Polar metal-formate frameworks templated with 1,2-diaminoethane-water assemblies showing ferromagnetic and ferroelectric properties

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Electronic Supplementary Information

Single-crystal X-ray diffraction

Table S1. The geometry of hydrogen bonding (Å, °).

DAEMgF

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
C1—H1···O3	0.93	2.56	3.116 (4)	118.5
C2—H2···O4^{i}	0.93	2.57	3.141 (4)	120.3
C2—H2···O5	0.93	2.65	3.126 (4)	112.2
C3—H3···O8^{ii}	0.93	2.55	3.116 (4)	119.8
C4—H4···O7	0.93	2.54	3.137 (4)	122.1
C21—H21E···O4^{iii}	0.97	2.67	3.325 (4)	124.9
C22—H22D···O2	0.97	2.50	3.142 (4)	123.2
N21—H21A···O3^{iii}	0.89	2.14	2.932 (4)	147.7
N21—H21A···O11^{iii}	0.89	2.52	3.129 (4)	126.4
N21—H21B···OW^{iv}	0.89	1.92	2.733 (4)	150.6
N21—H21C···O1	0.89	1.97	2.836 (4)	163.3
N21—H21C···O2	0.89	2.63	3.335 (4)	136.3
N22—H22A···OW	0.89	1.94	2.749 (4)	149.6
N22—H22B···O6^{v}	0.89	1.94	2.813 (4)	167.1
N22—H22C···O12^{vi}	0.89	2.11	2.893 (4)	146.9
OW—HW1···O8^{vii}	0.83 (5)	2.70 (5)	3.163 (3)	117 (4)
OW—HW1···O7^{vii}	0.83 (5)	1.94 (5)	2.758 (4)	171 (5)
OW—HW2···O9^{viii}	0.94 (4)	2.54 (4)	3.172 (4)	125 (3)
OW—HW2···O10^{viii}	0.94 (4)	1.85 (5)	2.784 (4)	172 (4)

Symmetry code(s): (i) −*x*+*y*+1, −*x*+2, *z*; (ii) −*y*+2, *x*−*y*+1, *z*; (iii) −*y*+1, *x*−*y*, *z*; (iv) −*y*+2/3, *x*−*y*+1/3, *z*+1/3; (v) −*x*+*y*, −*x*+1, *z*; (vi) *x*−2/3, *y*−1/3, *z*−1/3; (vii) −*y*+4/3, *x*−*y*+2/3, *z*−1/3; (viii) −*x*+*y*+1/3, −*x*+2/3, *z*−1/3.

DAEMnF

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
C1—H1···O3	0.93	2.63	3.222 (6)	122.1
C2—H2···O4^{i}	0.93	2.63	3.233 (6)	123.4
C4—H4···O8^{ii}	0.93	2.63	3.227 (6)	122.7
C5—H5···O7	0.93	2.64	3.256 (6)	124.6
C21—H21D···O6^{iii}	0.97	2.69	3.367 (7)	127.7
C21—H21E···O4^{iv}	0.97	2.65	3.302 (7)	124.9
C22—H22D···O2	0.97	2.50	3.152 (7)	124.3
N21—H21A···OW^{v}	0.89	1.93	2.754 (7)	154.0
N21—H21B···O1	0.89	1.96	2.839 (6)	171.2

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N21—H21C···O3^{iv}	0.89	2.14	2.912 (6)	144.8
N22—H22A···OW	0.89	1.94	2.758 (7)	151.2
N22—H22B···O6^{iii}	0.89	1.97	2.828 (6)	161.2
N22—H22C···O12^{vi}	0.89	2.20	2.908 (6)	136.2
OW—HW1···O7^{vii}	0.79 (6)	2.00 (6)	2.788 (5)	178 (7)
OW—HW2···O9^{viii}	1.06 (6)	2.60 (6)	3.168 (5)	113 (4)
OW—HW2···O10^{viii}	1.06 (6)	1.74 (6)	2.786 (5)	169 (5)

Symmetry code(s): (i) −*y*+2, *x*−*y*+1, *z*; (ii) −*x*+*y*+1, −*x*+2, *z*; (iii) −*y*+1, *x*−*y*, *z*; (iv) −*x*+*y*, −*x*+1, *z*; (v) −*x*+*y*+1/3, −*x*+2/3, *z*−1/3; (vi) *x*−1/3, *y*−2/3, *z*+1/3; (vii) −*x*+*y*+2/3, −*x*+4/3, *z*+1/3; (viii) −*y*+2/3, *x*−*y*+1/3, *z*+1/3.

