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Electronic Supplementary Information

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,[1] Natalie A. Mannino,[1] Laura M. Mendoza,[1] K. Tauni Dissanayake,[1]

Philip D. Martin,[1] Leopoldo Suescun,[2] and Federico A. Rabuffetti[1,*]

[1]Department of Chemistry, Wayne State University, Detroit, MI 48202, USA

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

*To whom correspondence should be addressed. Email: far@chem.wayne.edu

Single-Crystal Structures

1. $Mg(tfa)_2 \cdot 4H_2O$ at 100 K

Table S1 Fractional Atomic Coordinates and Isotropic or Equivalent Displacement Parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mg1	0.26844 (11)	0.59719 (9)	0.39021 (9)	0.0120 (2)
O1W	0.3082 (3)	0.7415 (2)	0.2184 (2)	0.0179 (4)
H1	0.275 (4)	0.835 (3)	0.247 (3)	0.027*
H1'	0.280 (4)	0.726 (3)	0.151 (3)	0.027*
O2W	-0.0307 (2)	0.7107 (2)	0.50527 (19)	0.0140 (4)
H2B	-0.083 (3)	0.808 (3)	0.512 (3)	0.021*
H2A	-0.084 (4)	0.677 (3)	0.589 (3)	0.021*
O2W'	0.5641 (2)	0.47703 (19)	0.2891 (2)	0.0140 (4)
H2A'	0.603 (4)	0.392 (3)	0.318 (3)	0.021*
H2B'	0.627 (3)	0.470 (3)	0.190 (3)	0.021*
O3W	0.2423 (3)	0.4455 (2)	0.5576 (2)	0.0153 (4)
H3	0.294 (4)	0.438 (3)	0.613 (3)	0.023*
H3'	0.187 (4)	0.385 (3)	0.567 (3)	0.023*
O1	0.3070 (2)	0.74446 (18)	0.53310 (18)	0.0133 (4)
O2	0.2138 (2)	0.97713 (18)	0.44734 (19)	0.0186 (4)
C1	0.2619 (3)	0.8914 (3)	0.5382 (3)	0.0142 (6)
C2	0.2612 (4)	0.9744 (3)	0.6795 (3)	0.0208 (6)
F1	0.3194 (2)	1.09865 (16)	0.64015 (18)	0.0298 (4)
F2	0.0818 (2)	1.02927 (19)	0.79596 (18)	0.0415 (5)
F3	0.3734 (3)	0.88175 (17)	0.7389 (2)	0.0406 (5)
O1'	0.2219 (2)	0.44631 (18)	0.25627 (18)	0.0138 (4)
O2'	0.2611 (2)	0.55261 (19)	0.02979 (19)	0.0180 (4)
C1'	0.2339 (3)	0.4505 (3)	0.1174 (3)	0.0135 (6)
C2'	0.2082 (4)	0.3067 (3)	0.0556 (3)	0.0197 (6)
F1'	0.2213 (2)	0.31384 (19)	-0.09043 (16)	0.0357 (4)
F2'	0.3402 (2)	0.17348 (17)	0.0537 (2)	0.0390 (5)
F3'	0.0351 (2)	0.29730 (18)	0.14829 (17)	0.0329 (4)

Table S2 Anisotropic Atomic Displacement Parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg1	0.0155 (5)	0.0110 (4)	0.0123 (4)	-0.0054 (3)	-0.0081 (4)	0.0021 (3)
O1W	0.0292 (11)	0.0138 (9)	0.0175 (10)	-0.0096 (8)	-0.0148 (9)	0.0041 (8)
O2W	0.0177 (10)	0.0094 (9)	0.0155 (10)	-0.0048 (8)	-0.0078 (8)	0.0039 (8)
O2W'	0.0179 (10)	0.0134 (10)	0.0112 (9)	-0.0046 (8)	-0.0075 (8)	0.0037 (8)
O3W	0.0215 (11)	0.0168 (10)	0.0183 (10)	-0.0118 (8)	-0.0148 (8)	0.0065 (7)
O1	0.0176 (10)	0.0087 (9)	0.0164 (9)	-0.0048 (7)	-0.0098 (8)	0.0021 (7)
O2	0.0272 (11)	0.0110 (9)	0.0221 (10)	-0.0047 (8)	-0.0163 (8)	0.0028 (8)
C1	0.0085 (14)	0.0161 (15)	0.0175 (14)	-0.0046 (11)	-0.0049 (11)	0.0001 (11)
C2	0.0277 (17)	0.0123 (14)	0.0257 (16)	-0.0048 (12)	-0.0161 (14)	0.0019 (12)
F1	0.0471 (10)	0.0191 (9)	0.0373 (10)	-0.0176 (7)	-0.0266 (8)	0.0021 (7)
F2	0.0404 (11)	0.0504 (12)	0.0231 (9)	-0.0158 (9)	-0.0028 (8)	-0.0144 (8)
F3	0.0754 (13)	0.0183 (9)	0.0519 (11)	-0.0082 (8)	-0.0551 (10)	0.0033 (8)
O1'	0.0179 (10)	0.0152 (9)	0.0113 (9)	-0.0069 (7)	-0.0081 (7)	0.0016 (7)
O2'	0.0274 (11)	0.0165 (10)	0.0134 (9)	-0.0093 (8)	-0.0107 (8)	0.0036 (8)
C1'	0.0078 (14)	0.0152 (14)	0.0154 (14)	-0.0016 (11)	-0.0046 (11)	-0.0026 (11)
C2'	0.0232 (16)	0.0229 (16)	0.0138 (14)	-0.0105 (13)	-0.0067 (12)	0.0005 (11)
F1'	0.0605 (11)	0.0474 (11)	0.0150 (9)	-0.0370 (9)	-0.0171 (8)	0.0028 (7)
F2'	0.0471 (11)	0.0165 (9)	0.0540 (12)	-0.0057 (8)	-0.0257 (9)	-0.0062 (8)
F3'	0.0336 (10)	0.0461 (11)	0.0236 (9)	-0.0298 (8)	-0.0042 (8)	-0.0042 (7)

Table S3 Geometric Parameters (Å, º)

Mg1—O1W	2.0259 (18)	O3W—H3'	0.79 (2)
Mg1—O3W	2.0405 (18)	O1—C1	1.256 (3)
Mg1—O2W'	2.0672 (18)	O2—C1	1.234 (3)
Mg1—O2W	2.0819 (18)	C1—C2	1.537 (3)
Mg1—O1	2.0946 (16)	C2—F3	1.321 (3)
Mg1—O1'	2.0995 (16)	C2—F2	1.331 (3)
O1W—H1	0.82 (2)	C2—F1	1.339 (3)
O1W—H1'	0.79 (2)	O1'—C1'	1.262 (3)
O2W—H2B	0.83 (2)	O2'—C1'	1.228 (3)
O2W—H2A	0.82 (2)	C1'—C2'	1.546 (3)
O2W'—H2A'	0.81 (2)	C2'—F2'	1.322 (3)
O2W'—H2B'	0.84 (2)	C2'—F1'	1.327 (3)
O3W—H3	0.78 (2)	C2'—F3'	1.331 (3)
O1W—Mg1—O3W	177.23 (8)	Mg1—O3W—H3	122.2 (19)
O1W—Mg1—O2W'	89.56 (8)	Mg1—O3W—H3'	123.3 (19)
O3W—Mg1—O2W'	87.69 (8)	H3—O3W—H3'	114 (3)
O1W—Mg1—O2W	94.14 (8)	C1—O1—Mg1	126.12 (15)
O3W—Mg1—O2W	88.62 (8)	O2—C1—O1	128.5 (2)
O2W'—Mg1—O2W	176.20 (8)	O2—C1—C2	116.3 (2)
O1W—Mg1—O1	91.11 (7)	O1—C1—C2	115.1 (2)
O3W—Mg1—O1	89.11 (7)	F3—C2—F2	107.6 (2)
O2W'—Mg1—O1	88.62 (7)	F3—C2—F1	107.1 (2)
O2W—Mg1—O1	90.42 (7)	F2—C2—F1	106.53 (19)
O1W—Mg1—O1'	91.17 (7)	F3—C2—C1	113.5 (2)
O3W—Mg1—O1'	88.67 (7)	F2—C2—C1	110.0 (2)
O2W'—Mg1—O1'	92.60 (7)	F1—C2—C1	111.8 (2)
O2W—Mg1—O1'	88.22 (7)	C1'—O1'—Mg1	129.90 (15)
O1—Mg1—O1'	177.42 (7)	O2'—C1'—O1'	128.4 (2)
Mg1—O1W—H1	117.0 (19)	O2'—C1'—C2'	118.1 (2)
Mg1—O1W—H1'	115.9 (19)	O1'—C1'—C2'	113.5 (2)

H1—O1W—H1'	113 (3)	F2'—C2'—F1'	107.52 (19)
Mg1—O2W—H2B	123.1 (17)	F2'—C2'—F3'	107.3 (2)
Mg1—O2W—H2A	113.8 (18)	F1'—C2'—F3'	107.10 (19)
H2B—O2W—H2A	111 (2)	F2'—C2'—C1'	111.51 (19)
Mg1—O2W'—H2A'	117.9 (18)	F1'—C2'—C1'	112.4 (2)
Mg1—O2W'—H2B'	118.4 (17)	F3'—C2'—C1'	110.80 (19)
H2A'—O2W'—H2B'	109 (2)		
Mg1—O1—C1—O2	-11.7 (4)	Mg1—O1'—C1'—O2'	-6.5 (4)
Mg1—O1—C1—C2	166.26 (15)	Mg1—O1'—C1'—C2'	174.10 (14)
O2—C1—C2—F3	-157.8 (2)	O2'—C1'—C2'—F2'	121.3 (2)
O1—C1—C2—F3	24.0 (3)	O1'—C1'—C2'—F2'	-59.2 (3)
O2—C1—C2—F2	81.7 (3)	O2'—C1'—C2'—F1'	0.5 (3)
O1—C1—C2—F2	-96.5 (2)	O1'—C1'—C2'—F1'	180.0 (2)
O2—C1—C2—F1	-36.5 (3)	O2'—C1'—C2'—F3'	-119.3 (2)
O1—C1—C2—F1	145.3 (2)	O1'—C1'—C2'—F3'	60.2 (3)

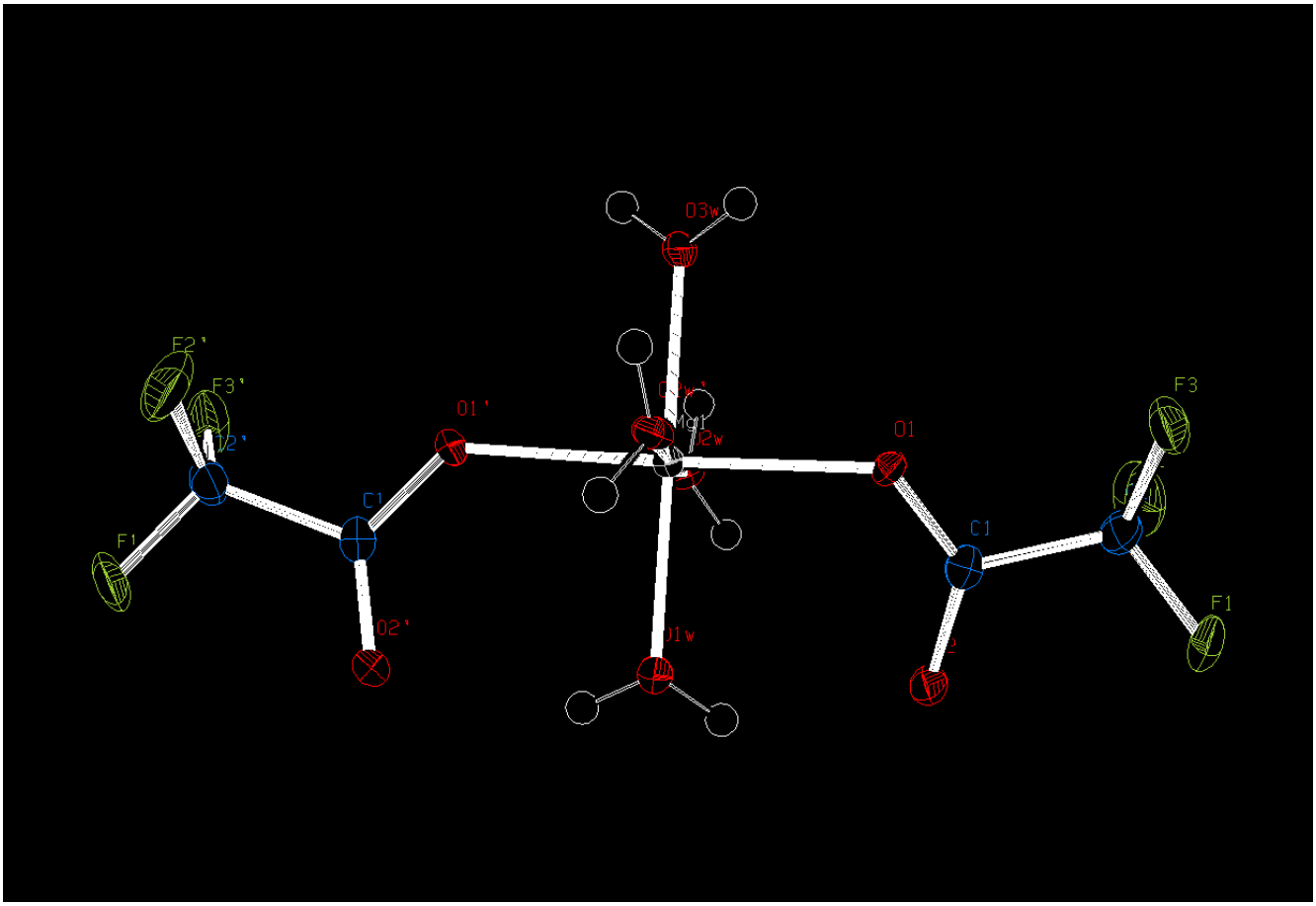

Figure S1. Thermal ellipsoids (50% probability).

2. $Mg(tfa)_2 \cdot 4H_2O$ at 143 K

Table S4 Fractional Atomic Coordinates and Isotropic or Equivalent Displacement Parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mg1	0.26488 (12)	0.59875 (10)	0.39174 (11)	0.0211 (2)
O1W	0.2968 (3)	0.7464 (2)	0.2233 (3)	0.0310 (5)
H1	0.2622	0.8418	0.2485	0.046*
H1'	0.2671	0.7311	0.1533	0.046*
O2W	-0.0324 (3)	0.7101 (2)	0.5063 (2)	0.0239 (4)
H2B	-0.0822	0.8062	0.5112	0.036*
H2A	-0.0824	0.6823	0.5939	0.036*
O2W'	0.5591 (3)	0.4797 (2)	0.2904 (2)	0.0237 (4)
H2A'	0.5941	0.3922	0.3174	0.036*
H2B'	0.6092	0.4696	0.1915	0.036*
O3W	0.2441 (3)	0.4445 (2)	0.5571 (2)	0.0253 (4)
H3	0.2989	0.4342	0.6152	0.038*
H3'	0.1885	0.3821	0.5699	0.038*
O1	0.3044 (3)	0.7443 (2)	0.5354 (2)	0.0241 (4)
O2	0.2135 (3)	0.9783 (2)	0.4501 (3)	0.0313 (5)
C1	0.2614 (4)	0.8903 (3)	0.5405 (3)	0.0242 (6)
C2	0.2645 (5)	0.9710 (4)	0.6823 (4)	0.0347 (7)
F1	0.3172 (4)	1.0960 (3)	0.6452 (3)	0.0526 (6)
F2	0.0891 (4)	1.0222 (4)	0.7988 (3)	0.0723 (8)
F3	0.3810 (5)	0.8773 (3)	0.7366 (4)	0.0702 (9)
O1'	0.2178 (3)	0.4494 (2)	0.2569 (2)	0.0252 (5)
O2'	0.2677 (3)	0.5508 (2)	0.0276 (3)	0.0316 (5)
C1'	0.2351 (4)	0.4522 (3)	0.1171 (3)	0.0246 (6)
C2'	0.2093 (5)	0.3084 (4)	0.0536 (4)	0.0343 (7)
F1'	0.2196 (4)	0.3177 (3)	-0.0905 (3)	0.0616 (7)
F2'	0.3427 (4)	0.1767 (3)	0.0509 (4)	0.0700 (8)
F3'	0.0392 (3)	0.2982 (3)	0.1455 (3)	0.0566 (7)

Table S5 Anisotropic Atomic Displacement Parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg1	0.0203 (5)	0.0205 (5)	0.0226 (5)	-0.0058 (3)	-0.0099 (3)	0.0005 (3)
O1W	0.0438 (12)	0.0255 (11)	0.0293 (12)	-0.0128 (9)	-0.0202 (9)	0.0039 (8)
O2W	0.0234 (10)	0.0206 (10)	0.0267 (11)	-0.0058 (7)	-0.0107 (8)	0.0010 (8)
O2W'	0.0222 (9)	0.0238 (10)	0.0226 (10)	-0.0047 (7)	-0.0093 (7)	0.0002 (8)
O3W	0.0281 (10)	0.0268 (11)	0.0274 (11)	-0.0118 (8)	-0.0162 (8)	0.0055 (8)
O1	0.0256 (10)	0.0203 (10)	0.0271 (11)	-0.0068 (7)	-0.0124 (8)	-0.0004 (8)
O2	0.0384 (12)	0.0204 (10)	0.0369 (13)	-0.0056 (8)	-0.0208 (9)	0.0000 (9)
C1	0.0187 (13)	0.0232 (14)	0.0284 (15)	-0.0056 (10)	-0.0085 (10)	-0.0018 (11)
C2	0.0406 (18)	0.0249 (16)	0.0389 (18)	-0.0045 (12)	-0.0217 (14)	-0.0024 (13)
F1	0.0772 (16)	0.0375 (12)	0.0631 (15)	-0.0272 (11)	-0.0423 (13)	-0.0009 (10)
F2	0.0598 (16)	0.097 (2)	0.0420 (15)	-0.0246 (14)	-0.0029 (11)	-0.0309 (14)
F3	0.119 (2)	0.0327 (12)	0.092 (2)	-0.0090 (12)	-0.0889 (19)	-0.0007 (12)
O1'	0.0248 (10)	0.0275 (11)	0.0241 (11)	-0.0085 (8)	-0.0112 (8)	-0.0006 (8)
O2'	0.0401 (12)	0.0323 (12)	0.0246 (11)	-0.0130 (9)	-0.0152 (9)	0.0009 (9)
C1'	0.0160 (13)	0.0273 (14)	0.0260 (15)	-0.0017 (10)	-0.0084 (10)	-0.0052 (11)
C2'	0.0363 (17)	0.0372 (18)	0.0273 (16)	-0.0147 (13)	-0.0093 (12)	-0.0045 (13)
F1'	0.0997 (19)	0.0787 (18)	0.0290 (12)	-0.0600 (15)	-0.0255 (12)	0.0006 (11)
F2'	0.0779 (18)	0.0309 (12)	0.099 (2)	-0.0039 (11)	-0.0451 (16)	-0.0151 (12)
F3'	0.0539 (13)	0.0745 (17)	0.0452 (13)	-0.0441 (12)	-0.0061 (10)	-0.0124 (11)

Table S6 Geometric Parameters (Å, º)

Mg1—O1W	2.023 (2)	O3W—H3'	0.8119
Mg1—O3W	2.042 (2)	O1—C1	1.251 (3)
Mg1—O2W'	2.077 (2)	O2—C1	1.233 (4)
Mg1—O2W	2.090 (2)	C1—C2	1.547 (4)
Mg1—O1	2.097 (2)	C2—F3	1.309 (4)
Mg1—O1'	2.101 (2)	C2—F1	1.328 (4)
O1W—H1	0.8262	C2—F2	1.329 (4)
O1W—H1'	0.8137	O1'—C1'	1.255 (4)
O2W—H2B	0.8254	O2'—C1'	1.222 (4)
O2W—H2A	0.8247	C1'—C2'	1.559 (4)
O2W'—H2A'	0.8200	C2'—F1'	1.315 (4)
O2W'—H2B'	0.8366	C2'—F2'	1.316 (4)
O3W—H3	0.8179	C2'—F3'	1.331 (4)
O1W—Mg1—O3W	177.70 (9)	Mg1—O3W—H3	122.9
O1W—Mg1—O2W'	89.96 (9)	Mg1—O3W—H3'	125.6
O3W—Mg1—O2W'	87.75 (8)	H3—O3W—H3'	111.4
O1W—Mg1—O2W	93.74 (9)	C1—O1—Mg1	126.60 (19)
O3W—Mg1—O2W	88.55 (8)	O2—C1—O1	128.9 (3)
O2W'—Mg1—O2W	176.25 (9)	O2—C1—C2	115.9 (3)
O1W—Mg1—O1	91.02 (9)	O1—C1—C2	115.1 (3)
O3W—Mg1—O1	89.16 (9)	F3—C2—F1	107.2 (3)
O2W'—Mg1—O1	88.70 (8)	F3—C2—F2	108.4 (3)
O2W—Mg1—O1	90.61 (8)	F1—C2—F2	106.5 (3)
O1W—Mg1—O1'	91.24 (9)	F3—C2—C1	112.9 (3)
O3W—Mg1—O1'	88.62 (8)	F1—C2—C1	111.9 (3)
O2W'—Mg1—O1'	92.48 (8)	F2—C2—C1	109.7 (3)
O2W—Mg1—O1'	88.06 (8)	C1'—O1'—Mg1	129.5 (2)
O1—Mg1—O1'	177.45 (8)	O2'—C1'—O1'	129.0 (3)
Mg1—O1W—H1	120.1	O2'—C1'—C2'	117.4 (3)
Mg1—O1W—H1'	116.1	O1'—C1'—C2'	113.6 (3)

