogen-bond geometry (Å) in Mg(tfa)_2·4H_2O at 100 K

316 2.08	137.85	. 2747
		2./4/
792 2.03	142.70) 2.711
332 1.85	173.61	2.680
323 1.98	3 161.92	2.777
314 2.04	5 152.25	2.791
314 2.47	79 136.42	3.120
340 1.85	3 172.10	2.687
340 2.58	115.61	3.041
783 2.06	4 150.28	3 2.771
794 2.06	149.80	2.783
	332 1.85 323 1.98 314 2.04 314 2.47 340 1.85 340 2.58 783 2.06 794 2.06	332 1.851 173.61 323 1.983 161.92 314 2.045 152.25 314 2.479 136.42 340 1.853 172.10 340 2.582 115.61 783 2.064 150.28 794 2.068 149.80

oxygen octahedral monomers are connected to each other via a complex three dimensional hydrogen-bond network depicted in Fig. 1b; the geometric parameters of the network are given in Table 4. Each magnesium-oxygen monomer is connected to four others via hydrogen-bond interactions involving all four coordinating water molecules and both pairs of oxygen atoms of the carboxylate groups. The carboxylate oxygen atoms O2'/ O2, which are not coordinated to the metal center, are simultaneously involved in both intra- and intermonomer hydrogenbond. Olejnik and Lis provided an hierarchy of the hydrogenbonding network for the high-temperature phase of Mn(tfa)₂·4H₂O,¹⁹ which is isostructural to the high-temperature phase of $Mg(tfa)_2 \cdot 4H_2O$ (vide infra). Although subjective, this hierarchy shows that interactions between $Mg(OH_2)_4(OCOCF_3)_2$ octahedra lead to the formation of zig-zag chains running along the [100] direction (Fig. 1c). Intra- and interchain hydrogen-bonding interactions can be distinguished (Fig. 1d). Intrachain interactions consist of four hydrogen bonds involving atoms O1' (acceptor), O3W (donor), and O2W (donor and acceptor), plus four hydrogen bonds involving atoms O1 (acceptor), O2W' (donor and acceptor), and O3W (donor). Each chain is connected to two equivalent chains along the [010] and [001] directions *via* the two strongest hydrogen bonds in the structure involving O2 and O2W on one side, and O2' and O2W' on the other side. Since the shortest hydrogen bonds are those connecting chains, the true nature of the hydrogen-bond network is three dimensional. As a result, each magnesium–oxygen monomer is connected to two monomers within the same chain and to two other monomers located in neighboring chains. Four adjacent chains define infinite channels running parallel to the [100] direction (Fig. 1e); these channels are lined with the –CF₃ groups of the trifluoroacetate ligands. Finally, it should be noted that weak O–H…F interactions involving O2W', F1', and F3 may play a role in determining the conformation of –CF₃ groups.

3.2. High-temperature phase of $Mg(tfa)_2 \cdot 4H_2O(300 \text{ K})$ and reversible phase transition

The crystal structure of the high-temperature phase of $Mg(tfa)_2 \cdot 4H_2O$ is shown in Fig. 2a using a stick representation. The structure of the low-temperature phase (100 K) is included in Fig. 2b using an identical representation to facilitate comparison. Inspection of these figures demonstrates the remarkable similarity between the monoclinic and triclinic crystal structures. Only two differences are observed: (i) at 300 K $Mg(tfa)_2 \cdot 4H_2O$ crystallizes in the monoclinic C2/c space-group with Z = 4 (Z' = 0.5), and (ii) –CF₃ groups are rotationally disordered at 300 K, with each fluorine atom distributed between three different positions with fractional occupancies of 53, 30, and 17%. No changes are observed in the hydrogen-bond network; the fluorine atom with the highest fractional occupation in the disordered, high-temperature phase has the same contacts as the fluorine atoms in the ordered, low-temperature phase (see Table 5).