DAECoF

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
C21A—H21E···O5^{i}	0.97	2.68	3.17 (2)	111.4
C21A—H21E···O6^{i}	0.97	2.77	3.43 (2)	125.4
C22B—H22I···O12^{ii}	0.97	2.39	3.10 (4)	129.4
C22A—H22E···O2	0.97	2.44	3.08 (2)	123.3
N21B—H21H···O11^{ii}	0.89	2.05	2.88 (3)	154.6
N21B—H21G···O1	0.89	2.48	3.02 (3)	118.9
N21B—H21G···O9	0.89	2.15	2.96 (3)	150.6
N21B—H21F···OWB	0.89	1.88	2.69 (4)	150.6
N21A—H21C···O1	0.89	1.89	2.768 (18)	167.2
N21A—H21B···O3^{ii}	0.89	2.29	3.026 (17)	140.5
N21A—H21B···O11^{ii}	0.89	2.52	3.052 (18)	119.1
N21A—H21A···OWA	0.89	2.06	2.84 (2)	145.9
N22B—H22G···O10	0.89	2.69	3.33 (3)	129.2
N22A—H22C···O6^{i}	0.89	1.97	2.839 (17)	163.9
N22A—H22B···O4^{ii}	0.89	2.55	3.224 (17)	133.4
N22A—H22B···O12^{iii}	0.89	2.24	2.899 (16)	130.5
N22A—H22A···OWA^{iv}	0.89	1.89	2.67 (2)	145.1
C1—H1···O3	0.93	2.60	3.159 (12)	119.3
C2—H2···O4^{v}	0.93	2.59	3.153 (13)	119.3
C2—H2···O5	0.93	2.63	3.146 (13)	115.6
C4—H4···O8^{vi}	0.93	2.59	3.160 (12)	119.8
C5—H5···O7	0.93	2.59	3.147 (12)	119.1
C6—H6···O12^{ii}	0.93	2.65	3.150 (12)	114.4
OWB—HWB1···O6^{i}	0.8400 (14)	2.66 (15)	3.24 (3)	128 (15)
OWA—HWA1···O10	0.843 (14)	1.91 (7)	2.728 (16)	162 (21)
OWA—HWA2···N21A	0.843 (14)	2.3 (2)	2.84 (2)	125 (22)

Symmetry code(s): (i) *z*, *x*+1, *y*−1; (ii) *y*, *z*, *x*; (iii) *x*, *y*, *z*−1; (iv) *z*, *x*, *y*−1; (v) *z*−1, *x*+1, *y*; (vi) *y*−1, *z*, *x*+1.

DAENiF

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
C1—H1···O1^{i}	1.02 (6)	2.57 (2)	3.130 (3)	114.1 (12)
C1—H1···O1^{ii}	1.02 (6)	2.57 (2)	3.130 (3)	114.1 (12)
C1—H1···OW^{iii}	1.02 (6)	2.54 (6)	3.56 (2)	180.000 (4)
C21—H21D···O1^{v}	0.9700 (14)	2.48 (9)	3.221 (2)	133 (9)
C21—H21D···OW	0.9700 (14)	2.67 (11)	3.035 (16)	103 (8)
N21—H21A···OW	0.92	1.49	2.339 (19)	152.4
N21—H21B···O1^{vi}	0.89	2.00	2.80 (3)	150.1
N21—H21C···O1	0.91	2.50	3.17 (4)	131.4
N21—H21C···O1^{vii}	0.91	2.21	2.95 (3)	138.2
OW—HW1···N21^{viii}	0.841 (14)	2.15 (8)	2.76 (2)	130 (7)
OW—HW1···N21^{ix}	0.841 (14)	1.67 (7)	2.339 (19)	135 (7)
OW—HW2···O1^{iv}	0.841 (14)	2.4 (3)	2.785 (11)	106 (22)
OW—HW2···O1^{ix}	0.841 (14)	2.7 (3)	3.194 (2)	121 (26)