H1—O1W—H1'	110.0	F1'—C2'—F2'	107.6 (3)
Mg1—O2W—H2B	121.2	F1'—C2'—F3'	107.4 (3)
Mg1—O2W—H2A	114.1	F2'—C2'—F3'	108.1 (3)
H2B—O2W—H2A	108.8	F1'—C2'—C1'	112.4 (3)
Mg1—O2W'—H2A'	115.3	F2'—C2'—C1'	110.7 (3)
Mg1—O2W'—H2B'	114.1	F3'—C2'—C1'	110.6 (3)
H2A'—O2W'—H2B'	107.0		
Mg1—O1—C1—O2	-11.4 (4)	Mg1—O1'—C1'—O2'	-7.1 (4)
Mg1—O1—C1—C2	166.92 (19)	Mg1—O1'—C1'—C2'	173.24 (17)
O2—C1—C2—F3	-155.3 (3)	O2'—C1'—C2'—F1'	-2.5 (4)
O1—C1—C2—F3	26.2 (4)	O1'—C1'—C2'—F1'	177.1 (3)
O2—C1—C2—F1	-34.2 (4)	O2'—C1'—C2'—F2'	117.8 (3)
O1—C1—C2—F1	147.2 (3)	O1'—C1'—C2'—F2'	-62.5 (3)
O2—C1—C2—F2	83.8 (4)	O2'—C1'—C2'—F3'	-122.5 (3)
O1—C1—C2—F2	-94.8 (3)	O1'—C1'—C2'—F3'	57.2 (4)

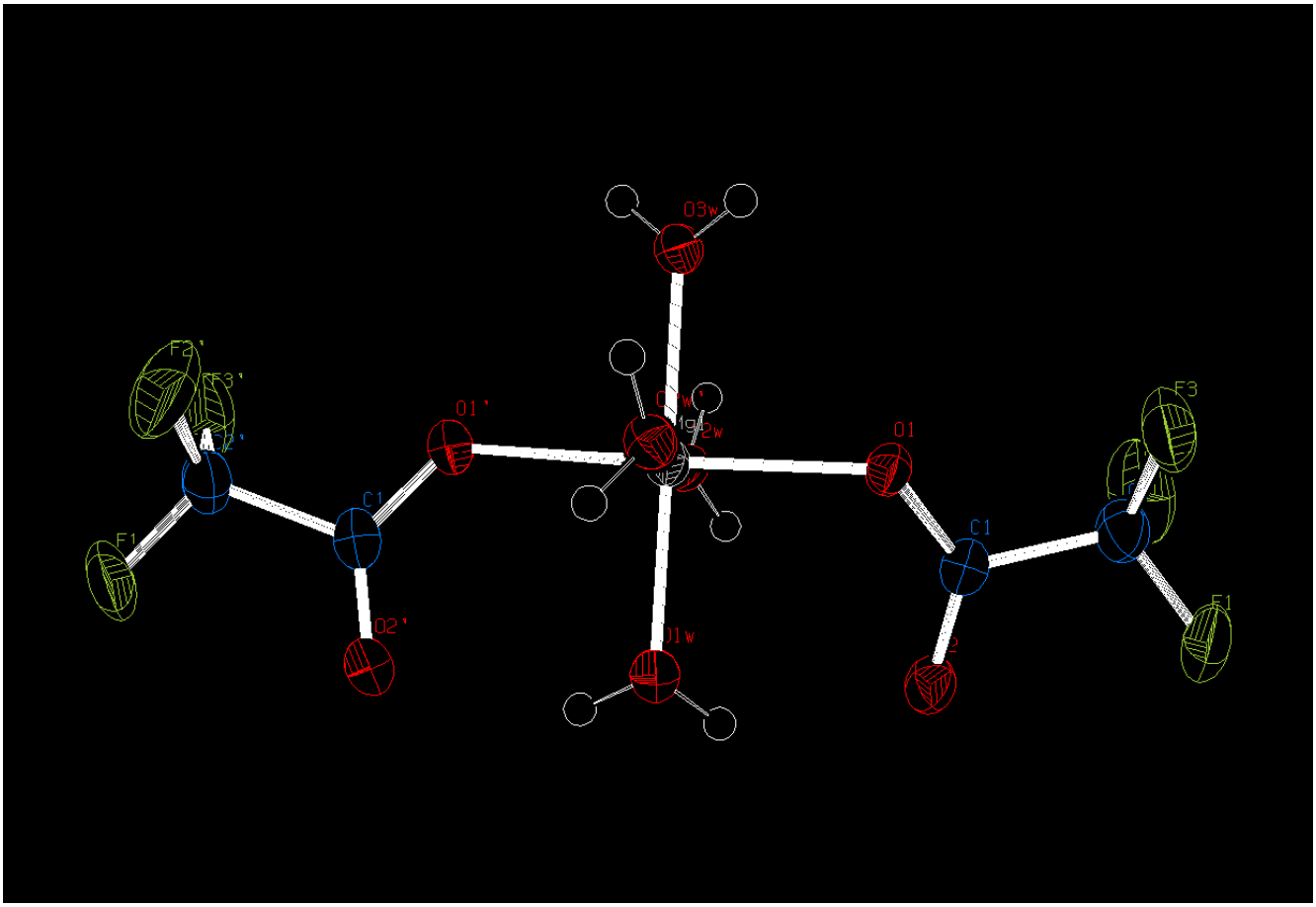

Figure S2. Thermal ellipsoids (50% probability).

3. $Mg(tfa)_2 \cdot 4H_2O$ at 160 K (triclinic)

Table S7 Fractional Atomic Coordinates and Isotropic or Equivalent Displacement Parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Mg1	0.2605 (4)	0.5998 (3)	0.3930 (3)	0.0248 (6)
O1W	0.2829 (10)	0.7498 (6)	0.2290 (6)	0.0411 (16)
H1	0.2484	0.8452	0.2541	0.062*
H1'	0.2532	0.7345	0.1589	0.062*
O2W	-0.0361 (8)	0.7087 (6)	0.5081 (6)	0.0268 (13)
H2B	-0.0860	0.8048	0.5130	0.040*
H2A	-0.0861	0.6810	0.5957	0.040*
O2W'	0.5537 (7)	0.4824 (6)	0.2898 (6)	0.0268 (13)
H2A'	0.5887	0.3948	0.3168	0.040*
H2B'	0.6038	0.4723	0.1910	0.040*
O3W	0.2463 (9)	0.4443 (6)	0.5575 (6)	0.0297 (12)
H3	0.3011	0.4341	0.6157	0.045*
H3'	0.1907	0.3820	0.5703	0.045*
O1	0.2994 (8)	0.7444 (7)	0.5383 (6)	0.0281 (14)
O2	0.2150 (9)	0.9774 (6)	0.4519 (7)	0.0334 (15)
C1	0.2566 (12)	0.8894 (10)	0.5429 (10)	0.028 (2)
C2	0.2671 (16)	0.9667 (11)	0.6846 (13)	0.044 (3)
F1	0.3111 (11)	1.0940 (7)	0.6522 (8)	0.067 (2)
F2	0.0972 (11)	1.0085 (10)	0.8058 (8)	0.098 (3)
F3	0.3912 (12)	0.8725 (7)	0.7324 (9)	0.083 (3)
O1'	0.2142 (8)	0.4515 (6)	0.2574 (7)	0.0287 (14)
O2'	0.2716 (9)	0.5502 (7)	0.0259 (7)	0.0387 (17)
C1'	0.2340 (12)	0.4524 (10)	0.1172 (10)	0.025 (2)
C2'	0.2118 (15)	0.3098 (12)	0.0503 (11)	0.039 (2)
F1'	0.2169 (12)	0.3226 (8)	-0.0914 (7)	0.079 (3)
F2'	0.3495 (12)	0.1821 (8)	0.0436 (11)	0.096 (3)
F3'	0.0482 (10)	0.2975 (8)	0.1422 (7)	0.073 (2)

Table S8 Anisotropic Atomic Displacement Parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg1	0.0337 (13)	0.0197 (17)	0.0237 (18)	-0.0087 (12)	-0.0149 (12)	0.0002 (9)
O1W	0.071 (5)	0.031 (4)	0.033 (4)	-0.024 (3)	-0.028 (3)	0.006 (2)
O2W	0.029 (3)	0.021 (3)	0.031 (4)	-0.008 (2)	-0.014 (2)	-0.001 (2)
O2W'	0.036 (3)	0.022 (3)	0.020 (3)	-0.008 (2)	-0.010 (2)	0.000 (2)
O3W	0.040 (3)	0.027 (4)	0.031 (4)	-0.016 (3)	-0.020 (3)	0.006 (2)
O1	0.038 (3)	0.023 (4)	0.027 (3)	-0.011 (3)	-0.016 (3)	0.000 (3)
O2	0.053 (4)	0.019 (3)	0.034 (4)	-0.011 (3)	-0.025 (3)	0.004 (3)
C1	0.027 (5)	0.026 (6)	0.032 (5)	-0.009 (4)	-0.012 (4)	-0.002 (4)
C2	0.060 (7)	0.017 (5)	0.052 (7)	-0.004 (5)	-0.027 (6)	-0.004 (4)
F1	0.108 (6)	0.048 (4)	0.079 (5)	-0.042 (4)	-0.060 (4)	0.003 (3)
F2	0.086 (6)	0.142 (8)	0.049 (5)	-0.043 (5)	-0.002 (4)	-0.047 (5)
F3	0.141 (6)	0.032 (3)	0.113 (6)	-0.010 (4)	-0.106 (5)	-0.007 (3)
O1'	0.037 (3)	0.028 (4)	0.027 (4)	-0.013 (3)	-0.017 (3)	0.000 (3)
O2'	0.051 (4)	0.047 (5)	0.024 (4)	-0.021 (3)	-0.018 (3)	-0.003 (3)
C1'	0.029 (4)	0.025 (5)	0.018 (5)	-0.008 (4)	-0.006 (4)	-0.001 (4)
C2'	0.050 (6)	0.037 (6)	0.035 (6)	-0.022 (5)	-0.016 (5)	-0.004 (4)
F1'	0.139 (7)	0.102 (6)	0.034 (4)	-0.089 (5)	-0.033 (4)	-0.001 (3)
F2'	0.112 (6)	0.036 (4)	0.152 (7)	0.000 (4)	-0.083 (6)	-0.033 (4)
F3'	0.083 (5)	0.099 (5)	0.059 (4)	-0.069 (4)	-0.015 (4)	-0.013 (4)

Table S9 Geometric Parameters (Å, º)

Mg1—O1W	2.000 (5)	O3W—H3'	0.8214
Mg1—O3W	2.037 (5)	O1—C1	1.238 (10)
Mg1—O2W'	2.065 (6)	O2—C1	1.203 (10)
Mg1—O2W	2.085 (6)	C1—C2	1.555 (12)
Mg1—O1	2.095 (5)	C2—F3	1.289 (12)
Mg1—O1'	2.095 (5)	C2—F1	1.319 (12)
O1W—H1	0.8242	C2—F2	1.331 (13)
O1W—H1'	0.8059	O1'—C1'	1.243 (10)
O2W—H2B	0.8188	O2'—C1'	1.238 (10)
O2W—H2A	0.8285	C1'—C2'	1.553 (11)
O2W'—H2A'	0.8121	C2'—F2'	1.284 (13)
O2W'—H2B'	0.8369	C2'—F1'	1.297 (12)
O3W—H3	0.8064	C2'—F3'	1.313 (12)
O1W—Mg1—O3W	178.3 (3)	Mg1—O3W—H3	122.7
O1W—Mg1—O2W'	89.5 (3)	Mg1—O3W—H3'	125.5
O3W—Mg1—O2W'	88.8 (3)	H3—O3W—H3'	111.7
O1W—Mg1—O2W	94.1 (3)	C1—O1—Mg1	127.0 (6)
O3W—Mg1—O2W	87.6 (3)	O2—C1—O1	129.7 (8)
O2W'—Mg1—O2W	176.4 (2)	O2—C1—C2	115.7 (7)
O1W—Mg1—O1	90.7 (2)	O1—C1—C2	114.5 (8)
O3W—Mg1—O1	89.1 (2)	F3—C2—F1	106.7 (10)
O2W'—Mg1—O1	89.0 (2)	F3—C2—F2	107.1 (10)
O2W—Mg1—O1	90.8 (2)	F1—C2—F2	108.1 (8)
O1W—Mg1—O1'	91.7 (2)	F3—C2—C1	113.1 (7)
O3W—Mg1—O1'	88.5 (2)	F1—C2—C1	112.9 (9)
O2W'—Mg1—O1'	92.3 (2)	F2—C2—C1	108.8 (9)
O2W—Mg1—O1'	87.7 (2)	C1'—O1'—Mg1	129.4 (6)
O1—Mg1—O1'	177.3 (2)	O2'—C1'—O1'	128.3 (7)
Mg1—O1W—H1	120.9	O2'—C1'—C2'	117.1 (7)
Mg1—O1W—H1'	115.6	O1'—C1'—C2'	114.6 (8)

H1—O1W—H1'	110.9	F2'—C2'—F1'	107.2 (8)
Mg1—O2W—H2B	119.4	F2'—C2'—F3'	109.1 (10)
Mg1—O2W—H2A	116.0	F1'—C2'—F3'	108.4 (9)
H2B—O2W—H2A	108.6	F2'—C2'—C1'	109.7 (9)
Mg1—O2W'—H2A'	113.3	F1'—C2'—C1'	112.5 (9)
Mg1—O2W'—H2B'	115.9	F3'—C2'—C1'	110.0 (7)
H2A'—O2W'—H2B'	106.9		
Mg1—O1—C1—O2	-14.0 (14)	Mg1—O1'—C1'—O2'	-6.5 (14)
Mg1—O1—C1—C2	168.9 (6)	Mg1—O1'—C1'—C2'	172.3 (6)
O2—C1—C2—F3	-148.9 (10)	O2'—C1'—C2'—F2'	112.5 (11)
O1—C1—C2—F3	28.7 (14)	O1'—C1'—C2'—F2'	-66.4 (12)
O2—C1—C2—F1	-27.7 (13)	O2'—C1'—C2'—F1'	-6.7 (13)
O1—C1—C2—F1	149.9 (8)	O1'—C1'—C2'—F1'	174.4 (8)
O2—C1—C2—F2	92.3 (11)	O2'—C1'—C2'—F3'	-127.5 (10)
O1—C1—C2—F2	-90.2 (10)	O1'—C1'—C2'—F3'	53.5 (12)

Symmetry codes: (i) -*x*, -*y*+2, -*z*+1; (ii) -*x*, -*y*+1, -*z*+1; (iii) -*x*+1, -*y*+1, -*z*+1; (iv) -*x*+1, -*y*+1, -*z*.

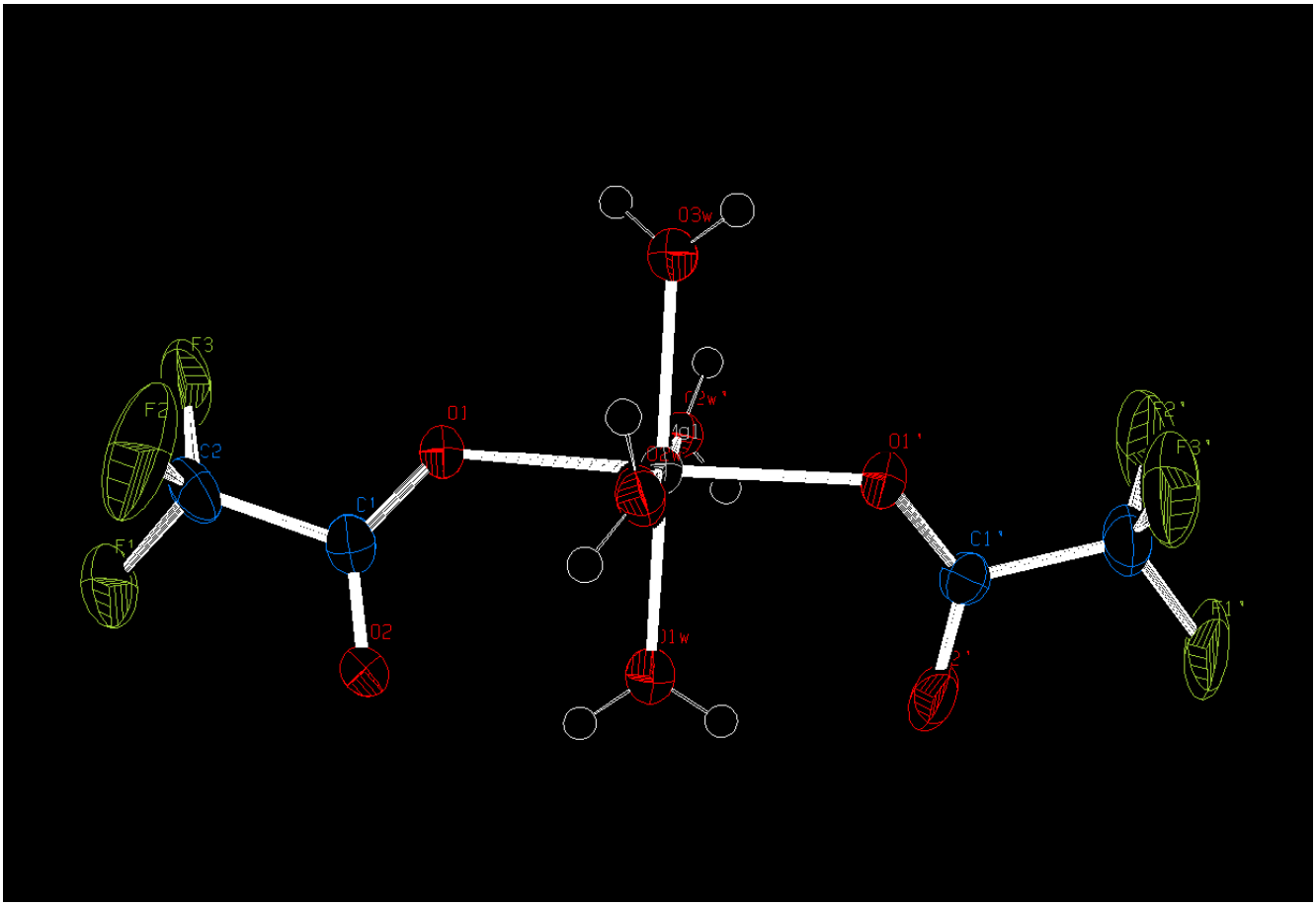

Figure S3. Thermal ellipsoids (50% probability).