Fig. 2 Stick representations of the crystal structures of Mg(tfa)₂·4H₂O at (a) 300 and (b) 100 K. Mg: orange, C: brown, O: red; fluorine and hydrogen atoms have been omitted for clarity. Unit cells are depicted with solid lines.

Table 5 Donor (D)–acceptor (A) hydrogen-bond geometry (Å) in Mg(tfa)_2·4H_2O at 300 K

$\begin{array}{ccc} O2W-H2A\cdotsO1^{i} & 0.8\\ O2W-H2B\cdotsO2^{ii} & 0.8\end{array}$	4 2.02	0.7000(1)	
$\Omega 2W - H 2B \cdots \Omega 2^{ii}$ 0.8		2./963(10)) 154
010 01 01	4 1.87	2.6978(10) 170
O1W-H1…O2 0.8	3 2.10	2.7545(8)	135
O3W–H3…O2W ⁱⁱⁱ 0.8	2 2.10	2.8363(7)	149
O1W-H1…O2 0.8	3 2.10	2.7545(8)	135
O2W-H2B····O2 ⁱⁱ 0.8	4 1.87	2.6978(10) 170
O2W-H2B…F1 ⁱⁱ 0.8	4 2.72	3.220(5)	120
O3W-H3…O2W ⁱⁱⁱ 0.8	2 2.10	2.8363(7)	149

Following the structure determination at 300 K, the triclinic-to-monoclinic phase transition was investigated to elucidate (i) the transition temperature, (ii) whether it is reversible, and (iii) the driving force for the transition. To this end, the crystal was subjected to the following cooling/heating sequence: 300 K \rightarrow 200 K \rightarrow 143 K \rightarrow 160 K \rightarrow 143 K \rightarrow 200 K. Diffraction data for structure determination were collected in the last three steps of this sequence. The evolution with temperature of the unit cell constants and volume is plotted in Fig. 3; data points at 100 and 143 K correspond to pseudomonoclinic cell constants. Inspection of Fig. 3a–c demonstrates that Mg(tfa)₂·4H₂O undergoes a triclinic-to-monoclinic



Fig. 3 Evolution with temperature of the unit cell edges' length (top panel), angles (middle panel), and volume (bottom panel) of Mg(tfa)₂·4H₂O. For the triclinic unit cell (100 and 143 K), pseudo-monoclinic cell constants are plotted. The dotted line depicts the estimated triclinic-to-monoclinic transition temperature (160 K). Dashed lines are guides-to-the-eye.

phase transition at ~160 K. Diffraction data at 160 K was modeled using both triclinic and monoclinic symmetries (see Table 1). Both models yielded consistent results, demonstrating that at 160 K the crystal is on the verge of the phase transition; splitting of the -CF3 groups was reduced to two crystallographically distinct positions in both cases. Judging from the refinement residuals, the monoclinic model performed slightly better; thus, unit cell constants extracted from the monoclinic structure at 160 K were employed in the plots shown in Fig. 3. Temperature-dependent changes in the unit cell are accommodated through a monotonous expansion of the *c* axis and a contraction of the β angle upon increasing the temperature; overall, this results in an increase in the unit cell volume. Splitting of the reflections was observed upon cooling from 200 to 143 K and was partially reversed upon heating to 200 K (see ESI[†]). Upon cooling to 143 K the crystal was observed to be a twin with two triclinic components, as expected for a C2/c to $P\overline{1}$ phase transition. Furthermore, the geometric relationship between these two components was found to be identical to that observed at 100 K and consistent with a C2/c to $P\overline{1}$ twin-domain splitting.²⁷ Altogether, these observations demonstrate that Mg(tfa)₂·4H₂O undergoes a reversible monoclinic-to-triclinic phase transition upon cooling below 160 K and that this transition leads to crystal twinning. An identical phase transition was observed by Olejnik and Lis in Mn(tfa)₂·4H₂O at 215 K;¹⁹ this confirms the structural similarity between the magnesium and manganese trifluoroacetates. As mentioned earlier, the only difference between the low-temperature (triclinic) and high-temperature (monoclinic) phases is the rotational disorder of the $-CF_3$ groups in the latter. Thus, the transition from a $P\bar{1}$ to a C2/csymmetry upon increasing the temperature appears to be related to this phenomenon. Indeed, when the -CF₃ groups are disordered, the magnesium-oxygen monomer possesses a twofold rotation axis, which combined with the inversion symmetry of the lattice leads to a 2/m symmetry.