Symmetry code(s): (i) −*x*+*y*+1, −*x*+1, *z*; (ii) −*x*+1, −*x*+*y*+1, −*z*+1; (iii) −*y*+1, *x*−*y*+1, *z*; (iv) −*y*, *x*−*y*, *z*; (v) −*x*+*y*, *y*, −*z*+1/2; (vi) −*x*+*y*, −*x*, *z*; (vii) *x*, *x*−*y*, −*z*+1/2; (viii) *y*, −*x*+*y*, *z*+1/2; (ix) −*x*, −*x*+*y*, −*z*+1.

DAEZnF

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
C1—H1···O3	0.93	2.57	3.140 (15)	120.3
C2—H2···O4^{i}	0.93	2.60	3.170 (16)	119.8
C3—H3···O1	0.93	2.63	3.178 (14)	118.4
C4—H4···O8^{ii}	0.93	2.62	3.183 (15)	119.2
C4—H4···O11	0.93	2.58	3.124 (15)	117.6
C5—H5···O7	0.93	2.60	3.168 (14)	120.1
N21A—H21A···OWA	0.89	1.99	2.79 (3)	148.9
N21A—H21B···O9	0.89	1.91	2.77 (2)	164.2
N21A—H21C···O5^{iii}	0.89	2.50	3.05 (2)	120.1
N21A—H21C···O7^{iii}	0.89	2.21	2.96 (2)	142.6
N22A—H22A···OWA^{iv}	0.89	1.90	2.67 (3)	143.8
N22A—H22B···O12^{v}	0.89	1.91	2.78 (2)	164.2
N22A—H22C···O6^{vi}	0.89	2.24	2.91 (2)	132.1
N22A—H22C···O8^{iii}	0.89	2.62	3.29 (2)	132.7
C21A—H21D···O11^{v}	0.97	2.69	3.14 (3)	109.0
C21A—H21D···O12^{v}	0.97	2.63	3.30 (2)	126.5
C22A—H22D···O10	0.97	2.44	3.07 (2)	122.8
OWA—HW1A···O2	0.840 (14)	1.91 (6)	2.726 (18)	162 (17)
OWA—HW2A···N22A^{vii}	0.840 (14)	2.1 (2)	2.67 (3)	125 (20)
N21B—H21F···OWB	0.89	1.91	2.74 (4)	155.4
N21B—H21H···O1	0.89	2.26	2.99 (3)	138.9
N21B—H21H···O9	0.89	2.39	3.01 (3)	126.6
N22B—H22H···O2	0.89	2.60	3.26 (4)	132.1

Symmetry code(s): (i) −*y*, *x*−*y*, *z*; (ii) −*x*+*y*, −*x*, *z*; (iii) −*y*, *x*−*y*+1, *z*; (iv) −*x*+*y*−2/3, −*x*+2/3, *z*−1/3; (v) −*x*+*y*, −*x*+1, *z*; (vi) *x*+1/3, *y*+2/3, *z*−1/3; (vii) −*y*+2/3, *x*−*y*+4/3, *z*+1/3.

Table S2. The selected geometric parameters (Å, °).