4. $Mg(tfa)_2 \cdot 4H_2O$ at 160 K (monoclinic)

Table S10 Fractional Atomic Coordinates and Isotropic or Equivalent Displacement Parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Mg1	0.5000	0.6025 (2)	0.7500	0.0381 (9)	
O1W	0.5000	0.7604 (6)	0.7500	0.083 (4)	
H1	0.4487	0.7991	0.7465	0.125*	
O2W	0.3885 (4)	0.5977 (3)	0.4529 (7)	0.0400 (13)	
H2A	0.3586	0.5393	0.4173	0.060*	
H2B	0.3335	0.6400	0.4081	0.060*	
O3W	0.5000	0.4433 (5)	0.7500	0.0387 (17)	
H3	0.4693	0.4049	0.7938	0.058*	
O1	0.3572 (4)	0.5996 (4)	0.7931 (7)	0.0406 (13)	
O2	0.2863 (4)	0.7630 (4)	0.7208 (9)	0.0520 (16)	
C1	0.2840 (6)	0.6713 (6)	0.7614 (11)	0.0434 (18)	
C2	0.1768 (6)	0.6364 (6)	0.7728 (12)	0.059 (2)	
F1	0.1101 (16)	0.7120 (13)	0.769 (3)	0.083 (5)	0.62 (4)
F2	0.1129 (15)	0.5654 (17)	0.645 (3)	0.098 (5)	0.62 (4)
F3	0.2153 (11)	0.5826 (11)	0.943 (2)	0.068 (4)	0.62 (4)
F1A	0.134 (2)	0.7153 (16)	0.829 (4)	0.058 (5)	0.38 (4)
F2A	0.0891 (15)	0.613 (2)	0.591 (2)	0.071 (5)	0.38 (4)
F3A	0.187 (2)	0.5514 (18)	0.862 (5)	0.087 (7)	0.38 (4)

Table S11 Anisotropic Atomic Displacement Parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg1	0.0226 (14)	0.0311 (16)	0.053 (2)	0.000	0.0139 (14)	0.000
O1W	0.071 (6)	0.030 (4)	0.175 (12)	0.000	0.082 (7)	0.000
O2W	0.022 (2)	0.034 (2)	0.051 (3)	0.0031 (17)	0.010 (2)	0.002 (2)
O3W	0.027 (3)	0.033 (3)	0.047 (4)	0.000	0.013 (3)	0.000
O1	0.025 (2)	0.038 (2)	0.055 (3)	0.0053 (18)	0.018 (2)	0.004 (2)
O2	0.029 (2)	0.040 (3)	0.076 (4)	0.008 (2)	0.018 (2)	0.004 (3)
C1	0.024 (3)	0.045 (4)	0.048 (4)	0.003 (3)	0.009 (3)	-0.001 (3)
C2	0.031 (4)	0.054 (4)	0.076 (6)	0.005 (3)	0.017 (4)	0.008 (4)
F1	0.055 (7)	0.094 (7)	0.110 (11)	0.028 (5)	0.050 (7)	0.020 (6)
F2	0.065 (7)	0.098 (9)	0.126 (9)	-0.040 (6)	0.046 (6)	-0.034 (7)
F3	0.054 (6)	0.064 (6)	0.106 (7)	0.007 (4)	0.056 (5)	0.015 (5)
F1A	0.040 (8)	0.071 (8)	0.069 (10)	0.011 (6)	0.032 (7)	0.018 (6)
F2A	0.039 (7)	0.083 (11)	0.084 (7)	-0.024 (7)	0.025 (5)	0.002 (6)
F3A	0.084 (10)	0.077 (8)	0.105 (11)	0.012 (8)	0.052 (9)	0.020 (8)

Table S12 Geometric Parameters (Å, º)

Mg1—O1W	2.032 (8)	O1—C1	1.265 (8)
Mg1—O3W	2.049 (7)	O2—C1	1.230 (9)
Mg1—O1^{i}	2.094 (5)	C1—C2	1.536 (11)
Mg1—O1	2.094 (5)	C2—F3A	1.281 (15)
Mg1—O2W^{i}	2.098 (5)	C2—F1	1.304 (13)
Mg1—O2W	2.098 (5)	C2—F2	1.315 (12)
O1W—H1	0.8306	C2—F1A	1.354 (16)
O2W—H2A	0.8292	C2—F2A	1.371 (14)
O2W—H2B	0.8302	C2—F3	1.391 (13)
O3W—H3	0.8282		
O1W—Mg1—O3W	180.0	H2A—O2W—H2B	106.5
O1W—Mg1—O1^{i}	91.01 (15)	Mg1—O3W—H3	126.6
O3W—Mg1—O1^{i}	88.99 (15)	C1—O1—Mg1	128.0 (5)
O1W—Mg1—O1	91.01 (15)	O2—C1—O1	129.3 (7)
O3W—Mg1—O1	88.99 (15)	O2—C1—C2	116.6 (6)
O1^{i}—Mg1—O1	178.0 (3)	O1—C1—C2	114.2 (6)
O1W—Mg1—O2W^{i}	91.70 (15)	F1—C2—F2	110.1 (11)
O3W—Mg1—O2W^{i}	88.30 (15)	F3A—C2—F1A	112.9 (17)
O1^{i}—Mg1—O2W^{i}	91.72 (19)	F3A—C2—F2A	102.2 (14)
O1—Mg1—O2W^{i}	88.22 (19)	F1A—C2—F2A	105.2 (13)
O1W—Mg1—O2W	91.70 (15)	F1—C2—F3	107.1 (11)
O3W—Mg1—O2W	88.30 (15)	F2—C2—F3	101.6 (10)
O1^{i}—Mg1—O2W	88.22 (19)	F3A—C2—C1	116.7 (12)
O1—Mg1—O2W	91.72 (19)	F1—C2—C1	114.6 (11)
O2W^{i}—Mg1—O2W	176.6 (3)	F2—C2—C1	113.4 (10)
Mg1—O1W—H1	126.8	F1A—C2—C1	111.3 (12)
Mg1—O2W—H2A	111.1	F2A—C2—C1	107.3 (10)
Mg1—O2W—H2B	115.5	F3—C2—C1	109.0 (7)
Mg1—O1—C1—O2	-10.0 (12)	O1—C1—C2—F2	-62.2 (16)

Mg1—O1—C1—C2	168.9 (5)	O2—C1—C2—F1A	-30.6 (16)
O2—C1—C2—F3A	-162 (2)	O1—C1—C2—F1A	150.4 (14)
O1—C1—C2—F3A	19 (2)	O2—C1—C2—F2A	84.0 (15)
O2—C1—C2—F1	-10.8 (16)	O1—C1—C2—F2A	-95.1 (15)
O1—C1—C2—F1	170.1 (13)	O2—C1—C2—F3	-130.8 (11)
O2—C1—C2—F2	116.8 (16)	O1—C1—C2—F3	50.1 (12)

Symmetry code: (i) -*x*+1, *y*, -*z*+3/2.

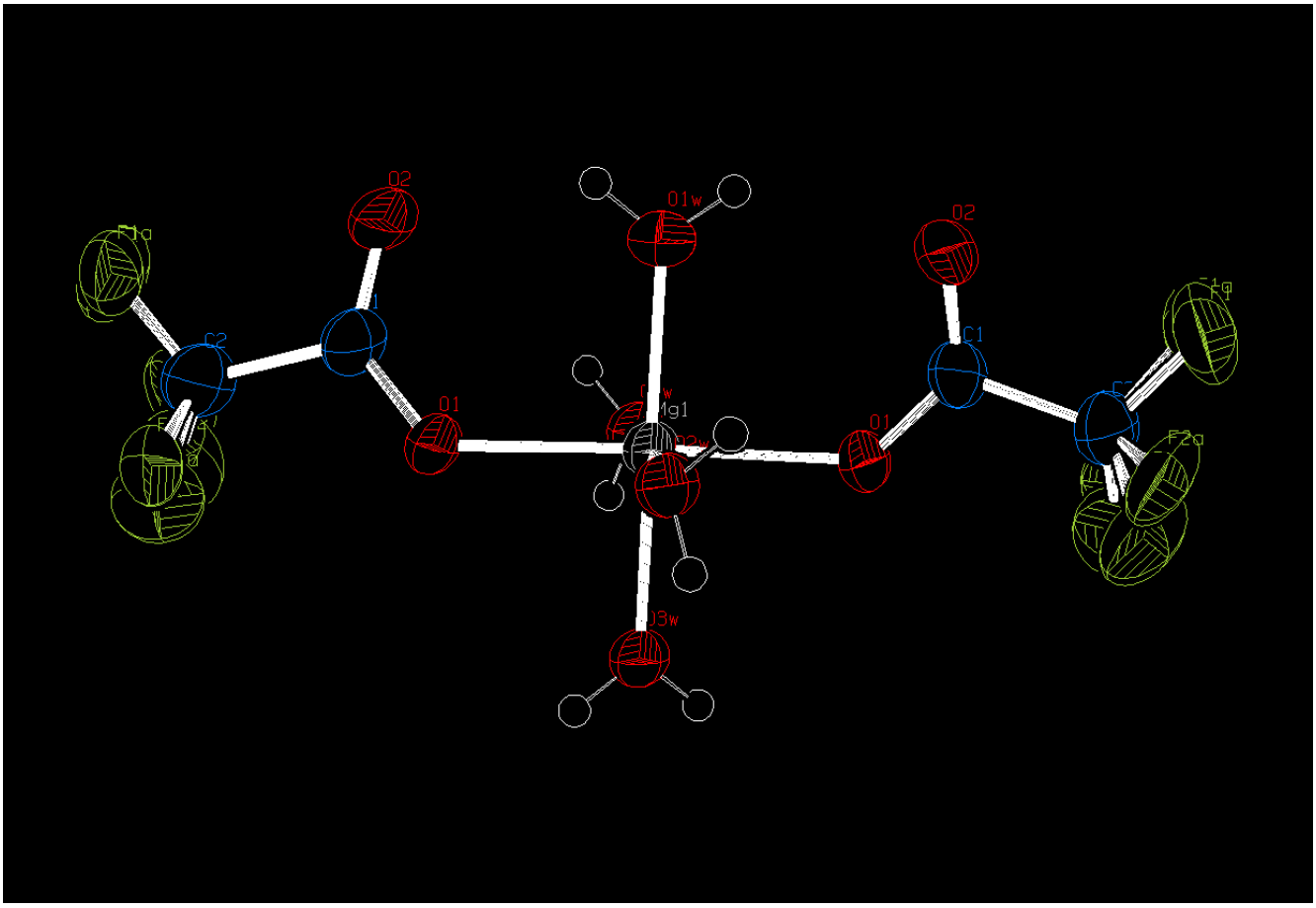

Figure S4. Thermal ellipsoids (50% probability).

5. $Mg(tfa)_2 \cdot 4H_2O$ at 200 K

Table S13 Fractional Atomic Coordinates and Isotropic or Equivalent Displacement Parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Mg1	0.5000	0.60300 (7)	0.7500	0.0293 (3)	
O1W	0.5000	0.76098 (17)	0.7500	0.0510 (7)	
H1	0.4486	0.7932	0.7447	0.076*	
O2W	0.38926 (12)	0.59818 (10)	0.4568 (2)	0.0334 (4)	
H2A	0.3758	0.5373	0.4430	0.050*	
H2B	0.3477	0.6473	0.4126	0.050*	
O3W	0.5000	0.44311 (15)	0.7500	0.0349 (5)	
H3	0.5202	0.4092	0.6921	0.052*	
O1	0.35689 (13)	0.59960 (10)	0.7929 (2)	0.0339 (4)	
O2	0.28465 (14)	0.76170 (12)	0.7179 (3)	0.0451 (5)	
C1	0.28340 (17)	0.66990 (17)	0.7602 (3)	0.0339 (5)	
C2	0.1772 (2)	0.6337 (2)	0.7759 (4)	0.0495 (6)	
F1	0.1228 (6)	0.7156 (4)	0.8007 (13)	0.0686 (16)	0.688 (17)
F2	0.1016 (5)	0.5845 (7)	0.6206 (9)	0.089 (2)	0.688 (17)
F3	0.2089 (5)	0.5729 (6)	0.9238 (11)	0.073 (2)	0.688 (17)
F1A	0.0911 (12)	0.6984 (13)	0.708 (3)	0.064 (4)	0.205 (14)
F2A	0.2139 (19)	0.615 (2)	0.9589 (19)	0.080 (5)	0.205 (14)
F3A	0.1361 (18)	0.5413 (14)	0.692 (4)	0.077 (5)	0.205 (14)
F1B	0.0803 (15)	0.640 (2)	0.606 (2)	0.055 (5)	0.108 (9)
F2B	0.155 (3)	0.693 (3)	0.885 (5)	0.086 (8)	0.108 (9)
F3B	0.1782 (16)	0.5332 (14)	0.821 (4)	0.055 (5)	0.108 (9)

Table S14 Anisotropic Atomic Displacement Parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg1	0.0265 (5)	0.0282 (5)	0.0320 (5)	0.000	0.0138 (4)	0.000
O1W	0.0479 (14)	0.0303 (11)	0.087 (2)	0.000	0.0436 (14)	0.000
O2W	0.0302 (8)	0.0309 (7)	0.0339 (8)	0.0042 (5)	0.0126 (6)	0.0025 (5)
O3W	0.0410 (11)	0.0297 (10)	0.0382 (11)	0.000	0.0232 (9)	0.000
O1	0.0284 (8)	0.0360 (8)	0.0376 (8)	0.0031 (5)	0.0171 (6)	0.0022 (6)
O2	0.0384 (9)	0.0420 (9)	0.0566 (11)	0.0099 (6)	0.0254 (8)	0.0092 (7)
C1	0.0275 (9)	0.0436 (11)	0.0282 (9)	0.0033 (8)	0.0124 (7)	0.0000 (8)
C2	0.0362 (12)	0.0551 (14)	0.0593 (15)	0.0092 (10)	0.0258 (11)	0.0134 (11)
F1	0.057 (3)	0.076 (2)	0.098 (4)	0.0299 (19)	0.057 (3)	0.028 (2)
F2	0.046 (2)	0.100 (5)	0.104 (3)	-0.030 (3)	0.027 (2)	-0.013 (3)
F3	0.066 (3)	0.079 (4)	0.102 (4)	0.027 (3)	0.063 (3)	0.046 (3)
F1A	0.040 (5)	0.080 (7)	0.081 (9)	0.012 (5)	0.037 (6)	0.019 (7)
F2A	0.098 (8)	0.099 (11)	0.060 (5)	0.001 (7)	0.052 (5)	0.018 (5)
F3A	0.061 (8)	0.078 (7)	0.101 (10)	-0.024 (5)	0.047 (7)	-0.024 (7)
F1B	0.036 (7)	0.054 (10)	0.051 (7)	-0.015 (7)	0.005 (5)	0.008 (6)
F2B	0.087 (13)	0.110 (13)	0.086 (11)	0.000 (9)	0.062 (10)	-0.017 (9)
F3B	0.032 (7)	0.068 (7)	0.066 (11)	0.005 (6)	0.026 (7)	0.020 (7)

Table S15 Geometric Parameters (Å, º)

Mg1—O1W	2.020 (2)	O2—C1	1.226 (3)
Mg1—O3W	2.044 (2)	C1—C2	1.548 (3)
Mg1—O2W	2.0842 (15)	C2—F1A	1.285 (11)
Mg1—O2W^{i}	2.0842 (15)	C2—F2	1.312 (5)
Mg1—O1	2.0987 (14)	C2—F3	1.315 (5)
Mg1—O1^{i}	2.0987 (14)	C2—F2B	1.316 (16)
Mg1—H2A	2.3526	C2—F1B	1.332 (13)
O1W—H1	0.7781	C2—F3A	1.336 (11)
O2W—H2A	0.7939	C2—F3B	1.336 (14)
O2W—H2B	0.7914	C2—F2A	1.343 (13)
O3W—H3	0.7836	C2—F1	1.346 (5)
O1—C1	1.251 (2)		
O1W—Mg1—O3W	180.0	H2A—O2W—H2B	131.2
O1W—Mg1—O2W	91.70 (4)	Mg1—O3W—H3	123.6
O3W—Mg1—O2W	88.30 (4)	C1—O1—Mg1	128.44 (14)
O1W—Mg1—O2W^{i}	91.70 (4)	O2—C1—O1	128.9 (2)
O3W—Mg1—O2W^{i}	88.30 (4)	O2—C1—C2	117.0 (2)
O2W—Mg1—O2W^{i}	176.61 (9)	O1—C1—C2	114.2 (2)
O1W—Mg1—O1	91.19 (4)	F2—C2—F3	109.9 (4)
O3W—Mg1—O1	88.81 (4)	F2B—C2—F1B	104.1 (15)
O2W—Mg1—O1	91.45 (6)	F1A—C2—F3A	107.9 (10)
O2W^{i}—Mg1—O1	88.48 (6)	F2B—C2—F3B	109.9 (15)
O1W—Mg1—O1^{i}	91.19 (4)	F1B—C2—F3B	102.5 (11)
O3W—Mg1—O1^{i}	88.81 (4)	F1A—C2—F2A	109.6 (10)
O2W—Mg1—O1^{i}	88.48 (6)	F3A—C2—F2A	103.7 (10)
O2W^{i}—Mg1—O1^{i}	91.45 (6)	F2—C2—F1	108.4 (3)
O1—Mg1—O1^{i}	177.62 (8)	F3—C2—F1	105.4 (3)
O1W—Mg1—H2A	110.9	F1A—C2—C1	114.7 (7)
O3W—Mg1—H2A	69.1	F2—C2—C1	110.0 (3)
O2W—Mg1—H2A	19.4	F3—C2—C1	112.0 (3)

$O2W^{i}$—Mg1—H2A	157.2	F2B—C2—C1	114.2 (12)
O1—Mg1—H2A	88.3	F1B—C2—C1	109.3 (9)
$O1^{i}$—Mg1—H2A	90.8	F3A—C2—C1	111.8 (7)
Mg1—O1W—H1	121.9	F3B—C2—C1	115.5 (8)
Mg1—O2W—H2A	99.7	F2A—C2—C1	108.6 (9)
Mg1—O2W—H2B	115.0	F1—C2—C1	111.1 (3)
Mg1—O1—C1—O2	-10.0 (3)	O2—C1—C2—F1B	64.8 (13)
Mg1—O1—C1—C2	169.79 (15)	O1—C1—C2—F1B	-115.0 (13)
O2—C1—C2—F1A	12.5 (12)	O2—C1—C2—F3A	135.8 (14)
O1—C1—C2—F1A	-167.3 (12)	O1—C1—C2—F3A	-44.1 (14)
O2—C1—C2—F2	99.8 (6)	O2—C1—C2—F3B	179.7 (16)
O1—C1—C2—F2	-80.0 (5)	O1—C1—C2—F3B	-0.2 (16)
O2—C1—C2—F3	-137.7 (5)	O2—C1—C2—F2A	-110.5 (12)
O1—C1—C2—F3	42.4 (5)	O1—C1—C2—F2A	69.7 (12)
O2—C1—C2—F2B	-51 (2)	O2—C1—C2—F1	-20.2 (5)
O1—C1—C2—F2B	129 (2)	O1—C1—C2—F1	160.0 (4)

Symmetry code: (i) -*x*+1, *y*, -*z*+3/2.

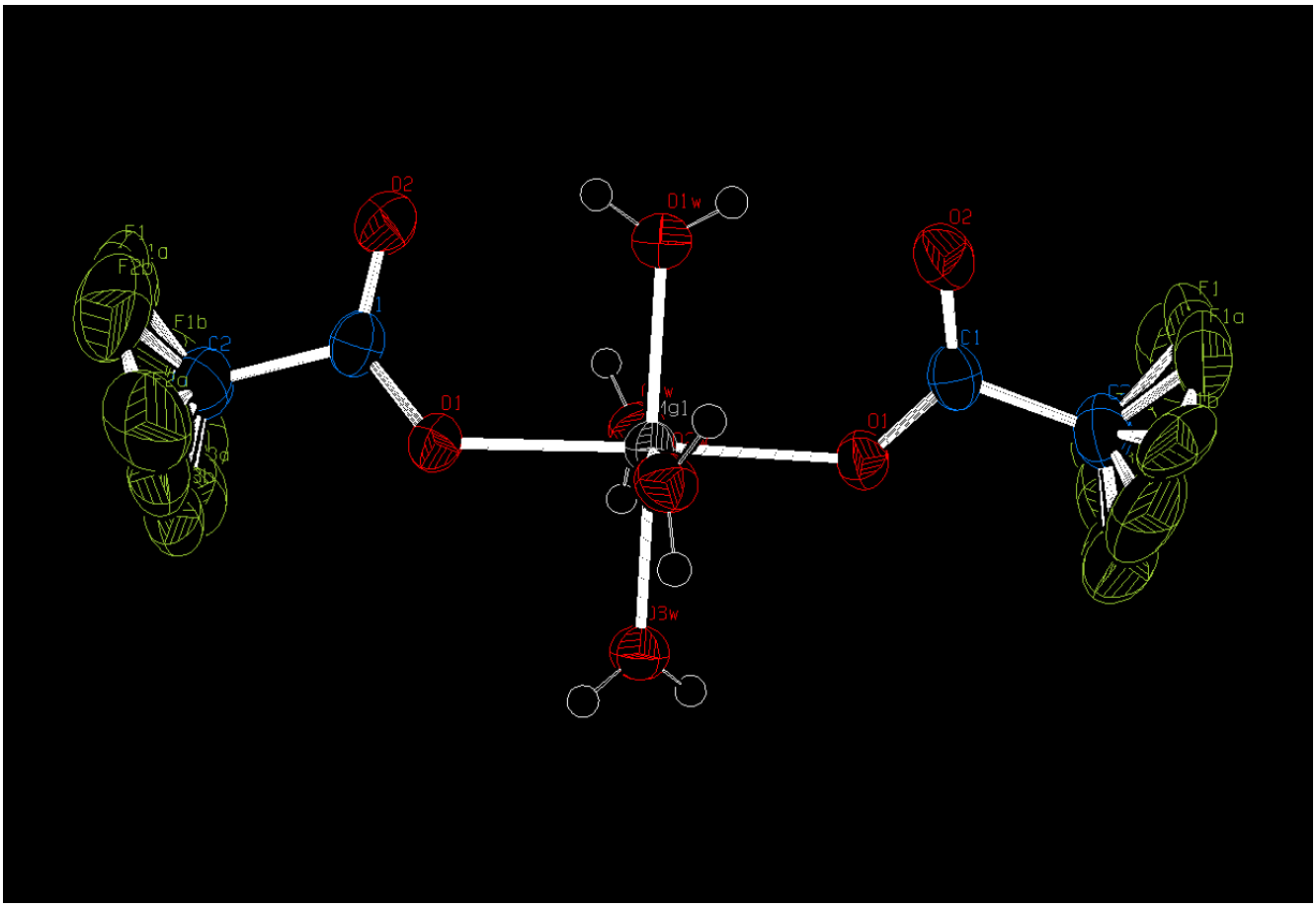

Figure S5. Thermal ellipsoids (50% probability).