3.3. Map of structural relationships in $Mg(tfa)_2 \cdot 4H_2O$, $Mn(tfa)_2 \cdot 4H_2O$, $Mn_3(tfa)_6 \cdot 4H_2O$, and $Ca_3(tfa)_6 \cdot 4H_2O$

Our next step was to establish chemical and structural relationships between monometallic trifluoroacetates. In the following, we focus on relationships existing between alkaline-earth and manganese trifluoroacetates; for completeness, a systematic comparison of the crystal-chemistries of Mg, Ca, Sr, and Ba trifluoroacetates is provided in the ESI (Table S29 and Fig. S10[†]). As mentioned earlier, the high-temperature phase of $Mg(tfa)_2 \cdot 4H_2O$ is isostructural to the high-temperature phase of Mn(tfa)₂·4H₂O reported by Olejnik and Lis.¹⁹ This led us to investigate whether this relationship holds at low temperatures as well. Although Olejnik and Lis acknowledged a phase transition leading to crystal twinning at 215 K,¹⁵ they did not provide a structural model for the low-temperature phase of $Mn(tfa)_2 \cdot 4H_2O$. Our attempt to perform a structural investigation of Mn(tfa)₂·4H₂O at 100 K resulted in two interesting findings: (i) a new compound of formula $Mn_3(tfa)_6 \cdot 4H_2O$, which is stable in the 100–298 K temperature

	References	Low Temperature		High Temperature		Transition Temperature	
Mg(tfa) ₂ ·4H ₂ O	This work	$P\overline{1}$, mor	nomeric			160 K	
Mn _x (tfa) _{2x} ·4H ₂ O —	Ref. 19 (x = 1)	not rep	ported C2/c,		nonomeric	215 K	
	This work $(x = 3)$					no transition observed between 100 and 298 K	
Ca ₃ (tfa) ₆ ·4H ₂ O	Ref. 20 Ref. 28		PZ_1/n , trimeric			temperature dependence not investigated	

Scheme 1 Structural relationships in Mg, Mn, and Ca trifluoroacetates. The ability of $Mn_x(tfa)_{2x}$ ·4H₂O compounds to pivot between their magnesium and calcium counterparts is highlighted.

range; and (ii) the observation that this new compound is isostructural to $Ca_3(tfa)_6\cdot 4H_2O$.^{20,28} These findings allowed us to construct a map of structural relationships between Mg(tfa)₂·4H₂O, Mn(tfa)₂·4H₂O, Mn_3(tfa)₆·4H₂O, and Ca₃(tfa)₆·4H₂O (Scheme 1).

The crystal structure of Mn₃(tfa)₆·4H₂O at 100 K is shown in Fig. 4. The structure is monoclinic (space-group $P2_1/n$) and features (i) trimers of manganese-oxygen corner-sharing octahedra, and (ii) layers running parallel to the b axis and the trifluoromethyl groups directed outwards. The central manganese atom is coordinated to six oxygen atoms belonging to carboxylate groups, whereas the terminal manganese atoms are coordinated to four oxygen atoms belonging to carboxylate groups and two oxygen atoms from two water molecules. The two coordinating water molecules are cis positioned. The structure shows severe disorder of: (i) one of the two crystallographically distinct manganese atoms (displaced ~0.15 Å off the center of symmetry), (ii) two trifluoroacetate moieties, (iii) both water molecules, and (iv) -CF₃ groups (rotationally disordered). Details on the fractional occupancies of the manganese, carbon, oxygen and fluorine sites are given in the



Fig. 4 Crystal structure of $Mn_3(tfa)_6 \cdot 4H_2O$ (100 K). Mn: purple; C: brown; O: red; F: light blue; H: pink. Manganese–oxygen octahedra are arranged in trimers (left panel). Layers running parallel to the *b* axis are observed (right panel). The structure remains unchanged in the 100–298 K temperature range. Severe structure disorder was observed; atom splitting is not shown for clarity (see text for details).