DAEMgF			
Bond (Å)			
Mg0—O9	2.073 (2)	C2—O3	1.258 (4)
Mg0—O3	2.076 (2)	C3—O8	1.242 (4)
Mg0—O5	2.090 (2)	C3—O7	1.259 (4)
Mg0—O11	2.093 (2)	Mg3—O8	2.090 (2)
Mg0—O1	2.095 (2)	Mg3—O8^{viii}	2.090 (2)
Mg0—O7	2.107 (2)	Mg3—O8^{ix}	2.090 (2)
C1—O1	1.241 (4)	Mg3—O6^{x}	2.093 (2)
C1—O2	1.243 (4)	Mg3—O6^{xi}	2.093 (2)
Mg1—O2^{i}	2.073 (2)	Mg3—O6^{xii}	2.093 (2)
Mg1—O2^{ii}	2.073 (2)	C4—O9	1.236 (4)
Mg1—O2	2.073 (2)	C4—O10	1.241 (4)
Mg1—O10^{iii}	2.090 (2)	O10—Mg1^{xiii}	2.090 (2)
Mg1—O10^{iv}	2.090 (2)	O5—C6	1.225 (4)
Mg1—O10^{v}	2.090 (2)	C5—O11	1.235 (4)
Mg2—O12^{vi}	2.073 (2)	C5—O12	1.249 (4)
Mg2—O12^{iii}	2.073 (2)	C6—O6	1.252 (4)
Mg2—O12^{vii}	2.074 (2)	O6—Mg3^{xiv}	2.093 (2)
Mg2—O4^{viii}	2.096 (2)	O12—Mg2^{xv}	2.073 (2)
Mg2—O4	2.096 (2)	N21—C21	1.486 (5)
Mg2—O4^{ix}	2.096 (2)	C21—C22	1.512 (6)
C2—O4	1.235 (4)	N22—C22	1.469 (5)
Angle (°)			
O9—Mg0—O3	176.44 (10)	O12^{vii}—Mg2—O4	84.55 (9)
O9—Mg0—O5	90.51 (11)	O4^{viii}—Mg2—O4	92.18 (11)
O3—Mg0—O5	90.94 (10)	O12^{vi}—Mg2—O4^{ix}	90.46 (10)