6. $Mg(tfa)_2 \cdot 4H_2O$ at 300 K

Table S16 Fractional Atomic Coordinates and Isotropic or Equivalent Displacement Parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Mg1	0.5000	0.60404 (3)	0.7500	0.03179 (15)	
O1W	0.5000	0.76438 (9)	0.7500	0.0574 (3)	
H1	0.4445	0.7985	0.7448	0.086*	
O2W	0.39192 (6)	0.59973 (5)	0.46705 (10)	0.03848 (19)	
H2A	0.3648	0.5400	0.4249	0.058*	
H2B	0.3447	0.6488	0.4153	0.058*	
O3W	0.5000	0.44119 (8)	0.7500	0.0414 (3)	
H3	0.5252	0.4058	0.6938	0.062*	
O1	0.35844 (6)	0.59883 (5)	0.79884 (11)	0.0401 (2)	
O2	0.28049 (7)	0.75922 (7)	0.70991 (14)	0.0576 (3)	
C1	0.28211 (8)	0.66778 (9)	0.75993 (14)	0.0398 (2)	
C2	0.17672 (12)	0.63029 (13)	0.7767 (2)	0.0640 (4)	
F1	0.1259 (5)	0.7150 (3)	0.8122 (11)	0.0847 (14)	0.533 (11)
F2	0.1018 (4)	0.5850 (6)	0.6201 (9)	0.1192 (19)	0.533 (11)
F3	0.2014 (5)	0.5654 (5)	0.9080 (12)	0.100 (2)	0.533 (11)
F1A	0.0920 (5)	0.6945 (6)	0.7110 (18)	0.080 (3)	0.302 (11)
F2A	0.1384 (9)	0.5376 (8)	0.6998 (17)	0.099 (3)	0.302 (11)
F3A	0.2180 (10)	0.6064 (10)	0.9613 (11)	0.097 (3)	0.302 (11)
F1B	0.1642 (13)	0.6695 (17)	0.906 (2)	0.115 (5)	0.165 (7)
F2B	0.0796 (7)	0.6452 (12)	0.6172 (14)	0.075 (3)	0.165 (7)
F3B	0.1728 (9)	0.5229 (8)	0.801 (2)	0.075 (3)	0.165 (7)

Table S17 Anisotropic Atomic Displacement Parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg1	0.0283 (2)	0.0278 (2)	0.0433 (3)	0.000	0.0205 (2)	0.000
O1W	0.0529 (7)	0.0314 (5)	0.0999 (10)	0.000	0.0464 (7)	0.000
O2W	0.0338 (4)	0.0333 (4)	0.0459 (4)	0.0056 (3)	0.0173 (3)	0.0014 (3)
O3W	0.0505 (6)	0.0297 (5)	0.0576 (6)	0.000	0.0369 (5)	0.000
O1	0.0322 (4)	0.0395 (4)	0.0554 (4)	0.0064 (3)	0.0265 (3)	0.0052 (3)
O2	0.0461 (5)	0.0503 (5)	0.0849 (6)	0.0179 (4)	0.0383 (5)	0.0190 (4)
C1	0.0316 (5)	0.0479 (6)	0.0441 (5)	0.0080 (4)	0.0215 (4)	0.0031 (4)
C2	0.0447 (7)	0.0690 (9)	0.0929 (10)	0.0148 (6)	0.0448 (7)	0.0209 (8)
F1	0.071 (2)	0.0893 (17)	0.132 (4)	0.0351 (16)	0.079 (3)	0.028 (2)
F2	0.064 (2)	0.124 (4)	0.147 (3)	-0.040 (3)	0.033 (2)	-0.007 (3)
F3	0.084 (3)	0.106 (4)	0.151 (5)	0.031 (3)	0.091 (3)	0.064 (4)
F1A	0.041 (3)	0.097 (4)	0.119 (6)	0.024 (2)	0.053 (3)	0.025 (4)
F2A	0.069 (5)	0.111 (5)	0.125 (6)	-0.035 (4)	0.054 (4)	-0.014 (4)
F3A	0.108 (4)	0.125 (7)	0.094 (3)	0.008 (4)	0.078 (3)	0.026 (3)
F1B	0.123 (7)	0.160 (10)	0.121 (7)	0.000 (6)	0.106 (6)	-0.015 (6)
F2B	0.040 (3)	0.093 (7)	0.080 (5)	-0.005 (4)	0.019 (3)	0.009 (4)
F3B	0.049 (4)	0.087 (5)	0.103 (7)	-0.001 (3)	0.048 (5)	0.023 (5)

Table S18 Geometric Parameters (Å, º)

Mg1—O1W	2.0212 (12)	O2—C1	1.2221 (14)
Mg1—O3W	2.0530 (11)	C1—C2	1.5384 (16)
Mg1—O2W^{i}	2.0816 (7)	C2—F1B	1.262 (7)
Mg1—O2W	2.0816 (7)	C2—F1A	1.272 (5)
Mg1—O1	2.0969 (7)	C2—F3	1.274 (5)
Mg1—O1^{i}	2.0969 (7)	C2—F2A	1.311 (7)
O1W—H1	0.8321	C2—F2	1.325 (5)
O2W—H2A	0.8352	C2—F2B	1.341 (8)
O2W—H2B	0.8355	C2—F1	1.367 (4)
O3W—H3	0.8239	C2—F3B	1.372 (10)
O1—C1	1.2496 (12)	C2—F3A	1.392 (8)
O1W—Mg1—O3W	180.0	O2—C1—O1	128.59 (10)
O1W—Mg1—O2W^{i}	91.50 (2)	O2—C1—C2	116.90 (10)
O3W—Mg1—O2W^{i}	88.50 (2)	O1—C1—C2	114.51 (10)
O1W—Mg1—O2W	91.50 (2)	F1A—C2—F2A	107.8 (4)
O3W—Mg1—O2W	88.50 (2)	F3—C2—F2	109.0 (3)
O2W^{i}—Mg1—O2W	177.01 (4)	F1B—C2—F2B	109.3 (8)
O1W—Mg1—O1	91.80 (2)	F3—C2—F1	105.4 (3)
O3W—Mg1—O1	88.20 (2)	F2—C2—F1	109.7 (3)
O2W^{i}—Mg1—O1	88.26 (3)	F1B—C2—F3B	103.4 (8)
O2W—Mg1—O1	91.64 (3)	F2B—C2—F3B	101.3 (6)
O1W—Mg1—O1^{i}	91.80 (2)	F1A—C2—F3A	114.0 (5)
O3W—Mg1—O1^{i}	88.20 (2)	F2A—C2—F3A	101.4 (5)
O2W^{i}—Mg1—O1^{i}	91.64 (3)	F1B—C2—C1	116.9 (5)
O2W—Mg1—O1^{i}	88.26 (3)	F1A—C2—C1	114.4 (3)
O1—Mg1—O1^{i}	176.41 (4)	F3—C2—C1	114.0 (2)
Mg1—O1W—H1	121.1	F2A—C2—C1	112.5 (3)
Mg1—O2W—H2A	114.8	F2—C2—C1	108.8 (2)
Mg1—O2W—H2B	119.8	F2B—C2—C1	110.1 (4)
H2A—O2W—H2B	112.9	F1—C2—C1	109.8 (2)

Mg1—O3W—H3	122.8	F3B—C2—C1	114.5 (4)
C1—O1—Mg1	127.68 (7)	F3A—C2—C1	106.0 (5)
Mg1—O1—C1—O2	-11.70 (18)	O2—C1—C2—F2	93.0 (4)
Mg1—O1—C1—C2	167.71 (9)	O1—C1—C2—F2	-86.5 (4)
O2—C1—C2—F1B	-70.0 (13)	O2—C1—C2—F2B	55.4 (8)
O1—C1—C2—F1B	110.5 (13)	O1—C1—C2—F2B	-124.1 (8)
O2—C1—C2—F1A	9.6 (7)	O2—C1—C2—F1	-27.1 (4)
O1—C1—C2—F1A	-169.9 (7)	O1—C1—C2—F1	153.4 (4)
O2—C1—C2—F3	-145.1 (5)	O2—C1—C2—F3B	168.8 (8)
O1—C1—C2—F3	35.4 (5)	O1—C1—C2—F3B	-10.6 (8)
O2—C1—C2—F2A	133.1 (7)	O2—C1—C2—F3A	-116.9 (6)
O1—C1—C2—F2A	-46.4 (7)	O1—C1—C2—F3A	63.6 (6)

Symmetry code: (i) -*x*+1, *y*, -*z*+3/2.

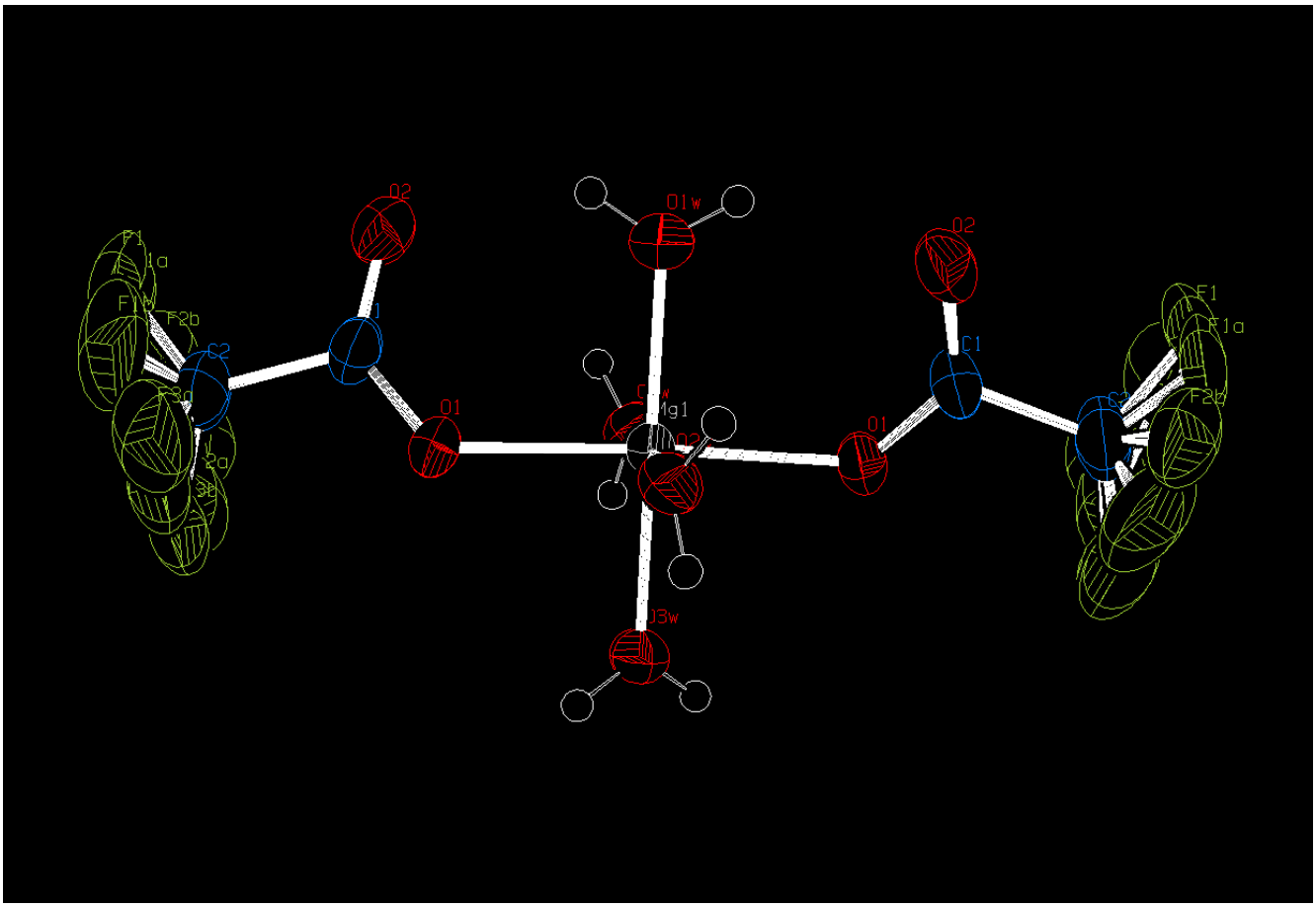

Figure S6. Thermal ellipsoids (50% probability).

7. $Mn_3(tfa)_6 \cdot 4H_2O$ at 100 K

Table S19 Fractional Atomic Coordinates and Isotropic or Equivalent Displacement Parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Mn1	0.70458 (8)	0.44189 (6)	0.29357 (3)	0.00863 (14)	
Mn2	0.5179 (9)	0.4968 (14)	0.5061 (7)	0.0163 (10)	0.5
O1A	0.4164 (8)	0.3488 (8)	0.4183 (5)	0.0183 (11)	0.513 (8)
O2A	0.5043 (12)	0.3073 (14)	0.2845 (6)	0.0118 (12)	0.513 (8)
C1A	0.4120 (11)	0.2989 (13)	0.3454 (6)	0.0183 (14)	0.513 (8)
C2A	0.2649 (15)	0.2294 (16)	0.3117 (9)	0.0280 (12)	0.513 (8)
F1A	0.2391 (9)	0.1015 (8)	0.3535 (6)	0.0280 (17)	0.513 (8)
F2A	0.1472 (11)	0.3105 (12)	0.3234 (7)	0.046 (2)	0.513 (8)
F3A	0.2702 (11)	0.1742 (13)	0.2302 (6)	0.037 (2)	0.513 (8)
O1AA	0.3657 (9)	0.3884 (9)	0.3976 (5)	0.0183 (11)	0.487 (8)
O2AA	0.5136 (12)	0.2970 (15)	0.2999 (6)	0.0118 (12)	0.487 (8)
C1AA	0.3900 (12)	0.3143 (14)	0.3333 (7)	0.0183 (14)	0.487 (8)
C2AA	0.2579 (16)	0.2156 (16)	0.3094 (9)	0.0280 (12)	0.487 (8)
F1AA	0.2137 (14)	0.1315 (13)	0.3736 (7)	0.052 (3)	0.487 (8)
F2AA	0.2821 (14)	0.1284 (12)	0.2463 (7)	0.044 (3)	0.487 (8)
F3AA	0.1450 (12)	0.3048 (11)	0.2889 (6)	0.041 (2)	0.487 (8)
O1B	0.7240 (10)	0.3889 (9)	0.5133 (5)	0.0238 (14)	0.551 (8)
O2B	0.8156 (16)	0.305 (3)	0.3886 (8)	0.0125 (17)	0.551 (8)
C1B	0.8037 (18)	0.311 (3)	0.4672 (8)	0.0267 (14)	0.551 (8)
C2B	0.9332 (14)	0.2305 (14)	0.5142 (7)	0.0361 (19)	0.551 (8)
F1B	0.9046 (10)	0.2034 (10)	0.5930 (5)	0.0356 (19)	0.551 (8)
F2B	0.9716 (9)	0.1051 (9)	0.4775 (5)	0.047 (2)	0.551 (8)
F3B	1.0524 (9)	0.3150 (9)	0.5148 (5)	0.049 (2)	0.551 (8)
O1BA	0.6670 (12)	0.3586 (12)	0.5045 (7)	0.0238 (14)	0.449 (8)
O2BA	0.789 (2)	0.299 (3)	0.3903 (10)	0.0125 (17)	0.449 (8)
C1BA	0.780 (2)	0.318 (3)	0.4683 (10)	0.0267 (14)	0.449 (8)
C2BA	0.9142 (16)	0.2674 (16)	0.5225 (9)	0.0361 (19)	0.449 (8)
F1BA	1.0162 (9)	0.1931 (12)	0.4773 (5)	0.040 (2)	0.449 (8)
F2BA	0.9965 (13)	0.3785 (12)	0.5499 (7)	0.065 (3)	0.449 (8)

F3BA	0.8639 (13)	0.1740 (14)	0.5839 (7)	0.046 (3)	0.449 (8)
O1C	0.7900 (5)	0.2707 (3)	0.2061 (2)	0.0198 (6)	
O2C	0.8865 (5)	0.1122 (3)	0.1149 (2)	0.0192 (6)	
C1C	0.8580 (7)	0.2401 (4)	0.1419 (3)	0.0156 (6)	
C2C	0.9141 (6)	0.3710 (4)	0.0887 (3)	0.0160 (7)	
F1C	0.8311 (7)	0.4901 (6)	0.0968 (4)	0.0252 (15)	0.505 (7)
F2C	1.0477 (7)	0.3972 (7)	0.1162 (4)	0.0282 (16)	0.505 (7)
F3C	0.9204 (7)	0.3389 (7)	0.0059 (3)	0.0255 (15)	0.505 (7)
F1CA	0.9458 (7)	0.4946 (6)	0.1356 (4)	0.0207 (14)	0.495 (7)
F2CA	1.0375 (7)	0.3455 (7)	0.0452 (4)	0.0245 (15)	0.495 (7)
F3CA	0.8086 (7)	0.4096 (7)	0.0366 (4)	0.0238 (15)	0.495 (7)
O1W	0.9137 (9)	0.5520 (11)	0.3106 (6)	0.0132 (12)	0.529 (11)
H1WA	0.982 (5)	0.522 (7)	0.342 (6)	0.020*	0.529 (11)
H1WB	0.941 (6)	0.625 (8)	0.284 (6)	0.020*	0.529 (11)
O2W	0.6067 (14)	0.543 (2)	0.1826 (8)	0.016 (2)	0.529 (11)
H2WA	0.652 (6)	0.601 (10)	0.152 (4)	0.024*	0.529 (11)
H2WB	0.530 (8)	0.515 (10)	0.160 (5)	0.024*	0.529 (11)
O1WA	0.9247 (11)	0.5283 (11)	0.2776 (7)	0.0132 (12)	0.471 (11)
H1WC	0.943 (4)	0.616 (5)	0.265 (8)	0.020*	0.471 (11)
H1WD	0.999 (3)	0.498 (9)	0.304 (6)	0.020*	0.471 (11)
O2WA	0.5689 (17)	0.548 (3)	0.2019 (11)	0.016 (2)	0.471 (11)
H2WC	0.580 (9)	0.630 (6)	0.180 (6)	0.024*	0.471 (11)
H2WD	0.548 (13)	0.496 (9)	0.150 (5)	0.024*	0.471 (11)

Table S20 Anisotropic Atomic Displacement Parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.0113 (3)	0.0078 (2)	0.0068 (3)	0.0009 (3)	0.00171 (18)	-0.0006 (2)
Mn2	0.032 (4)	0.0075 (9)	0.010 (3)	-0.002 (3)	0.0116 (19)	-0.0019 (16)
O1A	0.014 (3)	0.018 (3)	0.024 (3)	-0.001 (2)	0.004 (2)	0.001 (2)
O2A	0.0115 (14)	0.0105 (15)	0.013 (2)	-0.0003 (11)	-0.0006 (14)	0.0003 (15)
C1A	0.0181 (18)	0.0161 (19)	0.0206 (19)	-0.0010 (14)	0.0027 (13)	0.0022 (14)
C2A	0.019 (2)	0.024 (3)	0.041 (3)	-0.0063 (18)	0.0059 (19)	0.003 (2)
F1A	0.023 (3)	0.015 (2)	0.046 (3)	-0.007 (2)	0.005 (3)	0.000 (2)
F2A	0.037 (3)	0.042 (4)	0.057 (4)	0.009 (3)	0.000 (3)	0.007 (3)
F3A	0.026 (3)	0.048 (4)	0.037 (3)	-0.016 (3)	0.002 (2)	0.002 (3)
O1AA	0.014 (3)	0.018 (3)	0.024 (3)	-0.001 (2)	0.004 (2)	0.001 (2)
O2AA	0.0115 (14)	0.0105 (15)	0.013 (2)	-0.0003 (11)	-0.0006 (14)	0.0003 (15)
C1AA	0.0181 (18)	0.0161 (19)	0.0206 (19)	-0.0010 (14)	0.0027 (13)	0.0022 (14)
C2AA	0.019 (2)	0.024 (3)	0.041 (3)	-0.0063 (18)	0.0059 (19)	0.003 (2)
F1AA	0.052 (5)	0.054 (5)	0.050 (4)	-0.020 (3)	0.003 (3)	0.010 (3)
F2AA	0.037 (4)	0.036 (4)	0.060 (4)	-0.003 (3)	0.000 (3)	-0.012 (3)
F3AA	0.048 (3)	0.035 (3)	0.042 (4)	0.009 (3)	-0.009 (3)	-0.007 (3)
O1B	0.033 (4)	0.025 (4)	0.013 (2)	-0.007 (3)	-0.001 (3)	0.002 (2)
O2B	0.016 (4)	0.012 (2)	0.0098 (13)	-0.005 (4)	-0.004 (2)	0.0024 (12)
C1B	0.046 (4)	0.021 (3)	0.0128 (19)	0.002 (3)	-0.002 (2)	0.0080 (17)
C2B	0.055 (4)	0.040 (4)	0.013 (3)	0.010 (3)	-0.008 (2)	0.005 (3)
F1B	0.047 (4)	0.041 (3)	0.018 (3)	-0.008 (3)	-0.014 (2)	0.012 (2)
F2B	0.056 (4)	0.044 (3)	0.040 (3)	0.020 (3)	-0.022 (3)	0.001 (3)
F3B	0.051 (3)	0.054 (3)	0.043 (3)	0.002 (3)	-0.011 (3)	0.008 (3)
O1BA	0.033 (4)	0.025 (4)	0.013 (2)	-0.007 (3)	-0.001 (3)	0.002 (2)
O2BA	0.016 (4)	0.012 (2)	0.0098 (13)	-0.005 (4)	-0.004 (2)	0.0024 (12)
C1BA	0.046 (4)	0.021 (3)	0.0128 (19)	0.002 (3)	-0.002 (2)	0.0080 (17)
C2BA	0.055 (4)	0.040 (4)	0.013 (3)	0.010 (3)	-0.008 (2)	0.005 (3)
F1BA	0.034 (3)	0.050 (4)	0.037 (3)	0.006 (3)	-0.006 (3)	0.007 (3)
F2BA	0.073 (4)	0.054 (4)	0.067 (4)	0.000 (3)	-0.017 (3)	-0.001 (3)
F3BA	0.050 (5)	0.052 (4)	0.036 (4)	0.003 (3)	-0.010 (3)	0.019 (3)

O1C	0.035 (2)	0.0097 (13)	0.0154 (17)	0.0040 (15)	0.0152 (13)	0.0019 (12)
O2C	0.035 (2)	0.0074 (11)	0.0158 (17)	0.0056 (14)	0.0155 (13)	0.0025 (11)
C1C	0.022 (2)	0.0079 (14)	0.017 (2)	0.0026 (16)	0.0089 (16)	0.0044 (15)
C2C	0.025 (2)	0.0091 (16)	0.0147 (19)	0.0013 (17)	0.0106 (14)	0.0015 (14)
F1C	0.033 (2)	0.017 (2)	0.025 (2)	0.0058 (16)	0.0106 (17)	0.0043 (16)
F2C	0.028 (2)	0.027 (2)	0.031 (2)	-0.0067 (16)	0.0064 (16)	0.0010 (17)
F3C	0.039 (2)	0.020 (2)	0.018 (2)	-0.0004 (17)	0.0090 (16)	0.0030 (16)
F1CA	0.029 (2)	0.0143 (19)	0.019 (2)	-0.0055 (16)	0.0089 (16)	-0.0001 (16)
F2CA	0.027 (2)	0.020 (2)	0.027 (2)	0.0004 (16)	0.0166 (16)	0.0007 (17)
F3CA	0.028 (2)	0.022 (2)	0.021 (2)	0.0003 (16)	-0.0022 (16)	0.0074 (16)
O1W	0.014 (2)	0.011 (3)	0.015 (4)	-0.0008 (19)	0.000 (3)	0.003 (3)
O2W	0.012 (6)	0.0134 (19)	0.021 (6)	-0.007 (5)	-0.006 (3)	0.008 (4)
O1WA	0.014 (2)	0.011 (3)	0.015 (4)	-0.0008 (19)	0.000 (3)	0.003 (3)
O2WA	0.012 (6)	0.0134 (19)	0.021 (6)	-0.007 (5)	-0.006 (3)	0.008 (4)