ESI (Table S19[†]). The observation of a pseudo-tetragonal unit cell (*i.e.*, *a* and *b* differ by 0.03 Å and β = 90.69°) is likely to be at the origin of the observed structural disorder and crystal twinning. No structural changes were observed via singlecrystal X-ray diffraction in the 100-298 K temperature range. The structure is identical to that of Ca₃(tfa)₆·4H₂O reported by Khristov et al.²⁸ and Dissanayake et al.²⁰ (see ESI, Fig. S11[†]). The observation of a trimeric structure of manganese trifluoroacetate in the 100-298 K temperature range was unexpected considering the monomeric nature of the previously known high-temperature phase of Mn(tfa)₂·4H₂O. These observations were reconciled through Rietveld analysis of powder X-ray diffraction data (see ESI, Fig. S11[†]). The room-temperature X-ray diffraction pattern of polycrystalline Mn_x(tfa)_{2x}·4H₂O could be adequately fit as a mixture of the trimeric (space-group $P2_1/n$) and monomeric (space-group C2/c) phases in weight fractions of ~11 and 89%, respectively. Therefore, two compounds of formula $Mn_x(tfa)_{2x} \cdot 4H_2O$ can be distinguished: the C2/c monomeric tetrahydrate (x = 1) stable above 215 K and originally reported by Olejnik and Lis,¹⁹ and the previously unknown $P2_1/n$ trimeric hydrate (x = 3) stable in the 100–298 K range. Both compounds coexist at room temperature. More important, Mn_x(tfa)_{2x}·4H₂O compounds are isostructural to the hightemperature phase of Mg(tfa)₂·4H₂O (monomeric) on the one hand, and to Ca₃(tfa)₆·4H₂O (trimeric) on the other hand. As will be shown in the next section, the chemical and structural flexibility of $Mn_x(tfa)_{2x} \cdot 4H_2O$ to behave as its magnesium or calcium counterparts constitutes a synthetic principle to direct the preparation of Mg-Mn and Ca-Mn bimetallic trifluoroacetates.

3.4. Crystal structures of Mg–Mn and Ca–Mn bimetallic trifluoroacetates

Crystallization of Mg–Mn and Ca–Mn bimetallic trifluoroacetates was attempted using mixtures containing $Mg^{2+}:Mn^{2+}$ and $Ca^{2+}:Mn^{2+}$ in a 1:1 molar ratio, respectively. The crystal structures of the resulting $Mg_{0.45}Mn_{0.55}(tfa)_2\cdot 4H_2O$ and $Ca_{1.72}Mn_{1.28}(tfa)_6\cdot 4H_2O$ are shown in Fig. 5a and b, respect-



Fig. 5 Crystal structures of (a) $Mg_{0.45}Mn_{0.55}(tfa)_2\cdot 4H_2O$ and (b) $Ca_{1.72}Mn_{1.28}(tfa)_6\cdot 4H_2O$ (100 K). Mg: orange; Mn: purple; Ca: blue; C: brown; O: red; F: light blue; H: pink. Mg^{2+} and Mn^{2+} are nearly equally distributed over the octahedral sites (Mg/Mn: 45/55). Ca^{2+} and Mn^{2+} are unequally distributed over the central (Ca/Mn: 96/4) and terminal (Ca/Mn: 38/62) octahedral sites of the corner-sharing metal-oxygen trimers. $Ca_{1.72}Mn_{1.28}(tfa)_6\cdot 4H_2O$ exhibits structural disorder (see text for details).