O9—Mg0—O11	92.14 (10)	O12^{iii}—Mg2—O4^{ix}	84.56 (9)
O3—Mg0—O11	86.38 (10)	O12^{vii}—Mg2—O4^{ix}	175.88 (9)
O5—Mg0—O11	177.30 (12)	O4^{viii}—Mg2—O4^{ix}	92.18 (11)
O9—Mg0—O1	86.42 (10)	O4—Mg2—O4^{ix}	92.18 (11)
O3—Mg0—O1	90.32 (10)	C1—O2—Mg1	129.3 (2)
O5—Mg0—O1	90.46 (11)	O4—C2—O3	126.7 (3)
O11—Mg0—O1	89.21 (10)	O8—C3—O7	125.7 (3)
O9—Mg0—O7	92.40 (10)	O8—Mg3—O8^{viii}	91.58 (11)
O3—Mg0—O7	90.85 (10)	O8—Mg3—O8^{ix}	91.58 (11)
O5—Mg0—O7	89.76 (10)	O8^{viii}—Mg3—O8^{ix}	91.58 (11)
O11—Mg0—O7	90.63 (10)	O8—Mg3—O6^{x}	178.27 (10)
O1—Mg0—O7	178.80 (11)	O8^{viii}—Mg3—O6^{x}	86.93 (9)
O1—C1—O2	125.5 (3)	O8^{ix}—Mg3—O6^{x}	89.34 (9)
O2^{i}—Mg1—O2^{ii}	88.05 (12)	O8—Mg3—O6^{xi}	86.92 (9)
O2^{i}—Mg1—O2	88.05 (12)	O8^{viii}—Mg3—O6^{xi}	89.34 (9)
O2^{ii}—Mg1—O2	88.05 (12)	O8^{ix}—Mg3—O6^{xi}	178.27 (10)
O2^{i}—Mg1—O10^{iii}	87.37 (9)	O6^{x}—Mg3—O6^{xi}	92.18 (11)
O2^{ii}—Mg1—O10^{iii}	175.14 (10)	O8—Mg3—O6^{xii}	89.34 (9)
O2—Mg1—O10^{iii}	93.44 (10)	O8^{viii}—Mg3—O6^{xii}	178.27 (10)
O2^{i}—Mg1—O10^{iv}	175.14 (10)	O8^{ix}—Mg3—O6^{xii}	86.93 (9)
O2^{ii}—Mg1—O10^{iv}	93.44 (10)	O6^{x}—Mg3—O6^{xii}	92.18 (11)
O2—Mg1—O10^{iv}	87.38 (9)	O6^{xi}—Mg3—O6^{xii}	92.18 (11)
O10^{iii}—Mg1—O10^{iv}	91.26 (12)	C2—O3—Mg0	124.4 (2)
O2^{i}—Mg1—O10^{v}	93.44 (10)	O9—C4—O10	127.5 (3)
O2^{ii}—Mg1—O10^{v}	87.37 (9)	C2—O4—Mg2	125.4 (2)
O2—Mg1—O10^{v}	175.14 (10)	C4—O9—Mg0	127.4 (2)
O10^{iii}—Mg1—O10^{v}	91.25 (12)	C3—O8—Mg3	125.8 (2)
O10^{iv}—Mg1—O10^{v}	91.26 (12)	C3—O7—Mg0	125.5 (2)
C1—O1—Mg0	129.8 (2)	C4—O10—Mg1^{xiii}	126.1 (2)
O12^{vi}—Mg2—O12^{iii}	92.95 (11)	C6—O5—Mg0	130.7 (2)
O12^{vi}—Mg2—O12^{vii}	92.95 (11)	O11—C5—O12	127.0 (3)
O12^{iii}—Mg2—O12^{vii}	92.95 (11)	O5—C6—O6	126.5 (3)
O12^{vi}—Mg2—O4^{viii}	84.55 (9)	C6—O6—Mg3^{xiv}	132.4 (2)
O12^{iii}—Mg2—O4^{viii}	175.89 (9)	C5—O12—Mg2^{xv}	130.7 (2)
O12^{vii}—Mg2—O4^{viii}	90.45 (10)	C5—O11—Mg0	127.1 (2)
O12^{vi}—Mg2—O4	175.88 (9)	N21—C21—C22	111.2 (3)
O12^{iii}—Mg2—O4	90.45 (10)	N22—C22—C21	111.1 (3)
Dihedral (Å)			
O2—C1—O1—Mg0	−179.3 (3)	O9—C4—O10—Mg1^{xiii}	−173.8 (3)
O1—C1—O2—Mg1	−157.8 (3)	Mg0—O5—C6—O6	−177.6 (3)
O4—C2—O3—Mg0	−176.9 (3)	O5—C6—O6—Mg3^{xiv}	168.2 (3)
O3—C2—O4—Mg2	175.4 (3)	O11—C5—O12—Mg2^{xv}	−178.7 (3)
O10—C4—O9—Mg0	174.7 (3)	O12—C5—O11—Mg0	−174.5 (3)
O7—C3—O8—Mg3	174.9 (3)	N21—C21—C22—N22	174.1 (3)
O8—C3—O7—Mg0	−175.8 (3)		
DAEMnF			
Bond (Å)			
Mn0—O9	2.155 (4)	Mn3—O8^{xii}	2.185 (3)
Mn0—O3	2.174 (3)	Mn3—O8^{xiii}	2.185 (3)
Mn0—O5	2.188 (4)	Mn3—O8^{iv}	2.185 (3)
Mn0—O1	2.192 (3)	O1—C1	1.247 (6)
Mn0—O11	2.193 (4)	O2—C1	1.238 (6)
Mn0—O7	2.204 (3)	O3—C2	1.263 (6)
Mn1—O2^{i}	2.167 (3)	O4—C2	1.236 (6)
Mn1—O2^{ii}	2.167 (4)	O5—C3	1.229 (6)
Mn1—O2	2.167 (3)	O6—C3	1.254 (6)
Mn1—O10^{iii}	2.185 (4)	O7—C4	1.250 (6)