Table S21 Geometric Parameters (Å, º)

Mn1—O2WA	2.121 (19)	O1B—C1B	1.249 (12)
Mn1—O2BA	2.14 (2)	O1B—Mn2^{ii}	2.431 (12)
Mn1—O1W	2.147 (9)	O2B—C1B	1.258 (11)
Mn1—O1WA	2.152 (10)	C1B—C2B	1.562 (11)
Mn1—O2AA	2.167 (12)	C2B—F1B	1.306 (12)
Mn1—O2W	2.168 (16)	C2B—F3B	1.319 (14)
Mn1—O2A	2.182 (11)	C2B—F2B	1.324 (12)
Mn1—O2B	2.188 (18)	O1BA—C1BA	1.230 (13)
Mn1—O1C	2.226 (3)	O1BA—Mn2^{ii}	2.125 (14)
Mn1—O2C^{i}	2.280 (3)	O2BA—C1BA	1.258 (13)
Mn2—Mn2^{ii}	0.380 (10)	C1BA—C2BA	1.549 (13)
Mn2—O1BA	1.836 (15)	C2BA—F2BA	1.320 (15)
Mn2—O1A^{ii}	1.930 (13)	C2BA—F1BA	1.352 (14)
Mn2—O1B	2.101 (13)	C2BA—F3BA	1.374 (15)
Mn2—O1AA^{ii}	2.118 (12)	O1C—C1C	1.230 (4)
Mn2—O1BA^{ii}	2.125 (14)	O2C—C1C	1.262 (5)
Mn2—O1A	2.133 (13)	O2C—Mn1^{iv}	2.280 (3)
Mn2—O2C^{iii}	2.328 (14)	O2C—Mn2^{v}	2.328 (14)
Mn2—O2C^{i}	2.362 (13)	O2C—Mn2^{iv}	2.362 (13)
Mn2—O1AA	2.402 (12)	C1C—C2C	1.544 (5)
Mn2—O1B^{ii}	2.431 (12)	C2C—F2C	1.299 (8)
O1A—C1A	1.246 (10)	C2C—F3CA	1.302 (8)
O1A—Mn2^{ii}	1.930 (13)	C2C—F1C	1.318 (7)
O2A—C1A	1.287 (11)	C2C—F2CA	1.338 (7)
C1A—C2A	1.558 (11)	C2C—F3C	1.352 (7)
C2A—F2A	1.305 (16)	C2C—F1CA	1.372 (7)
C2A—F1A	1.355 (12)	O1W—H1WA	0.83 (2)
C2A—F3A	1.390 (14)	O1W—H1WB	0.82 (2)
O1AA—C1AA	1.246 (11)	O2W—H2WA	0.83 (2)
O1AA—Mn2^{ii}	2.118 (12)	O2W—H2WB	0.82 (2)
O2AA—C1AA	1.250 (11)	O1WA—H1WC	0.83 (2)

C1AA—C2AA	1.533 (12)	O1WA—H1WD	0.83 (2)
C2AA—F2AA	1.298 (15)	O2WA—H2WC	0.827 (17)
C2AA—F3AA	1.337 (15)	O2WA—H2WD	0.96 (7)
C2AA—F1AA	1.338 (13)		
O2WA—Mn1—O1WA	106.3 (5)	O1AA—C1AA—O2AA	125.6 (10)
O1W—Mn1—O2W	104.8 (5)	O1AA—C1AA—C2AA	111.9 (10)
O2WA—Mn1—O1C	94.9 (6)	O2AA—C1AA—C2AA	121.1 (11)
O2BA—Mn1—O1C	84.6 (6)	F2AA—C2AA—F3AA	108.2 (11)
O1W—Mn1—O1C	95.2 (3)	F2AA—C2AA—F1AA	107.5 (12)
O1WA—Mn1—O1C	81.5 (3)	F3AA—C2AA—F1AA	107.2 (13)
O2AA—Mn1—O1C	83.7 (3)	F2AA—C2AA—C1AA	114.1 (12)
O2W—Mn1—O1C	85.7 (4)	F3AA—C2AA—C1AA	107.3 (11)
O2A—Mn1—O1C	82.1 (3)	F1AA—C2AA—C1AA	112.3 (11)
O2B—Mn1—O1C	83.1 (5)	C1B—O1B—Mn2	138.1 (9)
O2WA—Mn1—O2C^{i}	85.7 (5)	C1B—O1B—Mn2^{ii}	133.3 (8)
O2BA—Mn1—O2C^{i}	94.4 (6)	C1B—O2B—Mn1	128.1 (14)
O1W—Mn1—O2C^{i}	85.9 (3)	O1B—C1B—O2B	131.8 (14)
O1WA—Mn1—O2C^{i}	99.8 (3)	O1B—C1B—C2B	114.4 (10)
O2AA—Mn1—O2C^{i}	94.9 (3)	O2B—C1B—C2B	112.5 (11)
O2W—Mn1—O2C^{i}	95.1 (4)	F1B—C2B—F3B	105.8 (10)
O2A—Mn1—O2C^{i}	96.6 (3)	F1B—C2B—F2B	108.6 (10)
O2B—Mn1—O2C^{i}	96.1 (5)	F3B—C2B—F2B	106.4 (10)
O1C—Mn1—O2C^{i}	178.38 (10)	F1B—C2B—C1B	113.1 (10)
Mn2^{ii}—Mn2—O1BA	136 (4)	F3B—C2B—C1B	109.7 (12)
Mn2^{ii}—Mn2—O1A^{ii}	118 (4)	F2B—C2B—C1B	112.8 (11)
Mn2^{ii}—Mn2—O1B	148 (4)	C1BA—O1BA—Mn2	145.0 (14)
Mn2^{ii}—Mn2—O1AA^{ii}	135 (4)	C1BA—O1BA—Mn2^{ii}	143.0 (12)
Mn2^{ii}—Mn2—O1BA^{ii}	37 (4)	C1BA—O2BA—Mn1	126.7 (19)
O1BA—Mn2—O1BA^{ii}	172.8 (6)	O1BA—C1BA—O2BA	124.7 (14)
Mn2^{ii}—Mn2—O1A	53 (4)	O1BA—C1BA—C2BA	118.3 (12)
O1A^{ii}—Mn2—O1A	170.9 (5)	O2BA—C1BA—C2BA	116.6 (13)
Mn2^{ii}—Mn2—O2C^{iii}	91 (4)	F2BA—C2BA—F1BA	99.8 (12)

O1BA—Mn2—O2C^{iii}	95.9 (6)	F2BA—C2BA—F3BA	114.9 (12)
O1A^{ii}—Mn2—O2C^{iii}	89.9 (5)	F1BA—C2BA—F3BA	107.8 (12)
O1B—Mn2—O2C^{iii}	102.8 (5)	F2BA—C2BA—C1BA	113.2 (15)
O1AA^{ii}—Mn2—O2C^{iii}	85.5 (5)	F1BA—C2BA—C1BA	112.6 (11)
O1BA^{ii}—Mn2—O2C^{iii}	85.0 (5)	F3BA—C2BA—C1BA	108.3 (15)
O1A—Mn2—O2C^{iii}	90.2 (5)	C1C—O1C—Mn1	148.9 (3)
Mn2^{ii}—Mn2—O2C^{i}	80 (4)	C1C—O2C—Mn1^{iv}	109.0 (2)
O1BA—Mn2—O2C^{i}	90.8 (6)	C1C—O2C—Mn2^{v}	138.5 (4)
O1A^{ii}—Mn2—O2C^{i}	94.4 (6)	C1C—O2C—Mn2^{iv}	139.5 (4)
O1B—Mn2—O2C^{i}	85.3 (5)	O1C—C1C—O2C	126.5 (3)
O1AA^{ii}—Mn2—O2C^{i}	101.0 (5)	O1C—C1C—C2C	116.9 (3)
O1BA^{ii}—Mn2—O2C^{i}	87.5 (5)	O2C—C1C—C2C	116.5 (3)
O1A—Mn2—O2C^{i}	84.3 (5)	F2C—C2C—F1C	110.1 (5)
O2C^{iii}—Mn2—O2C^{i}	170.7 (3)	F3CA—C2C—F2CA	108.8 (5)
Mn2^{ii}—Mn2—O1AA	39 (4)	F2C—C2C—F3C	108.5 (5)
O1AA^{ii}—Mn2—O1AA	173.6 (6)	F1C—C2C—F3C	107.5 (5)
O2C^{iii}—Mn2—O1AA	94.0 (4)	F3CA—C2C—F1CA	105.9 (5)
O2C^{i}—Mn2—O1AA	78.8 (4)	F2CA—C2C—F1CA	104.7 (5)
Mn2^{ii}—Mn2—O1B^{ii}	28 (4)	F2C—C2C—C1C	105.3 (5)
O1B—Mn2—O1B^{ii}	175.2 (6)	F3CA—C2C—C1C	108.2 (5)
O2C^{iii}—Mn2—O1B^{ii}	79.1 (4)	F1C—C2C—C1C	112.5 (4)
O2C^{i}—Mn2—O1B^{ii}	92.5 (4)	F2CA—C2C—C1C	115.6 (4)
C1A—O1A—Mn2^{ii}	148.0 (8)	F3C—C2C—C1C	112.8 (4)
C1A—O1A—Mn2	147.8 (8)	F1CA—C2C—C1C	113.2 (4)
C1A—O2A—Mn1	121.7 (8)	Mn1—O1W—H1WA	125 (3)
O1A—C1A—O2A	131.8 (10)	Mn1—O1W—H1WB	126 (3)
O1A—C1A—C2A	119.0 (9)	H1WA—O1W—H1WB	110 (4)
O2A—C1A—C2A	108.7 (9)	Mn1—O2W—H2WA	123 (3)
F2A—C2A—F1A	105.3 (11)	Mn1—O2W—H2WB	124 (3)
F2A—C2A—F3A	111.8 (11)	H2WA—O2W—H2WB	111 (4)
F1A—C2A—F3A	99.2 (10)	Mn1—O1WA—H1WC	124 (3)
F2A—C2A—C1A	114.5 (11)	Mn1—O1WA—H1WD	124 (3)
F1A—C2A—C1A	109.0 (10)	H1WC—O1WA—H1WD	106 (4)

F3A—C2A—C1A	115.3 (11)	Mn1—O2WA—H2WC	129 (4)
C1AA—O1AA—Mn2^{ii}	140.2 (8)	Mn1—O2WA—H2WD	118 (4)
C1AA—O1AA—Mn2	134.9 (7)	H2WC—O2WA—H2WD	96 (6)
C1AA—O2AA—Mn1	131.1 (10)		
Mn2^{ii}—O1A—C1A—O2A	32 (2)	O2C^{iii}—Mn2—O1BA—C1BA	175 (2)
Mn2—O1A—C1A—O2A	15 (3)	O2C^{i}—Mn2—O1BA—C1BA	2 (3)
Mn2^{ii}—O1A—C1A—C2A	-138.8 (13)	O2C^{iii}—Mn2—O1BA—Mn2^{ii}	97 (6)
Mn2—O1A—C1A—C2A	-156.0 (12)	O2C^{i}—Mn2—O1BA—Mn2^{ii}	-77 (6)
Mn1—O2A—C1A—O1A	-6 (2)	Mn2—O1BA—C1BA—O2BA	-50 (5)
Mn1—O2A—C1A—C2A	165.6 (8)	Mn2^{ii}—O1BA—C1BA—O2BA	-39 (5)
O1A—C1A—C2A—F2A	49.1 (16)	Mn2—O1BA—C1BA—C2BA	137.8 (16)
O2A—C1A—C2A—F2A	-123.5 (13)	Mn2^{ii}—O1BA—C1BA—C2BA	149.5 (14)
O1A—C1A—C2A—F1A	-68.6 (16)	Mn1—O2BA—C1BA—O1BA	44 (5)
O2A—C1A—C2A—F1A	118.8 (13)	Mn1—O2BA—C1BA—C2BA	-143.9 (17)
O1A—C1A—C2A—F3A	-179.0 (11)	O1BA—C1BA—C2BA—F2BA	-83 (3)
O2A—C1A—C2A—F3A	8.3 (16)	O2BA—C1BA—C2BA—F2BA	105 (3)
Mn2^{ii}—O1AA—C1AA—O2AA	-8 (2)	O1BA—C1BA—C2BA—F1BA	165 (2)
Mn2—O1AA—C1AA—O2AA	-13 (2)	O2BA—C1BA—C2BA—F1BA	-7 (3)
Mn2^{ii}—O1AA—C1AA—C2AA	159.0 (11)	O1BA—C1BA—C2BA—F3BA	46 (3)
Mn2—O1AA—C1AA—C2AA	153.5 (9)	O2BA—C1BA—C2BA—F3BA	-126 (3)
Mn1—O2AA—C1AA—O1AA	-31 (2)	Mn1—O1C—C1C—O2C	177.2 (5)
Mn1—O2AA—C1AA—C2AA	162.8 (9)	Mn1—O1C—C1C—C2C	-2.9 (13)
O1AA—C1AA—C2AA—F2AA	-175.3 (12)	Mn1^{iv}—O2C—C1C—O1C	-1.2 (9)
O2AA—C1AA—C2AA—F2AA	-7.7 (19)	Mn2^{v}—O2C—C1C—O1C	-175.3 (5)
O1AA—C1AA—C2AA—F3AA	64.8 (14)	Mn2^{iv}—O2C—C1C—O1C	170.6 (5)
O2AA—C1AA—C2AA—F3AA	-127.6 (14)	Mn1^{iv}—O2C—C1C—C2C	178.9 (4)
O1AA—C1AA—C2AA—F1AA	-52.7 (17)	Mn2^{v}—O2C—C1C—C2C	4.8 (10)
O2AA—C1AA—C2AA—F1AA	114.9 (15)	Mn2^{iv}—O2C—C1C—C2C	-9.3 (11)
Mn2—O1B—C1B—O2B	27 (4)	O1C—C1C—C2C—F2C	92.0 (7)
Mn2^{ii}—O1B—C1B—O2B	28 (4)	O2C—C1C—C2C—F2C	-88.1 (7)
Mn2—O1B—C1B—C2B	-166.6 (11)	O1C—C1C—C2C—F3CA	-87.3 (7)
Mn2^{ii}—O1B—C1B—C2B	-165.6 (10)	O2C—C1C—C2C—F3CA	92.6 (7)

Mn1—O2B—C1B—O1B	4 (4)	O1C—C1C—C2C—F1C	-28.0 (9)
Mn1—O2B—C1B—C2B	-162.6 (13)	O2C—C1C—C2C—F1C	151.9 (6)
O1B—C1B—C2B—F1B	27 (2)	O1C—C1C—C2C—F2CA	150.5 (6)
O2B—C1B—C2B—F1B	-163.7 (19)	O2C—C1C—C2C—F2CA	-29.6 (9)
O1B—C1B—C2B—F3B	-90 (2)	O1C—C1C—C2C—F3C	-149.8 (6)
O2B—C1B—C2B—F3B	78 (2)	O2C—C1C—C2C—F3C	30.1 (8)
O1B—C1B—C2B—F2B	151.2 (17)	O1C—C1C—C2C—F1CA	29.8 (9)
O2B—C1B—C2B—F2B	-40 (3)	O2C—C1C—C2C—F1CA	-150.3 (6)
Mn2^{ii}—Mn2—O1BA—C1BA	79 (7)		

Symmetry codes: (i) -*x*+3/2, *y*+1/2, -*z*+1/2; (ii) -*x*+1, -*y*+1, -*z*+1; (iii) *x*-1/2, -*y*+1/2, *z*+1/2; (iv) -*x*+3/2, *y*-1/2, -*z*+1/2; (v) *x*+1/2, -*y*+1/2, *z*-1/2.

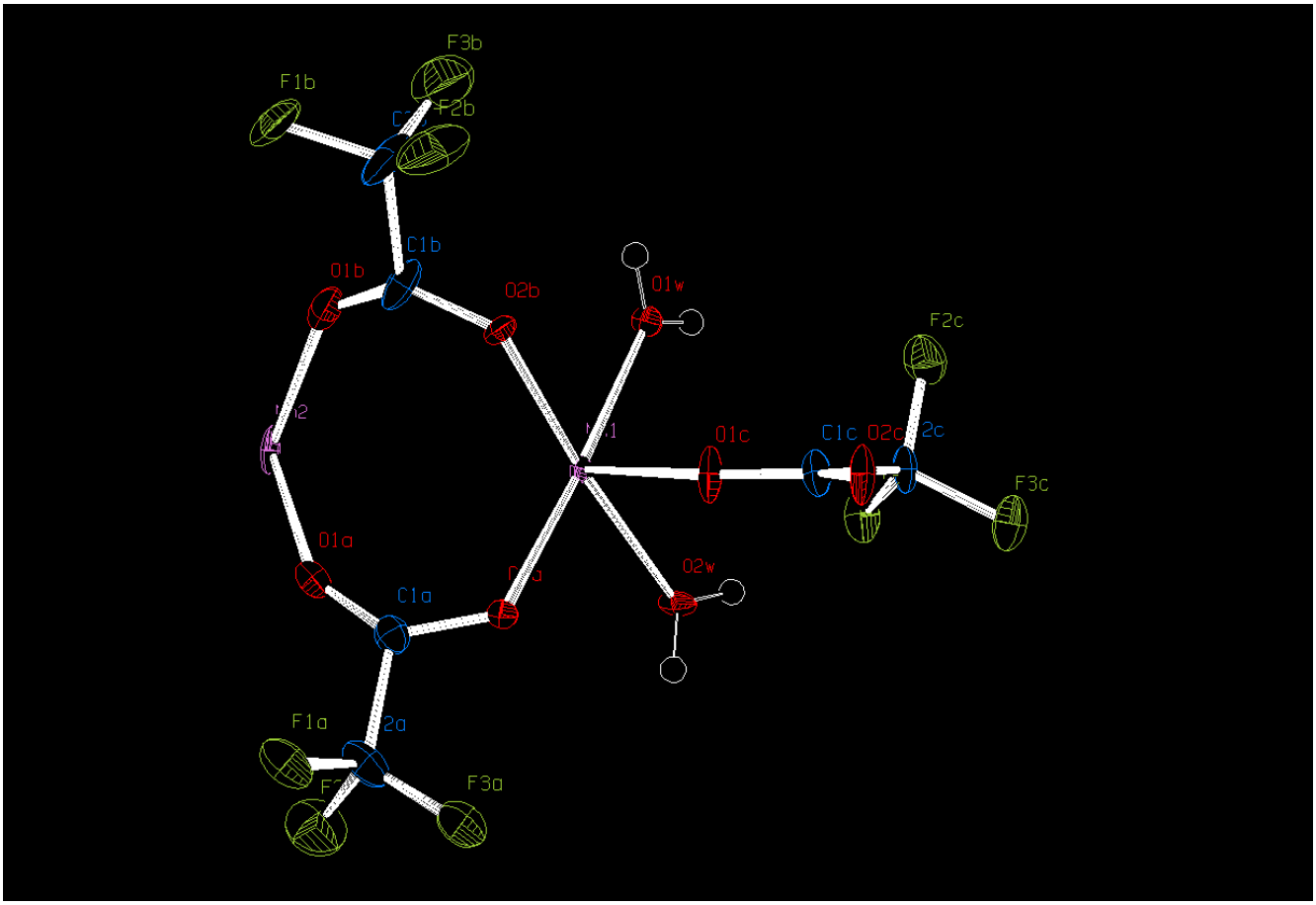

Figure S7. Thermal ellipsoids (50% probability). Severe structure disorder was observed; atom splitting is not shown for clarity.