ively. $Mg_{0.45}Mn_{0.55}(tfa)_2 \cdot 4H_2O$ is isostructural to the low-temperature phase of $Mg(tfa)_2 \cdot 4H_2O$ (triclinic, PI). Mg^{2+} and Mn^{2+} are nearly equally distributed over the metal–oxygen octahedra (Mg/Mn: 45/55). $Ca_{1.72}Mn_{1.28}(tfa)_6 \cdot 4H_2O$ is isostructural to $Ca_3(tfa)_6 \cdot 4H_2O$ and $Mn_3(tfa)_6 \cdot 4H_2O$ (monoclinic, $P2_1/n$). Metal–oxygen octahedra form corner-sharing trimers, with Ca^{2+} and Mn^{2+} unequally distributed over the central (Ca/Mn: 96/4) and terminal (Ca/Mn: 38/62) sites. As observed in $Mn_3(tfa)_6 \cdot 4H_2O$, the structure exhibits severe disorder. Metal–oxygen bond distances encountered in Mg–Mn and Ca–Mn bimetallic trifluor-oacetates and in their monometallic counterparts are given in Table 6 and plotted in Fig. 6. In the case of $Mg_{0.45}Mn_{0.55}(tfa)_2 \cdot 4H_2O$, the average metal–oxygen bond distance is 2.1298 Å. This is in excellent agreement with the com-



Fig. 6 Metal–oxygen bond distances in monometallic and bimetallic trifluoroacetates. All six distances are given for each octahedral site. Average distances are depicted with hollow symbols. For bimetallic compounds, the composition-weighted average distance for each site is depicted with red symbols.

position-weighted average of bond distances encountered in Mg(tfa)₂·4H₂O and Mn(tfa)₂·4H₂O, which equals 2.1293 Å (2.0683 × 0.45 + 2.1792 × 0.55). In the case of Ca_{1.72}Mn_{1.28}(tfa)₆·4H₂O, the average metal–oxygen bond distance for the central site of the trimer is 2.358 Å. This is in good agreement with the composition-weighted average of distances encountered in Mn₃(tfa)₆·4H₂O and Ca₃(tfa)₆·4H₂O, which equals 2.327 Å (2.195 × 0.04 + 2.332 × 0.96). The close agreement of these two values is consistent with the central site being almost exclusively occupied by Ca²⁺. Bond valence analysis using parameters $R_0 = 1.967$ Å and b = 0.37 gives further support to this finding: a bond valence sum of +2.13 is thus obtained for the central site of the trimer, consistent with

Table 6 Metal-oxygen bond distances (Å) in mono- and bimetallic trifluoroacetates

$Mg(tfa)_2 \cdot 4H_2O^a$	Mg _{0.45} Mn _{0.55} (tfa) ₂ ·4H ₂ O ^a	$Mn(tfa)_2 \cdot 4H_2O^b$	$Mn_3(tfa)_6 \cdot 4H_2O^a$	$Ca_{1.72}Mn_{1.28}(tfa)_{6} \cdot 4H_2O^a$	$Ca_3(tfa)_6 \cdot 4H_2O^c$
<i>P</i> 1, monomeric	<i>C</i> 2/ <i>c</i> , monomeric		$P2_1/n$, trimeric		
$4 H_2O + 2 tfa (trans)$			Central: 6 tfa		
. ,				Ca/Mn: 96/4	
2.0259(18)	2.0949(11)	2.136(4)	2.101(13)	2.264(7)	$2 \times 2.282(4)$
2.0405(18)	2.1053(10)	2.157(3)	2.118(12)	2.273(8)	$2 \times 2.294(4)$
2.0672(18)	2.1314(11)	$2 \times 2.193(2)$	2.125(14)	2.372(7)	$2 \times 2.421(2)$
2.0819(18)	2.1450(10)	$2 \times 2.198(2)$	2.133(13)	2.343(4)	
2.0946(16)	2.1510(10)		2.328(14)	2.447(3)	
2.0995(16)	2.1514(11)		2.362(13)	2.451(3)	
(2.0683)	(2.1298)	$\langle 2.1792 \rangle$	(2.195)	(2.358)	$\langle 2.332 \rangle$
			Terminal: 4 tfa + 2 $H_2O(cis)$		
				Ca/Mn: 38/62	
			2.147(9)	2.1860(13)	2.318(4)
			2.168(16)	2.1888(18)	2.332(4)
			2.182(11)	2.236(8)	2.368(3)
			2.188(18)	2.241(9)	2.379(4)
			2.226(3)	2.2681(11)	2.385(4)
			2.280(3)	2.3231(12)	2.464(3)
			(2.199)	(2.241)	(2.374)

^a Data at 100 K. This work. ^b Data at 220 K. Ref. 19. ^c Data at 298 K. Ref. 20.

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it being near fully occupied by Ca^{2+} ions.²⁹ Likewise, the average metal–oxygen bond distance for the terminal site is 2.241 Å, in good agreement with the composition-weighted average of distances encountered in the parent monometallic compounds, which equals 2.266 Å (2.199 × 0.62 + 2.374 × 0.38). The consistency of these results is quite remarkable, especially in the case of the Ca–Mn bimetallic trifluoroacetate, which features severe structural disorder. This agreement gives further support to site occupancies extracted from single-crystal X-ray diffraction. More important, the successful preparation of Mg–Mn and Ca–Mn bimetallic trifluoroacetates confirms that synthetic principles for the rational design of multimetallic trifluoroacetates can be established through a systematic investigation of the crystal-chemistry of their monometallic counterparts.

4. Conclusions

In conclusion, the synthesis of Mg-Mn and Ca-Mn bimetallic trifluoroacetates was accomplished following a systematic investigation of the crystal-chemistry of $A(tfa)_2 \cdot nH_2O$ (A = Mg, Ca, Sr, Ba, Mn) monometallic trifluoroacetates. Crystallochemical relationships were established between Mg(tfa)₂·4H₂O, $Mn(tfa)_2 \cdot 4H_2O$, $Mn_3(tfa)_6 \cdot 4H_2O$, and $Ca_3(tfa)_6 \cdot 4H_2O$. The evolution with temperature of the crystal structure of Mg(tfa)₂·4H₂O was found to be identical to that of Mn(tfa)₂·4H₂O, with both systems exhibiting a phase transition leading to crystal twinning at 160 and 215 K, respectively. The ability of $Mn_x(tfa)_{2x}$ ·4H₂O to pivot between the structures of the high-temperature phase of Mg(tfa)₂·4H₂O and that of Ca₃(tfa)₆·4H₂O enabled the synthesis of bimetallic trifluoroacetates containing Mg-Mn and Ca-Mn as metal centers. Mg_{0.45}Mn_{0.55}(tfa)₂·4H₂O was found to be isostructural to Mg(tfa)₂·4H₂O, with Mg²⁺ and Mn²⁺ nearly equally distributed over the octahedral sites (Mg/Mn: 45/55). Ca1.72Mn1.28(tfa)6.4H2O was found to be isostructural to $Ca_3(tfa)_6 \cdot 4H_2O$, with Ca^{2+} and Mn^{2+} unequally distributed over the central (Ca/Mn: 96/4) and terminal (Ca/Mn: 38/62) sites of the corner-sharing metal-oxygen trimers. Analysis of metaloxygen bond distances in the bimetallic trifluoroacetates gave further support to site occupancies extracted from single-crystal X-ray diffraction. This work demonstrates that chemical and structural principles enabling the rational design of multimetallic trifluoroacetates can be established through a systematic investigation of the crystal-chemistry of their monometallic counterparts.

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