8. $Mg_{0.45}Mn_{0.55}(tfa)_2 \cdot 4H_2O$ at 100 K

Table S22 Fractional Atomic Coordinates and Isotropic or Equivalent Displacement Parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Mg1	0.27111 (4)	0.59533 (3)	0.38853 (3)	0.01203 (10)	0.452 (2)
Mn1	0.27111 (4)	0.59533 (3)	0.38853 (3)	0.01203 (10)	0.548 (2)
O1W	0.31870 (17)	0.73863 (12)	0.20809 (13)	0.0208 (2)	
H1	0.281 (3)	0.8308 (14)	0.242 (2)	0.031*	
H1'	0.278 (3)	0.727 (2)	0.1454 (19)	0.031*	
O2W	-0.03737 (15)	0.71507 (12)	0.50793 (12)	0.0158 (2)	
H2B	-0.092 (2)	0.8127 (13)	0.519 (2)	0.024*	
H2A	-0.095 (2)	0.6871 (18)	0.5951 (16)	0.024*	
O2W'	0.57533 (15)	0.47150 (12)	0.28536 (12)	0.0162 (2)	
H2A'	0.612 (2)	0.3880 (16)	0.3159 (18)	0.024*	
H2B'	0.640 (2)	0.463 (2)	0.1869 (13)	0.024*	
O3W	0.23889 (17)	0.44289 (13)	0.56241 (13)	0.0182 (2)	
H3	0.291 (2)	0.434 (2)	0.619 (2)	0.027*	
H3'	0.185 (2)	0.3798 (19)	0.575 (2)	0.027*	
O1	0.30682 (15)	0.74625 (11)	0.53615 (12)	0.0159 (2)	
O2	0.21436 (17)	0.97336 (12)	0.44744 (13)	0.0211 (2)	
C1	0.2603 (2)	0.89200 (17)	0.53936 (18)	0.0154 (3)	
C2	0.2544 (3)	0.98008 (18)	0.6805 (2)	0.0229 (3)	
F1	0.31719 (16)	1.10021 (11)	0.63726 (13)	0.0338 (3)	
F2	0.07298 (17)	1.03956 (14)	0.79515 (13)	0.0464 (3)	
F3	0.35985 (19)	0.89023 (12)	0.74322 (14)	0.0445 (3)	
O1'	0.22717 (15)	0.43810 (12)	0.25268 (12)	0.0162 (2)	
O2'	0.25168 (16)	0.55195 (12)	0.03457 (12)	0.0201 (2)	
C1'	0.2328 (2)	0.44647 (17)	0.11691 (17)	0.0151 (3)	
C2'	0.2087 (2)	0.30361 (18)	0.05281 (18)	0.0210 (3)	
F1'	0.22924 (17)	0.30964 (13)	-0.09470 (11)	0.0368 (3)	
F2'	0.33632 (16)	0.17011 (11)	0.05238 (14)	0.0391 (3)	
F3'	0.03308 (15)	0.29806 (13)	0.14419 (12)	0.0342 (3)	

Table S23 Anisotropic Atomic Displacement Parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg1	0.01643 (16)	0.01107 (15)	0.01242 (15)	-0.00589 (11)	-0.00913 (12)	0.00281 (10)
Mn1	0.01643 (16)	0.01107 (15)	0.01242 (15)	-0.00589 (11)	-0.00913 (12)	0.00281 (10)
O1W	0.0309 (7)	0.0158 (5)	0.0222 (6)	-0.0097 (5)	-0.0165 (5)	0.0032 (4)
O2W	0.0209 (6)	0.0115 (5)	0.0165 (5)	-0.0063 (4)	-0.0094 (5)	0.0040 (4)
O2W'	0.0218 (6)	0.0152 (5)	0.0131 (5)	-0.0058 (4)	-0.0098 (4)	0.0033 (4)
O3W	0.0259 (6)	0.0185 (6)	0.0206 (6)	-0.0126 (5)	-0.0164 (5)	0.0073 (4)
O1	0.0213 (5)	0.0109 (5)	0.0184 (5)	-0.0059 (4)	-0.0113 (5)	0.0020 (4)
O2	0.0325 (6)	0.0126 (5)	0.0248 (6)	-0.0065 (4)	-0.0197 (5)	0.0034 (4)
C1	0.0160 (7)	0.0136 (7)	0.0180 (7)	-0.0060 (6)	-0.0084 (6)	0.0006 (5)
C2	0.0327 (9)	0.0155 (7)	0.0262 (8)	-0.0067 (7)	-0.0195 (8)	0.0017 (6)
F1	0.0550 (7)	0.0214 (5)	0.0417 (6)	-0.0195 (5)	-0.0321 (6)	0.0027 (4)
F2	0.0431 (7)	0.0544 (8)	0.0271 (6)	-0.0129 (6)	-0.0054 (5)	-0.0161 (5)
F3	0.0833 (9)	0.0220 (5)	0.0546 (7)	-0.0102 (6)	-0.0596 (7)	0.0044 (5)
O1'	0.0215 (5)	0.0173 (5)	0.0135 (5)	-0.0084 (4)	-0.0099 (4)	0.0031 (4)
O2'	0.0315 (6)	0.0178 (5)	0.0143 (5)	-0.0091 (5)	-0.0128 (5)	0.0029 (4)
C1'	0.0138 (7)	0.0161 (7)	0.0138 (7)	-0.0037 (6)	-0.0058 (6)	-0.0012 (6)
C2'	0.0260 (8)	0.0221 (8)	0.0151 (7)	-0.0114 (7)	-0.0073 (6)	-0.0014 (6)
F1'	0.0622 (8)	0.0451 (6)	0.0166 (5)	-0.0356 (6)	-0.0178 (5)	0.0024 (4)
F2'	0.0473 (7)	0.0165 (5)	0.0526 (7)	-0.0066 (5)	-0.0247 (6)	-0.0041 (5)
F3'	0.0331 (6)	0.0445 (6)	0.0263 (5)	-0.0266 (5)	-0.0051 (4)	-0.0048 (5)

Table S24 Geometric Parameters (Å, º)

Mg1—O1W	2.0949 (11)	O3W—H3'	0.808 (10)
Mg1—O3W	2.1053 (10)	O1—C1	1.2537 (17)
Mg1—O2W'	2.1314 (11)	O2—C1	1.2320 (18)
Mg1—O1	2.1450 (10)	C1—C2	1.541 (2)
Mg1—O1'	2.1510 (10)	C2—F3	1.3177 (18)
Mg1—O2W	2.1514 (11)	C2—F2	1.329 (2)
O1W—H1	0.813 (11)	C2—F1	1.3358 (19)
O1W—H1'	0.816 (11)	O1'—C1'	1.2604 (17)
O2W—H2B	0.841 (10)	O2'—C1'	1.2265 (18)
O2W—H2A	0.831 (11)	C1'—C2'	1.548 (2)
O2W'—H2A'	0.819 (10)	C2'—F2'	1.3226 (19)
O2W'—H2B'	0.832 (10)	C2'—F1'	1.3258 (18)
O3W—H3	0.811 (10)	C2'—F3'	1.3307 (19)
O1W—Mg1—O3W	176.87 (5)	Mg1—O3W—H3	122.6 (12)
O1W—Mg1—O2W'	89.40 (4)	Mg1—O3W—H3'	126.1 (12)
O3W—Mg1—O2W'	87.56 (4)	H3—O3W—H3'	111.0 (14)
O1W—Mg1—O1	91.95 (4)	C1—O1—Mg1	124.44 (9)
O3W—Mg1—O1	88.70 (4)	O2—C1—O1	128.59 (13)
O2W'—Mg1—O1	88.02 (4)	O2—C1—C2	116.32 (13)
O1W—Mg1—O1'	91.24 (4)	O1—C1—C2	115.07 (13)
O3W—Mg1—O1'	88.17 (4)	F3—C2—F2	107.84 (14)
O2W'—Mg1—O1'	93.03 (4)	F3—C2—F1	107.22 (13)
O1—Mg1—O1'	176.65 (4)	F2—C2—F1	106.88 (13)
O1W—Mg1—O2W	94.20 (4)	F3—C2—C1	113.22 (13)
O3W—Mg1—O2W	88.86 (4)	F2—C2—C1	109.80 (13)
O2W'—Mg1—O2W	176.08 (4)	F1—C2—C1	111.61 (13)
O1—Mg1—O2W	90.30 (4)	C1'—O1'—Mg1	128.64 (9)
O1'—Mg1—O2W	88.46 (4)	O2'—C1'—O1'	128.35 (13)
Mg1—O1W—H1	113.0 (14)	O2'—C1'—C2'	118.32 (13)
Mg1—O1W—H1'	114.6 (13)	O1'—C1'—C2'	113.33 (13)

H1—O1W—H1'	110.8 (15)	F2'—C2'—F1'	107.70 (13)
Mg1—O2W—H2B	124.4 (12)	F2'—C2'—F3'	107.43 (13)
Mg1—O2W—H2A	114.8 (12)	F1'—C2'—F3'	107.34 (13)
H2B—O2W—H2A	106.1 (14)	F2'—C2'—C1'	111.62 (13)
Mg1—O2W'—H2A'	117.6 (12)	F1'—C2'—C1'	112.14 (13)
Mg1—O2W'—H2B'	118.2 (12)	F3'—C2'—C1'	110.39 (12)
H2A'—O2W'—H2B'	109.3 (14)		
Mg1—O1—C1—O2	-11.6 (2)	Mg1—O1'—C1'—O2'	-5.5 (2)
Mg1—O1—C1—C2	166.35 (10)	Mg1—O1'—C1'—C2'	175.65 (9)
O2—C1—C2—F3	-159.68 (15)	O2'—C1'—C2'—F2'	126.56 (15)
O1—C1—C2—F3	22.1 (2)	O1'—C1'—C2'—F2'	-54.43 (17)
O2—C1—C2—F2	79.74 (18)	O2'—C1'—C2'—F1'	5.6 (2)
O1—C1—C2—F2	-98.46 (16)	O1'—C1'—C2'—F1'	-175.38 (13)
O2—C1—C2—F1	-38.6 (2)	O2'—C1'—C2'—F3'	-114.03 (15)
O1—C1—C2—F1	143.21 (13)	O1'—C1'—C2'—F3'	64.98 (17)

Table S25 Donor (D)–Acceptor (A) Hydrogen-Bond Geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1···O2	0.81 (1)	2.11 (1)	2.7777 (15)	140 (2)
O1*W*—H1′···O2′	0.82 (1)	2.04 (1)	2.7134 (14)	140 (2)
O2*W*—H2*B*···O2^{i}	0.84 (1)	1.84 (1)	2.6817 (14)	178 (2)
O2*W*—H2*A*···O1′^{ii}	0.83 (1)	1.97 (1)	2.7610 (15)	159 (2)
O2*W*′—H2*A*′···O1^{iii}	0.82 (1)	2.02 (1)	2.7807 (15)	154 (2)
O2*W*′—H2*A*′···F3^{iii}	0.82 (1)	2.52 (2)	3.1588 (15)	136 (2)
O2*W*′—H2*B*′···O2′^{iv}	0.83 (1)	1.86 (1)	2.6863 (14)	171 (2)
O3*W*—H3···O2*W*′^{iii}	0.81 (1)	2.06 (1)	2.7753 (15)	147 (2)
O3*W*—H3′···O2*W*^{ii}	0.81 (1)	2.09 (1)	2.7849 (15)	145 (2)

Symmetry codes: (i) -*x*, -*y*+2, -*z*+1; (ii) -*x*, -*y*+1, -*z*+1; (iii) -*x*+1, -*y*+1, -*z*+1; (iv) -*x*+1, -*y*+1, -*z*.

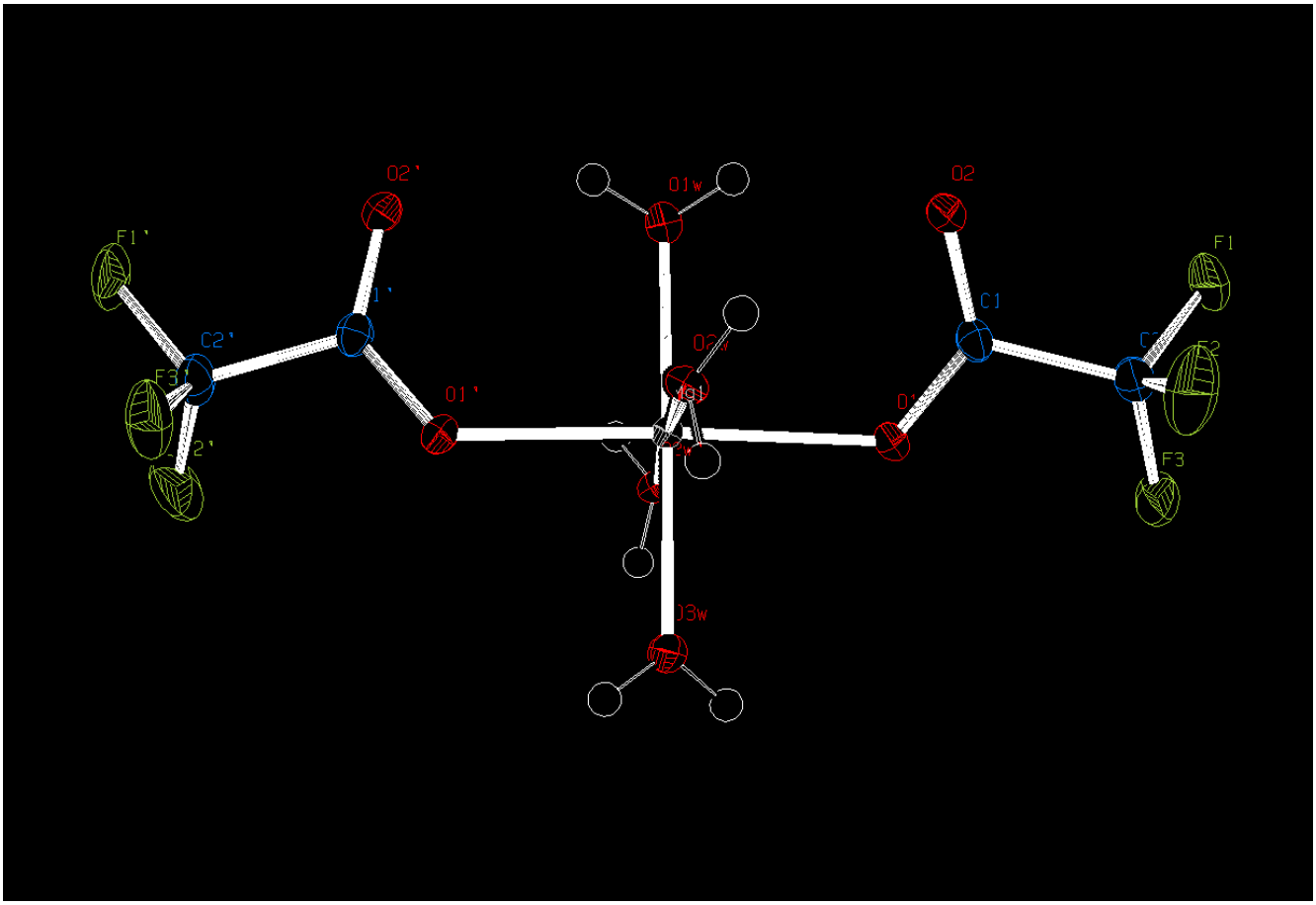

Figure S8. Thermal ellipsoids (50% probability).

9. $Ca_{1.72}Mn_{1.28}(tfa)_6 \cdot 4H_2O$ at 100 K

Table S26 Fractional Atomic Coordinates and Isotropic or Equivalent Displacement Parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Mn1	0.70709 (3)	0.43612 (3)	0.29193 (2)	0.01504 (7)	0.625 (7)
Ca1	0.70709 (3)	0.43612 (3)	0.29193 (2)	0.01504 (7)	0.375 (7)
Ca2	0.51953 (18)	0.4997 (3)	0.50606 (16)	0.0169 (3)	0.481 (4)
Mn2	0.51953 (18)	0.4997 (3)	0.50606 (16)	0.0169 (3)	0.019 (4)
O1W	0.58812 (15)	0.53994 (14)	0.18801 (9)	0.0313 (3)	
H1WA	0.608 (3)	0.615 (2)	0.1645 (17)	0.047*	
H1WB	0.532 (3)	0.500 (3)	0.1553 (15)	0.047*	
O2W	0.92648 (19)	0.53700 (16)	0.29604 (14)	0.0491 (5)	
H2WA	1.004 (3)	0.507 (4)	0.317 (2)	0.074*	
H2WB	0.947 (4)	0.616 (3)	0.276 (2)	0.074*	
O1A	0.4034 (5)	0.3595 (4)	0.4019 (3)	0.0361 (9)	0.697 (11)
O2A	0.5057 (10)	0.2946 (10)	0.2866 (7)	0.0186 (14)	0.697 (11)
C1A	0.3958 (7)	0.3041 (9)	0.3302 (5)	0.0282 (14)	0.697 (11)
C2A	0.2618 (6)	0.2103 (7)	0.3010 (4)	0.0278 (10)	0.697 (11)
F1A	0.2397 (4)	0.1040 (4)	0.3553 (3)	0.0459 (9)	0.697 (11)
F2A	0.1398 (4)	0.2909 (4)	0.2942 (4)	0.0579 (12)	0.697 (11)
F3A	0.2740 (3)	0.1460 (6)	0.2298 (2)	0.0647 (12)	0.697 (11)
O1AA	0.3608 (7)	0.3877 (6)	0.3781 (4)	0.0190 (11)	0.303 (11)
O2AA	0.511 (2)	0.293 (3)	0.2821 (17)	0.023 (4)	0.303 (11)
C1AA	0.4102 (15)	0.298 (2)	0.3293 (10)	0.021 (3)	0.303 (11)
C2AA	0.2585 (17)	0.2365 (17)	0.3022 (11)	0.037 (3)	0.303 (11)
F1AA	0.2385 (11)	0.2349 (19)	0.2242 (5)	0.080 (4)	0.303 (11)
F2AA	0.2523 (9)	0.0949 (7)	0.3193 (8)	0.051 (2)	0.303 (11)
F3AA	0.1474 (8)	0.2983 (10)	0.3340 (7)	0.0469 (19)	0.303 (11)
O1B	0.7389 (9)	0.3809 (5)	0.5071 (3)	0.0281 (9)	0.594 (18)
O2B	0.8144 (10)	0.2906 (14)	0.3876 (5)	0.0265 (18)	0.594 (18)
C1B	0.8230 (9)	0.3151 (10)	0.4640 (5)	0.0196 (12)	0.594 (18)
C2B	0.9542 (10)	0.2435 (10)	0.5122 (5)	0.0329 (15)	0.594 (18)
F1B	0.9176 (8)	0.1997 (7)	0.5860 (3)	0.0508 (11)	0.594 (18)

F2B	0.9999 (10)	0.1252 (8)	0.4750 (5)	0.062 (2)	0.594 (18)
F3B	1.0583 (6)	0.3403 (5)	0.5201 (4)	0.0540 (13)	0.594 (18)
O1BA	0.6883 (11)	0.3606 (8)	0.4991 (5)	0.0278 (13)	0.406 (18)
O2BA	0.8146 (11)	0.3011 (19)	0.3884 (7)	0.0160 (17)	0.406 (18)
C1BA	0.7920 (12)	0.3012 (14)	0.4638 (7)	0.0184 (17)	0.406 (18)
C2BA	0.9221 (15)	0.2453 (17)	0.5162 (9)	0.039 (3)	0.406 (18)
F1BA	1.0266 (12)	0.1708 (14)	0.4736 (7)	0.055 (2)	0.406 (18)
F2BA	1.0085 (16)	0.3499 (8)	0.5534 (10)	0.085 (3)	0.406 (18)
F3BA	0.8802 (15)	0.1593 (13)	0.5754 (6)	0.059 (2)	0.406 (18)
O1C	0.79163 (14)	0.26556 (12)	0.20497 (7)	0.0208 (2)	
O2C	0.88281 (13)	0.10668 (11)	0.11762 (7)	0.0208 (2)	
C1C	0.85612 (17)	0.23351 (14)	0.14249 (9)	0.0154 (3)	
C2C	0.90899 (18)	0.35985 (16)	0.08920 (10)	0.0203 (3)	
F1C	0.9434 (3)	0.4807 (2)	0.13259 (14)	0.0397 (8)	0.520 (3)
F2C	1.0238 (3)	0.3276 (3)	0.04565 (17)	0.0417 (8)	0.520 (3)
F3C	0.7988 (3)	0.3983 (3)	0.03716 (16)	0.0380 (7)	0.520 (3)
F4C	0.8228 (4)	0.4727 (3)	0.0868 (2)	0.0460 (10)	0.480 (3)
F5C	1.0422 (3)	0.3953 (3)	0.11781 (19)	0.0448 (9)	0.480 (3)
F6C	0.9239 (4)	0.3147 (3)	0.01141 (15)	0.0413 (8)	0.480 (3)

Table S27 Anisotropic Atomic Displacement Parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mn1	0.01924 (12)	0.01378 (11)	0.01247 (12)	0.00282 (8)	0.00491 (8)	-0.00074 (8)
Ca1	0.01924 (12)	0.01378 (11)	0.01247 (12)	0.00282 (8)	0.00491 (8)	-0.00074 (8)
Ca2	0.0218 (9)	0.01499 (19)	0.0147 (7)	0.0007 (7)	0.0103 (6)	-0.0031 (4)
Mn2	0.0218 (9)	0.01499 (19)	0.0147 (7)	0.0007 (7)	0.0103 (6)	-0.0031 (4)
O1W	0.0330 (7)	0.0207 (6)	0.0390 (8)	-0.0095 (5)	-0.0095 (6)	0.0094 (5)
O2W	0.0433 (9)	0.0221 (6)	0.0839 (13)	0.0076 (6)	0.0232 (9)	0.0235 (8)
O1A	0.0430 (18)	0.0316 (14)	0.0354 (17)	-0.0141 (13)	0.0201 (14)	-0.0120 (12)
O2A	0.017 (2)	0.013 (2)	0.026 (3)	-0.0032 (15)	0.0090 (18)	-0.0025 (17)
C1A	0.026 (2)	0.0156 (17)	0.046 (2)	-0.0055 (14)	0.0258 (17)	-0.0041 (14)
C2A	0.0131 (13)	0.020 (2)	0.051 (2)	-0.0015 (11)	0.0138 (12)	0.0009 (14)
F1A	0.0359 (11)	0.0392 (13)	0.062 (2)	-0.0216 (10)	-0.0081 (12)	0.0230 (13)
F2A	0.0346 (12)	0.0300 (11)	0.108 (4)	0.0143 (9)	-0.0042 (18)	0.0059 (18)
F3A	0.0298 (12)	0.088 (3)	0.0773 (19)	-0.0203 (14)	0.0096 (11)	-0.0471 (19)
O1AA	0.025 (2)	0.0183 (19)	0.014 (2)	0.0017 (16)	0.0020 (17)	-0.0008 (15)
O2AA	0.017 (5)	0.027 (7)	0.026 (6)	0.004 (4)	0.011 (4)	0.005 (4)
C1AA	0.021 (3)	0.018 (3)	0.025 (3)	-0.0017 (19)	0.005 (2)	-0.003 (2)
C2AA	0.034 (4)	0.021 (5)	0.058 (5)	0.001 (3)	0.013 (3)	-0.003 (3)
F1AA	0.053 (5)	0.126 (9)	0.061 (4)	-0.042 (5)	0.001 (3)	-0.011 (4)
F2AA	0.037 (3)	0.0182 (19)	0.096 (5)	0.0015 (16)	-0.014 (3)	0.002 (3)
F3AA	0.015 (2)	0.052 (3)	0.074 (5)	0.0052 (19)	0.006 (3)	-0.005 (4)
O1B	0.037 (2)	0.0243 (14)	0.0232 (13)	0.0051 (15)	0.0057 (15)	0.0014 (10)
O2B	0.046 (4)	0.018 (3)	0.016 (2)	-0.004 (2)	0.007 (2)	-0.0006 (17)
C1B	0.030 (3)	0.0104 (18)	0.0191 (16)	-0.006 (2)	0.0059 (17)	0.0031 (11)
C2B	0.050 (3)	0.030 (2)	0.018 (2)	0.007 (2)	-0.008 (2)	0.0040 (15)
F1B	0.081 (3)	0.045 (2)	0.0247 (14)	-0.0063 (18)	-0.0102 (14)	0.0154 (14)
F2B	0.087 (4)	0.050 (3)	0.046 (3)	0.041 (2)	-0.031 (2)	-0.019 (2)
F3B	0.053 (2)	0.0608 (19)	0.047 (2)	-0.0104 (15)	-0.0065 (15)	0.0066 (16)
O1BA	0.030 (3)	0.026 (2)	0.028 (2)	0.007 (2)	0.011 (2)	0.0018 (16)
O2BA	0.017 (3)	0.011 (2)	0.020 (3)	0.005 (2)	-0.001 (2)	0.000 (2)
C1BA	0.026 (4)	0.009 (3)	0.020 (2)	-0.006 (3)	0.006 (2)	0.0025 (16)

C2BA	0.049 (5)	0.038 (4)	0.029 (4)	0.002 (3)	-0.001 (3)	-0.004 (3)
F1BA	0.051 (3)	0.076 (6)	0.038 (3)	0.026 (4)	0.003 (2)	0.017 (4)
F2BA	0.090 (6)	0.074 (3)	0.086 (7)	-0.014 (4)	-0.033 (5)	-0.006 (4)
F3BA	0.086 (5)	0.054 (4)	0.037 (3)	0.022 (3)	0.007 (3)	0.026 (3)
O1C	0.0295 (6)	0.0158 (5)	0.0179 (6)	-0.0006 (4)	0.0114 (4)	-0.0002 (4)
O2C	0.0267 (5)	0.0124 (4)	0.0236 (5)	0.0032 (4)	0.0044 (4)	-0.0038 (4)
C1C	0.0195 (7)	0.0118 (5)	0.0153 (7)	0.0011 (5)	0.0044 (5)	0.0006 (4)
C2C	0.0255 (7)	0.0176 (6)	0.0185 (7)	-0.0013 (5)	0.0096 (5)	0.0014 (5)
F1C	0.071 (2)	0.0206 (10)	0.0277 (11)	-0.0246 (11)	0.0085 (11)	0.0002 (8)
F2C	0.0414 (15)	0.0489 (14)	0.0374 (15)	0.0059 (12)	0.0300 (12)	0.0101 (12)
F3C	0.0391 (13)	0.0395 (14)	0.0347 (13)	-0.0028 (10)	-0.0076 (10)	0.0203 (11)
F4C	0.0629 (19)	0.0234 (12)	0.055 (2)	0.0175 (12)	0.0341 (16)	0.0227 (13)
F5C	0.0391 (15)	0.0440 (16)	0.0517 (18)	-0.0268 (13)	0.0075 (12)	0.0073 (13)
F6C	0.068 (2)	0.0374 (14)	0.0205 (12)	-0.0019 (14)	0.0250 (13)	0.0023 (10)

Table S28 Geometric Parameters (Å, º)

Mn1—O1W	2.1860 (13)	C2AA—F3AA	1.284 (16)
Mn1—O2W	2.1888 (18)	C2AA—F2AA	1.329 (15)
Mn1—O2BA	2.196 (11)	O1B—C1B	1.220 (8)
Mn1—O2AA	2.20 (2)	O1B—Ca2^{ii}	2.583 (7)
Mn1—O2A	2.236 (8)	O2B—C1B	1.267 (9)
Mn1—O2B	2.241 (9)	C1B—C2B	1.541 (8)
Mn1—O1C	2.2681 (11)	C2B—F3B	1.297 (10)
Mn1—O2C^{i}	2.3231 (12)	C2B—F2B	1.318 (10)
Ca2—Mn2^{ii}	0.397 (2)	C2B—F1B	1.327 (9)
Ca2—Ca2^{ii}	0.397 (2)	O1BA—C1BA	1.248 (10)
Ca2—O1BA	1.996 (7)	O1BA—Mn2^{ii}	2.273 (8)
Ca2—O1A^{ii}	2.078 (4)	O1BA—Ca2^{ii}	2.273 (8)
Ca2—O1B	2.264 (7)	O2BA—C1BA	1.258 (12)
Ca2—O1BA^{ii}	2.273 (8)	C1BA—C2BA	1.513 (12)
Ca2—O1A	2.343 (4)	C2BA—F3BA	1.316 (15)
Ca2—O1AA^{ii}	2.372 (7)	C2BA—F2BA	1.362 (15)
Ca2—O2C^{i}	2.447 (3)	C2BA—F1BA	1.380 (14)
Ca2—O2C^{iii}	2.451 (3)	O1C—C1C	1.2340 (18)
Ca2—O1B^{ii}	2.583 (7)	O1C—Ca1^{iv}	3.0188 (11)
Ca2—O1AA	2.685 (7)	O2C—C1C	1.2580 (16)
O1W—H1WA	0.816 (19)	O2C—Ca1^{iv}	2.3231 (12)
O1W—H1WB	0.808 (19)	O2C—Mn1^{iv}	2.3231 (12)
O2W—H2WA	0.81 (2)	O2C—Mn2^{iv}	2.447 (3)
O2W—H2WB	0.82 (2)	O2C—Ca2^{iv}	2.447 (3)
O1A—C1A	1.275 (7)	O2C—Mn2^{v}	2.451 (3)
O1A—Mn2^{ii}	2.078 (4)	O2C—Ca2^{v}	2.451 (3)
O1A—Ca2^{ii}	2.078 (4)	C1C—C2C	1.538 (2)
O2A—C1A	1.252 (7)	C1C—Ca1^{iv}	2.9924 (13)
C1A—C2A	1.544 (6)	C2C—F4C	1.295 (3)
C2A—F3A	1.312 (7)	C2C—F5C	1.314 (3)
C2A—F2A	1.329 (6)	C2C—F2C	1.319 (3)

C2A—F1A	1.338 (7)	C2C—F3C	1.328 (3)
O1AA—C1AA	1.244 (14)	C2C—F1C	1.344 (3)
O1AA—Mn2^{ii}	2.372 (7)	C2C—F6C	1.349 (3)
O1AA—Ca2^{ii}	2.372 (7)	F2C—Ca2^{v}	3.068 (4)
O2AA—C1AA	1.225 (15)	F6C—Ca2^{iv}	2.947 (4)
C1AA—C2AA	1.530 (14)	F6C—Ca2^{v}	3.010 (4)
C2AA—F1AA	1.278 (18)		
O1W—Mn1—O2W	104.73 (6)	Mn2^{ii}—O1AA—Ca2	5.6
O1W—Mn1—O2BA	171.5 (4)	Ca2^{ii}—O1AA—Ca2	5.56 (11)
O2W—Mn1—O2BA	81.0 (4)	C1AA—O2AA—Mn1	123.7 (17)
O1W—Mn1—O2AA	80.6 (8)	O2AA—C1AA—O1AA	136.7 (18)
O2W—Mn1—O2AA	168.1 (6)	O2AA—C1AA—C2AA	119.5 (16)
O1W—Mn1—O2A	81.4 (3)	O1AA—C1AA—C2AA	94.9 (11)
O2W—Mn1—O2A	169.5 (3)	F1AA—C2AA—F3AA	109.3 (13)
O1W—Mn1—O2B	169.3 (3)	F1AA—C2AA—F2AA	101.1 (11)
O2W—Mn1—O2B	82.3 (3)	F3AA—C2AA—F2AA	107.7 (13)
O1W—Mn1—O1C	88.96 (5)	F1AA—C2AA—C1AA	112.1 (13)
O2W—Mn1—O1C	88.77 (6)	F3AA—C2AA—C1AA	115.5 (12)
O2BA—Mn1—O1C	84.8 (3)	F2AA—C2AA—C1AA	110.1 (14)
O2AA—Mn1—O1C	80.6 (5)	C1B—O1B—Ca2	143.5 (5)
O2A—Mn1—O1C	82.8 (2)	C1B—O1B—Ca2^{ii}	138.4 (5)
O2B—Mn1—O1C	83.0 (3)	Ca2—O1B—Ca2^{ii}	5.63 (12)
O1W—Mn1—O2C^{i}	91.52 (5)	C1B—O2B—Mn1	125.9 (8)
O2W—Mn1—O2C^{i}	92.30 (6)	O1B—C1B—O2B	130.2 (8)
O2BA—Mn1—O2C^{i}	94.6 (3)	O1B—C1B—C2B	113.7 (7)
O2AA—Mn1—O2C^{i}	98.2 (5)	O2B—C1B—C2B	116.0 (7)
O2A—Mn1—O2C^{i}	96.1 (2)	F3B—C2B—F2B	111.5 (8)
O2B—Mn1—O2C^{i}	96.3 (2)	F3B—C2B—F1B	109.1 (7)
O1C—Mn1—O2C^{i}	178.67 (4)	F2B—C2B—F1B	105.5 (7)
Mn2^{ii}—Ca2—Ca2^{ii}	0.0	F3B—C2B—C1B	107.5 (6)
Mn2^{ii}—Ca2—O1BA	130.2 (9)	F2B—C2B—C1B	111.4 (7)
Ca2^{ii}—Ca2—O1BA	130.2 (9)	F1B—C2B—C1B	112.0 (7)

$Mn2^{ii}$—Ca2—$O1A^{ii}$	127.9 (9)	C1BA—O1BA—Ca2	153.9 (7)
$Ca2^{ii}$—Ca2—$O1A^{ii}$	127.9 (9)	C1BA—O1BA—$Mn2^{ii}$	150.1 (7)
$Mn2^{ii}$—Ca2—O1B	140.4 (9)	Ca2—O1BA—$Mn2^{ii}$	7.7
$Ca2^{ii}$—Ca2—O1B	140.4 (9)	C1BA—O1BA—$Ca2^{ii}$	150.1 (7)
$Mn2^{ii}$—Ca2—$O1BA^{ii}$	42.1 (8)	Ca2—O1BA—$Ca2^{ii}$	7.67 (13)
$Ca2^{ii}$—Ca2—$O1BA^{ii}$	42.1 (8)	$Mn2^{ii}$—O1BA—$Ca2^{ii}$	0.0
O1BA—Ca2—$O1BA^{ii}$	172.33 (13)	C1BA—O2BA—Mn1	128.0 (9)
$Mn2^{ii}$—Ca2—O1A	44.4 (8)	O1BA—C1BA—O2BA	127.7 (10)
$Ca2^{ii}$—Ca2—O1A	44.4 (8)	O1BA—C1BA—C2BA	118.0 (10)
$O1A^{ii}$—Ca2—O1A	172.31 (11)	O2BA—C1BA—C2BA	113.3 (9)
$Mn2^{ii}$—Ca2—$O1AA^{ii}$	139.1 (9)	O1BA—C1BA—Ca2	16.1 (5)
$Ca2^{ii}$—Ca2—$O1AA^{ii}$	139.1 (9)	O2BA—C1BA—Ca2	112.2 (8)
$Mn2^{ii}$—Ca2—$O2C^{i}$	86.0 (8)	C2BA—C1BA—Ca2	131.7 (8)
$Ca2^{ii}$—Ca2—$O2C^{i}$	86.0 (8)	F3BA—C2BA—F2BA	105.8 (11)
O1BA—Ca2—$O2C^{i}$	84.4 (2)	F3BA—C2BA—F1BA	107.6 (11)
$O1A^{ii}$—Ca2—$O2C^{i}$	103.12 (15)	F2BA—C2BA—F1BA	100.4 (10)
O1B—Ca2—$O2C^{i}$	81.30 (15)	F3BA—C2BA—C1BA	112.0 (11)
$O1BA^{ii}$—Ca2—$O2C^{i}$	94.23 (19)	F2BA—C2BA—C1BA	115.5 (11)
O1A—Ca2—$O2C^{i}$	77.70 (12)	F1BA—C2BA—C1BA	114.6 (11)
$O1AA^{ii}$—Ca2—$O2C^{i}$	108.36 (17)	C1C—O1C—Mn1	150.20 (10)
$Mn2^{ii}$—Ca2—$O2C^{iii}$	84.7 (8)	C1C—O1C—$Ca1^{iv}$	76.96 (8)
$Ca2^{ii}$—Ca2—$O2C^{iii}$	84.7 (8)	Mn1—O1C—$Ca1^{iv}$	132.8
O1BA—Ca2—$O2C^{iii}$	101.7 (2)	C1C—O2C—$Ca1^{iv}$	109.75 (9)
$O1A^{ii}$—Ca2—$O2C^{iii}$	82.71 (13)	C1C—O2C—$Mn1^{iv}$	109.75 (9)
O1B—Ca2—$O2C^{iii}$	106.01 (17)	$Ca1^{iv}$—O2C—$Mn1^{iv}$	0.0
$O1BA^{ii}$—Ca2—$O2C^{iii}$	78.82 (19)	C1C—O2C—$Mn2^{iv}$	135.93 (12)
O1A—Ca2—$O2C^{iii}$	95.56 (12)	$Ca1^{iv}$—O2C—$Mn2^{iv}$	113.95 (8)
$O1AA^{ii}$—Ca2—$O2C^{iii}$	78.93 (17)	$Mn1^{iv}$—O2C—$Mn2^{iv}$	113.95 (8)
$O2C^{i}$—Ca2—$O2C^{iii}$	170.69 (5)	C1C—O2C—$Ca2^{iv}$	135.93 (12)
$Mn2^{ii}$—Ca2—$O1B^{ii}$	34.0 (8)	$Ca1^{iv}$—O2C—$Ca2^{iv}$	113.95 (8)
$Ca2^{ii}$—Ca2—$O1B^{ii}$	34.0 (8)	$Mn1^{iv}$—O2C—$Ca2^{iv}$	113.95 (8)
O1B—Ca2—$O1B^{ii}$	174.37 (12)	$Mn2^{iv}$—O2C—$Ca2^{iv}$	0.0
$O2C^{i}$—Ca2—$O1B^{ii}$	97.00 (14)	C1C—O2C—$Mn2^{v}$	135.92 (12)

O2C^{iii}—Ca2—O1B^{ii}	75.16 (13)	Ca1^{iv}—O2C—Mn2^{v}	114.12 (8)
Mn2^{ii}—Ca2—O1AA	35.4 (8)	Mn1^{iv}—O2C—Mn2^{v}	114.12 (8)
Ca2^{ii}—Ca2—O1AA	35.4 (8)	Mn2^{iv}—O2C—Mn2^{v}	9.31 (5)
O1AA^{ii}—Ca2—O1AA	174.43 (11)	Ca2^{iv}—O2C—Mn2^{v}	9.31 (5)
O2C^{i}—Ca2—O1AA	73.22 (15)	C1C—O2C—Ca2^{v}	135.92 (12)
O2C^{iii}—Ca2—O1AA	98.97 (15)	Ca1^{iv}—O2C—Ca2^{v}	114.12 (8)
Mn1—O1W—H1WA	128 (2)	Mn1^{iv}—O2C—Ca2^{v}	114.12 (8)
Mn1—O1W—H1WB	126 (2)	Mn2^{iv}—O2C—Ca2^{v}	9.3
H1WA—O1W—H1WB	103 (3)	Ca2^{iv}—O2C—Ca2^{v}	9.31 (5)
Mn1—O2W—H2WA	130 (3)	Mn2^{v}—O2C—Ca2^{v}	0.0
Mn1—O2W—H2WB	126 (2)	O1C—C1C—O2C	126.29 (13)
H2WA—O2W—H2WB	105 (3)	O1C—C1C—C2C	117.40 (12)
C1A—O1A—Mn2^{ii}	156.1 (4)	O2C—C1C—C2C	116.31 (12)
C1A—O1A—Ca2^{ii}	156.1 (4)	O1C—C1C—Ca1^{iv}	79.36 (8)
Mn2^{ii}—O1A—Ca2^{ii}	0.0	O2C—C1C—Ca1^{iv}	46.94 (7)
C1A—O1A—Ca2	152.7 (3)	C2C—C1C—Ca1^{iv}	163.25 (9)
Mn2^{ii}—O1A—Ca2	7.7	F4C—C2C—F5C	110.8 (2)
Ca2^{ii}—O1A—Ca2	7.69 (11)	F2C—C2C—F3C	107.5 (2)
C1A—O2A—Mn1	127.2 (6)	F2C—C2C—F1C	107.4 (2)
O2A—C1A—O1A	122.6 (7)	F3C—C2C—F1C	105.6 (2)
O2A—C1A—C2A	114.8 (6)	F4C—C2C—F6C	107.6 (2)
O1A—C1A—C2A	120.9 (5)	F5C—C2C—F6C	106.3 (2)
F3A—C2A—F2A	106.2 (5)	F4C—C2C—C1C	114.55 (16)
F3A—C2A—F1A	106.4 (5)	F5C—C2C—C1C	106.82 (17)
F2A—C2A—F1A	108.1 (4)	F2C—C2C—C1C	114.20 (16)
F3A—C2A—C1A	115.2 (4)	F3C—C2C—C1C	108.52 (16)
F2A—C2A—C1A	110.8 (5)	F1C—C2C—C1C	113.11 (15)
F1A—C2A—C1A	109.9 (6)	F6C—C2C—C1C	110.45 (16)
C1AA—O1AA—Mn2^{ii}	129.4 (8)	C2C—F2C—Ca2^{v}	109.26 (17)
C1AA—O1AA—Ca2^{ii}	129.4 (8)	C2C—F6C—Ca2^{iv}	114.64 (17)
Mn2^{ii}—O1AA—Ca2^{ii}	0.0	C2C—F6C—Ca2^{v}	111.23 (17)
C1AA—O1AA—Ca2	123.9 (8)	Ca2^{iv}—F6C—Ca2^{v}	7.55 (5)

Mn1—O2A—C1A—O1A	-26.1 (17)	O2BA—C1BA—C2BA—F2BA	100.5 (15)
Mn1—O2A—C1A—C2A	168.7 (7)	Ca2—C1BA—C2BA—F2BA	-58.7 (17)
Mn2^{ii}—O1A—C1A—O2A	33 (2)	O1BA—C1BA—C2BA—F1BA	175.1 (12)
Ca2^{ii}—O1A—C1A—O2A	33 (2)	O2BA—C1BA—C2BA—F1BA	-15.4 (18)
Ca2—O1A—C1A—O2A	17 (2)	Ca2—C1BA—C2BA—F1BA	-174.6 (11)
Mn2^{ii}—O1A—C1A—C2A	-162.9 (9)	Mn1—O1C—C1C—O2C	177.51 (15)
Ca2^{ii}—O1A—C1A—C2A	-162.9 (9)	Ca1^{iv}—O1C—C1C—O2C	0.23 (16)
Ca2—O1A—C1A—C2A	-179.0 (7)	Mn1—O1C—C1C—C2C	-2.7 (3)
O2A—C1A—C2A—F3A	-7.3 (12)	Ca1^{iv}—O1C—C1C—C2C	179.98 (15)
O1A—C1A—C2A—F3A	-172.8 (8)	Mn1—O1C—C1C—Ca1^{iv}	177.3 (2)
O2A—C1A—C2A—F2A	-127.9 (10)	Ca1^{iv}—O2C—C1C—O1C	-0.3 (2)
O1A—C1A—C2A—F2A	66.7 (11)	Mn1^{iv}—O2C—C1C—O1C	-0.3 (2)
O2A—C1A—C2A—F1A	112.8 (10)	Mn2^{iv}—O2C—C1C—O1C	172.08 (13)
O1A—C1A—C2A—F1A	-52.6 (11)	Ca2^{iv}—O2C—C1C—O1C	172.08 (13)
Mn1—O2AA—C1AA—O1AA	21 (4)	Mn2^{v}—O2C—C1C—O1C	-174.52 (13)
Mn1—O2AA—C1AA—C2AA	158.6 (17)	Ca2^{v}—O2C—C1C—O1C	-174.52 (13)
Mn2^{ii}—O1AA—C1AA—O2AA	-59 (4)	Ca1^{iv}—O2C—C1C—C2C	179.94 (11)
Ca2^{ii}—O1AA—C1AA—O2AA	-59 (4)	Mn1^{iv}—O2C—C1C—C2C	179.94 (11)
Ca2—O1AA—C1AA—O2AA	-59 (3)	Mn2^{iv}—O2C—C1C—C2C	-7.7 (2)
Mn2^{ii}—O1AA—C1AA—C2AA	156.8 (8)	Ca2^{iv}—O2C—C1C—C2C	-7.7 (2)
Ca2^{ii}—O1AA—C1AA—C2AA	156.8 (8)	Mn2^{v}—O2C—C1C—C2C	5.7 (2)
Ca2—O1AA—C1AA—C2AA	156.6 (8)	Ca2^{v}—O2C—C1C—C2C	5.7 (2)
O2AA—C1AA—C2AA—F1AA	-24 (3)	Mn1^{iv}—O2C—C1C—Ca1^{iv}	0.0
O1AA—C1AA—C2AA—F1AA	128.6 (15)	Mn2^{iv}—O2C—C1C—Ca1^{iv}	172.39 (19)
O2AA—C1AA—C2AA—F3AA	-150 (2)	Ca2^{iv}—O2C—C1C—Ca1^{iv}	172.39 (19)
O1AA—C1AA—C2AA—F3AA	3 (2)	Mn2^{v}—O2C—C1C—Ca1^{iv}	-174.21 (19)
O2AA—C1AA—C2AA—F2AA	88 (3)	Ca2^{v}—O2C—C1C—Ca1^{iv}	-174.21 (19)
O1AA—C1AA—C2AA—F2AA	-119.6 (17)	O1C—C1C—C2C—F4C	-34.8 (3)
Ca2—O1B—C1B—O2B	3.0 (16)	O2C—C1C—C2C—F4C	145.0 (2)
Ca2^{ii}—O1B—C1B—O2B	7.0 (15)	Ca1^{iv}—C1C—C2C—F4C	145.2 (4)
Ca2—O1B—C1B—C2B	-172.7 (6)	O1C—C1C—C2C—F5C	88.3 (2)
Ca2^{ii}—O1B—C1B—C2B	-168.8 (6)	O2C—C1C—C2C—F5C	-91.9 (2)
Mn1—O2B—C1B—O1B	30.9 (16)	Ca1^{iv}—C1C—C2C—F5C	-91.7 (4)

Mn1—O2B—C1B—C2B	-153.5 (7)	O1C—C1C—C2C—F2C	153.5 (2)
O1B—C1B—C2B—F3B	-87.0 (8)	O2C—C1C—C2C—F2C	-26.7 (3)
O2B—C1B—C2B—F3B	96.7 (10)	Ca1^{iv}—C1C—C2C—F2C	-26.6 (5)
O1B—C1B—C2B—F2B	150.7 (9)	O1C—C1C—C2C—F3C	-86.6 (2)
O2B—C1B—C2B—F2B	-25.7 (12)	O2C—C1C—C2C—F3C	93.2 (2)
O1B—C1B—C2B—F1B	32.8 (10)	Ca1^{iv}—C1C—C2C—F3C	93.3 (4)
O2B—C1B—C2B—F1B	-143.6 (10)	O1C—C1C—C2C—F1C	30.2 (3)
Ca2—O1BA—C1BA—O2BA	-17 (3)	O2C—C1C—C2C—F1C	-150.0 (2)
Mn2^{ii}—O1BA—C1BA—O2BA	-2 (2)	Ca1^{iv}—C1C—C2C—F1C	-149.9 (3)
Ca2^{ii}—O1BA—C1BA—O2BA	-2 (2)	O1C—C1C—C2C—F6C	-156.5 (2)
Ca2—O1BA—C1BA—C2BA	151.2 (16)	O2C—C1C—C2C—F6C	23.3 (3)
Mn2^{ii}—O1BA—C1BA—C2BA	165.4 (12)	Ca1^{iv}—C1C—C2C—F6C	23.5 (5)
Ca2^{ii}—O1BA—C1BA—C2BA	165.4 (12)	F3C—C2C—F2C—Ca2^{v}	-91.47 (19)
Mn2^{ii}—O1BA—C1BA—Ca2	14.2 (6)	F1C—C2C—F2C—Ca2^{v}	155.32 (16)
Ca2^{ii}—O1BA—C1BA—Ca2	14.2 (6)	C1C—C2C—F2C—Ca2^{v}	29.0 (2)
Mn1—O2BA—C1BA—O1BA	12 (2)	F4C—C2C—F6C—Ca2^{iv}	-151.3 (2)
Mn1—O2BA—C1BA—C2BA	-156.0 (11)	F5C—C2C—F6C—Ca2^{iv}	89.9 (2)
Mn1—O2BA—C1BA—Ca2	7.4 (17)	C1C—C2C—F6C—Ca2^{iv}	-25.6 (3)
O1BA—C1BA—C2BA—F3BA	52.2 (17)	F4C—C2C—F6C—Ca2^{v}	-158.6 (2)
O2BA—C1BA—C2BA—F3BA	-138.3 (14)	F5C—C2C—F6C—Ca2^{v}	82.6 (2)
Ca2—C1BA—C2BA—F3BA	62.5 (18)	C1C—C2C—F6C—Ca2^{v}	-32.9 (2)
O1BA—C1BA—C2BA—F2BA	-69.0 (16)		

Symmetry codes: (i) -*x*+3/2, *y*+1/2, -*z*+1/2; (ii) -*x*+1, -*y*+1, -*z*+1; (iii) *x*-1/2, -*y*+1/2, *z*+1/2; (iv) -*x*+3/2, *y*-1/2, -*z*+1/2; (v) *x*+1/2, -*y*+1/2, *z*-1/2.

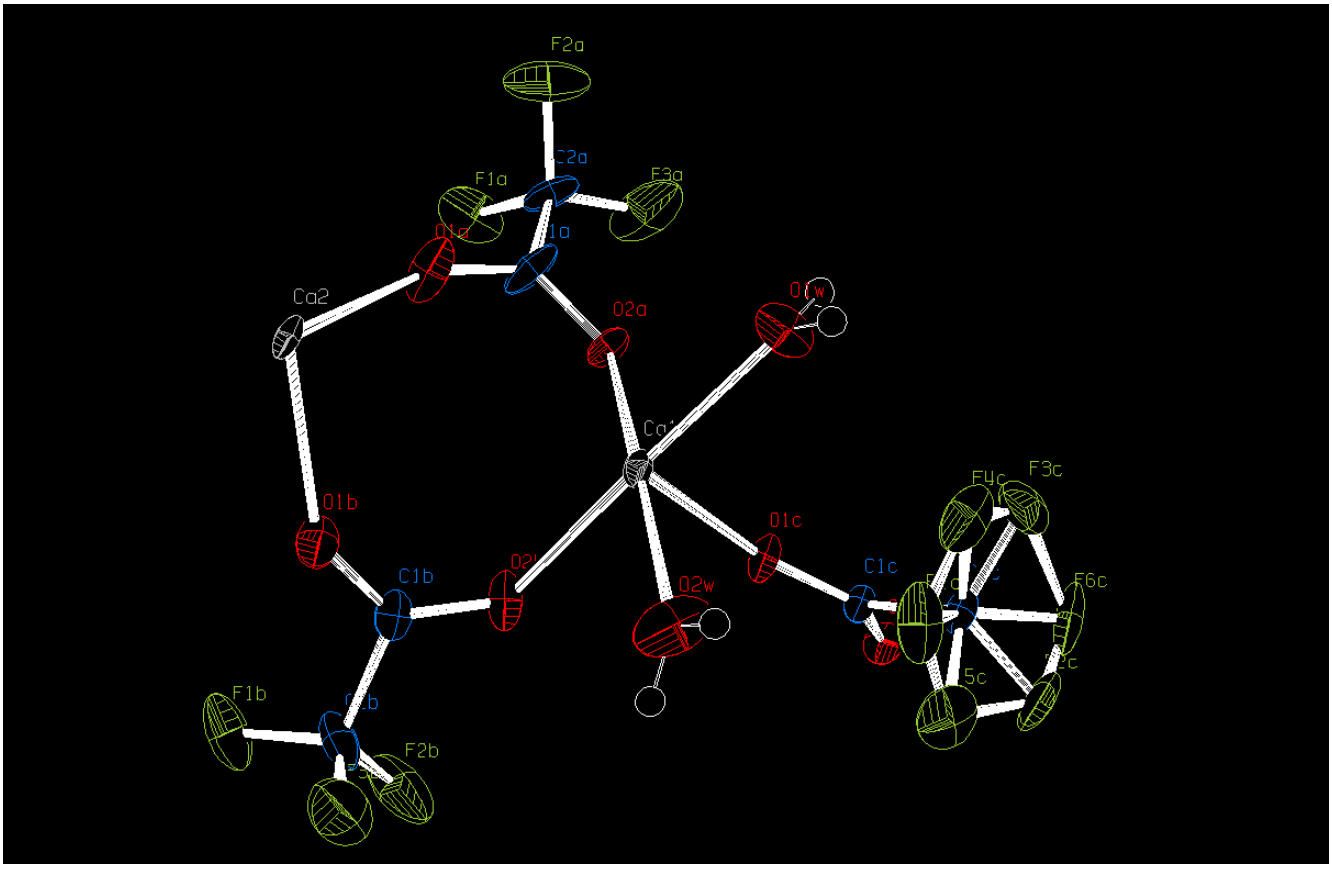

Figure S9. Thermal ellipsoids (50% probability). Severe structure disorder was observed; atom splitting is not shown for clarity.

Reversibility of Phase Transition of $Mg(tfa)_2 \cdot 4H_2O$

Macroscopic strain acting over the crystals under cold nitrogen flux resulted in the multiplication of nearly identical twin domains after each cooling cycle. This reduced the quality of the diffraction data collected at 200 K with respect to that at 300 K (after passing twice through the phase transition). Further, it confirmed the that twinning first observed at 100 K resulted from a $C2/c$ to $P\bar{1}$ phase transition, with one domain being rotated around the [0 –1 1] axis with a twin law {[–0.992 0.016 –0.027][0.083 0.006 –1.013][–0.062 –0.992 –0.014]} as determined by Bruker CELLNOW indexing software.

Crystal-Chemistry of Alkaline-earth Trifluoroacetates

Table S29 Crystallochemical Features of Alkaline-Earth Trifluoroacetates

	$Mg(tfa)_2 \cdot 4H_2O$	$Ca_3(tfa)_6 \cdot 4H_2O$	$Sr(tfa)_2$	$Ba(tfa)_2$
Space-group (Temperature)	$P\bar{1}$ (100 K)	$P2_1/n$ (298 K)	$R\bar{3}$ (100 K)	
A^{2+} coordination number	6	6	7	9
A^{2+} coordination geometry	Octahedral	Octahedral	Irregular	
Coordinating ligands	4 H_2O + 2 tfa (*trans*)	Central Ca^{2+}: 6 tfa Terminal Ca^{2+}: 4 tfa + 2 H_2O (*cis*)	tfa	
A–O Bond Length Range (Å)	2.0259–2.0995	Central Ca: 2.282–2.421 Terminal Ca: 2.318–2.464	2.462–2.712	2.654–3.050
Connectivity of metal–oxygen polyhedra	H-bonded octahedral monomers	H-bonded trimers of edge-sharing octahedra	Honeycomb arrangement of edge- and face-sharing polyhedra	
Layout of metal–oxygen polyhedra	Zig-zag chains and channels along [100]	Layers perpendicular to [010]	Channels along [001]	

A systematic comparison of the crystal structures of alkaline-earth trifluoroacetates provides insight into their crystal-chemistry; the most relevant crystallochemical features of this family of compounds is summarized in Table S29. The structural layout of the calcium and strontium compounds is shown in Figure S11 to facilitate discussion; further details on their crystal structures can be found in Dissanayake et al.[7] The coordination number (C.N.) of the metal center increases upon increasing the ionic radii of

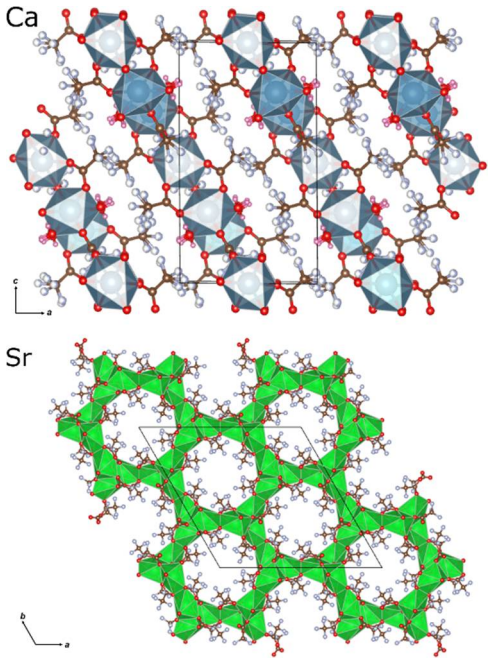

Figure S10. Crystal structures of $Ca_3(tfa)_6{\cdot}4H_2O$ (298 K) and $Sr(tfa)_2$ (100K). Ca: blue; Sr: green; C: brown; O: red; F: light blue; H: pink. $Ba(tfa)_2$ is isostructural with the strontium compound.

the alkaline-earth cation (Mg^{2+} 72 pm, C.N. = 6; Ca^{2+} 100 pm, C.N. = 6; Sr^{2+} 121 pm, C.N. = 7; Ba^{2+} 147 pm, C.N. = 9).[8] The increase in coordination number is accompanied by a reduction in the number of coordinating water molecules and by an increase in the connectivity of metal–oxygen polyhedra. Four water molecules coordinate to Mg^{2+} and the magnesium–oxygen network consists of octahedral monomers connected through hydrogen bonds. In contrast, the central calcium atom of the calcium–oxygen trimers in $Ca_3(tfa)_6{\cdot}4H_2O$ is bonded to trifluoroacetate ligands only, while the two terminal calcium atoms are coordinated by both water and trifluoroacetates. These edge-sharing octahedra are arranged to form a layered structure in which hydrogen bonds between coordinated water molecules play a significant role in terms of shaping the three-dimensional structural layout. No coordinating water

molecules are observed in the cases of $Sr(tfa)_2$ and $Ba(tfa)_2$, which display a three-dimensional network of edge- and face-sharing polyhedra. Considering that the synthesis conditions were the same for all four alkaline-earth trifluoroacetates (i.e., evaporation of H_2O and tfaH under dry nitrogen flow), it is clear that the trifluoroacetate ligand alone is not capable of stabilizing the harder Mg^{2+} and Ca^{2+} alkaline-earth cations and, as a result, the corresponding anhydrous trifluoroacetates are not obtained. In addition, the observation that magnesium and calcium compounds retain coordinating water molecules while the strontium and barium counterparts do not, illustrates to the increasing flexibility of the coordination polyhedra of alkaline-earth cations as their size increases. Magnesium–oxygen octahedra are close to regular and it is likely that no regular octahedra would be observed if the cation was surrounded only by trifluoroacetate anions. In contrast, calcium–oxygen octahedra in $Ca_3(tfa)_6{\cdot}4H_2O$ exhibit significantly larger geometric distortions. Indeed, Ca–O bond distances are in the 2.318–2.464 Å (terminal Ca) and 2.282–2.421 (central Ca) Å ranges (*vs* 2.0259 (18)–2.0995 (16) Å for Mg–O). Similarly, O–Ca–O bond angles are in the 166.7–178.76° (*trans*) and 77.94–110.07° (*cis*) ranges for the terminal Ca atom, and 180° (*trans*) 79.23–100.77° (*cis*) range for the central Ca atom (*vs* 176.19 (8)–177.43 (7)° (*trans*) and 87.67 (7)–94.15 (7)° (*cis*) for O–Mg–O).[7] Thus, the magnesium and calcium trifluoroacetates keep water molecules in the coordination sphere for both electronic and geometric reasons. Finally, we note that the structures of all four trifluoroacetates display a significant fraction of void space: channels in $Mg(tfa)_2{\cdot}4H_2O$, $Sr(tfa)_2$, and $Ba(tfa)_2$, and an interlayer gap in $Ca_3(tfa)_6{\cdot}4H_2O$. Further, in all cases those voids are lined with the trifluoromethyl groups of the trifluoroacetate ligands. All together, these observations suggest that the crystal structures of the alkaline-earth trifluoroacetates result from a balance between the electronic demand of the alkaline-earth cation, the relative abilities of the water and

trifluoroacetate ligands to satisfy that demand under the synthesis conditions employed in this work, and the stereochemical interactions between the trifluoromethyl groups.

Rietveld Analysis of Polycrystalline $Mn_x(tfa)_{2x}\cdot 4H_2O$ (298 K)

Rietveld analysis was conducted using the General Structure Analysis System (GSAS) with the graphical user interphase (EXPGUI) software.[1-4] The pattern was fit using a mixture of the two hydrates of $Mn_x(tfa)_{2x}\cdot 4H_2O$: trimeric (space-group $P2_1/n$, x = 3) and monomeric (space-group $C2/c$, x = 1). The following parameters were refined: (1) scale factor for each phase; (2) background, which was modeled using a shifted Chebyschev polynomial function; (3) peak shape, which was modeled using a modified Thompson–Cox–Hasting pseudo-Voight function;[5] and (4) lattice constants for the monomeric phase. R_{wp} and χ^2 residuals were employed to assess the quality of the refined structural models.[6] The resulting Rietveld fit and the refined lattice constants are given in Figure S10.

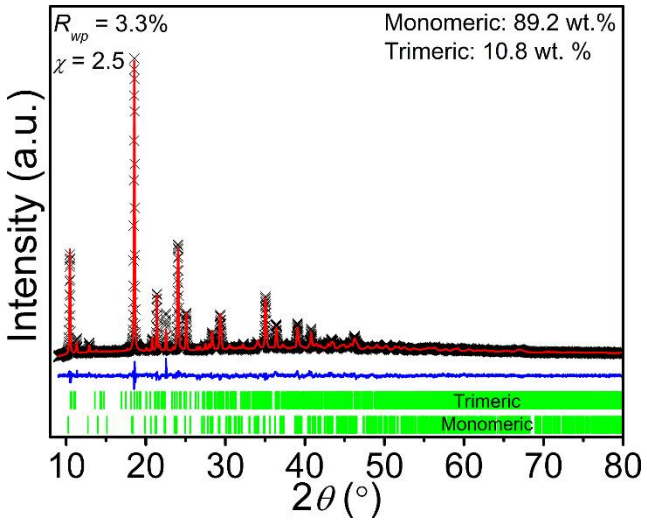

Figure S11. Rietveld analysis of the room-temperature X-ray diffraction data of polycrystalline $Mn_x(tfa)_{2x}\cdot 4H_2O$. Experimental data was fit using a mixture of the trimeric (x = 3) and monomeric (x = 1) compounds. Experimental data (○), calculated pattern (—), and difference curve (—) are shown. Tick

marks (|) corresponding to the calculated position of the diffraction maxima of the two hydrates are included. Refined lattice constants for the monomeric phase: a = 13.3432(5) Å, b = 12.6814(6) Å, c = 8.4702(4) Å, β = 118.463(3)°, V = 1260.00(10) Å^3.

Thermal Analyses of $Mg(tfa)_2 \cdot 4H_2O$ and $Mn_x(tfa)_{2x} \cdot 4H_2O$

Thermogravimetric analysis (TGA) was conducted using a Pyris 1 TGA analyzer (Perkin-Elmer). ~5–10 mg of sample were heated at 35 °C for 30 min under flowing nitrogen (20 mL min^{-1}), and then ramped to 600 °C at a rate of 10 °C min^{-1}. Differential thermal analysis (DTA) was conducted using an SDT2960 TGA-DTA analyzer (TA Instruments) under identical conditions.

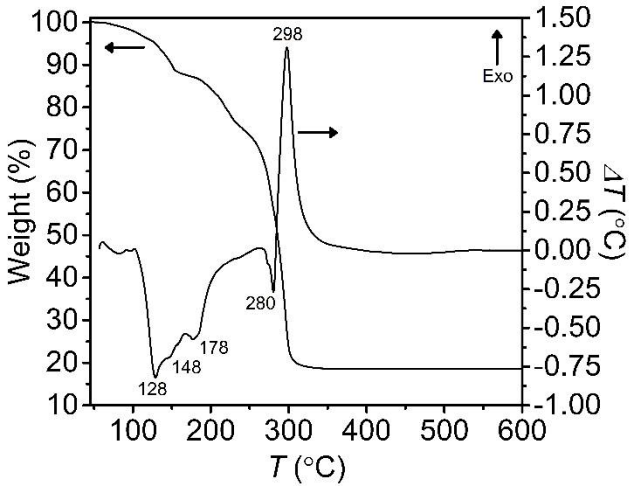

Figure S12. Thermogravimetric and differential thermogravimetric analyses of $Mg(tfa)_2 \cdot 4H_2O$.

Thermogravimetric analysis of $Mg(tfa)_2 \cdot 4H_2O$ resulted in a total weight loss of ~81.6 wt. % at 600 °C, in excellent agreement with the expected value (77.6 wt. %) for its complete transformation into MgF_2. The differential thermogram shows four endothermic peaks at 128, 148, 178, and 280 °C, resulting from the release of coordinating water molecules and decomposition of the trifluoroacetate ligands. The exothermic peak at 298 °C corresponds to the crystallization of MgF_2.

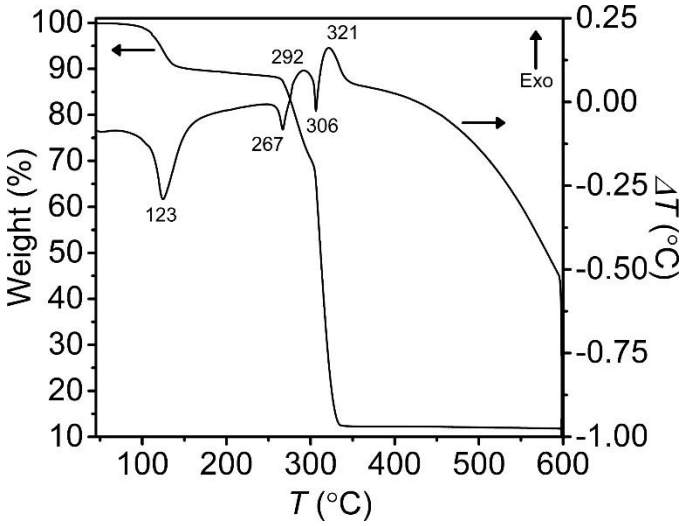

Figure S13. Thermogravimetric and differential thermogravimetric analyses of $Mn_x(tfa)_{2x}\cdot 4H_2O$ (mixture of two hydrates).

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