Mn1—O10^{iv}	2.185 (4)	O8—C4	1.240 (6)
Mn1—O10^{v}	2.185 (3)	O8—Mn3^{xiv}	2.185 (3)
Mn2—O12^{vi}	2.166 (3)	O9—C5	1.235 (6)
Mn2—O12^{iv}	2.166 (3)	O10—C5	1.238 (6)
Mn2—O12^{vii}	2.166 (3)	O10—Mn1^{xv}	2.185 (3)
Mn2—O4^{viii}	2.186 (3)	O11—C6	1.238 (6)
Mn2—O4	2.186 (3)	O12—C6	1.240 (6)
Mn2—O4^{ix}	2.186 (3)	O12—Mn2^{xvi}	2.166 (3)
Mn3—O6^{x}	2.175 (3)	N22—C22	1.482 (8)
Mn3—O6	2.175 (3)	C22—C21	1.502 (9)
Mn3—O6^{xi}	2.175 (3)	N21—C21	1.497 (8)
Angle (°)			
O9—Mn0—O3	174.53 (14)	O12^{vi}—Mn2—O4^{ix}	91.74 (14)
O9—Mn0—O5	91.83 (15)	O12^{iv}—Mn2—O4^{ix}	82.24 (13)
O3—Mn0—O5	90.23 (14)	O12^{vii}—Mn2—O4^{ix}	173.37 (13)
O9—Mn0—O1	83.98 (14)	O4^{viii}—Mn2—O4^{ix}	92.44 (15)
O3—Mn0—O1	90.95 (14)	O4—Mn2—O4^{ix}	92.44 (15)
O5—Mn0—O1	90.18 (15)	O6^{x}—Mn3—O6	93.23 (15)
O9—Mn0—O11	93.30 (15)	O6^{x}—Mn3—O6^{xi}	93.23 (15)
O3—Mn0—O11	84.65 (13)	O6—Mn3—O6^{xi}	93.23 (15)
O5—Mn0—O11	174.87 (15)	O6^{x}—Mn3—O8^{xii}	179.07 (17)
O1—Mn0—O11	90.27 (15)	O6—Mn3—O8^{xii}	87.61 (14)
O9—Mn0—O7	93.22 (14)	O6^{xi}—Mn3—O8^{xii}	87.14 (15)
O3—Mn0—O7	91.88 (13)	O6^{x}—Mn3—O8^{xiii}	87.14 (15)
O5—Mn0—O7	88.95 (14)	O6—Mn3—O8^{xiii}	179.07 (17)
O1—Mn0—O7	177.04 (14)	O6^{xi}—Mn3—O8^{xiii}	87.60 (13)
O11—Mn0—O7	90.85 (15)	O8^{xii}—Mn3—O8^{xiii}	92.02 (16)
O2^{i}—Mn1—O2^{ii}	88.21 (17)	O6^{x}—Mn3—O8^{iv}	87.61 (14)
O2^{i}—Mn1—O2	88.21 (17)	O6—Mn3—O8^{iv}	87.14 (15)
O2^{ii}—Mn1—O2	88.21 (17)	O6^{xi}—Mn3—O8^{iv}	179.07 (17)
O2^{i}—Mn1—O10^{iii}	94.78 (15)	O8^{xii}—Mn3—O8^{iv}	92.02 (16)
O2^{ii}—Mn1—O10^{iii}	172.89 (14)	O8^{xiii}—Mn3—O8^{iv}	92.02 (16)
O2—Mn1—O10^{iii}	85.44 (14)	C1—O1—Mn0	127.7 (3)
O2^{i}—Mn1—O10^{iv}	172.89 (14)	C1—O2—Mn1	127.3 (3)
O2^{ii}—Mn1—O10^{iv}	85.44 (15)	C2—O3—Mn0	123.1 (3)
O2—Mn1—O10^{iv}	94.78 (15)	C2—O4—Mn2	123.2 (3)
O10^{iii}—Mn1—O10^{iv}	91.89 (16)	C3—O5—Mn0	130.0 (3)
O2^{i}—Mn1—O10^{v}	85.44 (15)	C3—O6—Mn3	131.2 (3)
O2^{ii}—Mn1—O10^{v}	94.78 (15)	C4—O7—Mn0	124.4 (3)
O2—Mn1—O10^{v}	172.89 (14)	C4—O8—Mn3^{xiv}	124.3 (3)
O10^{iii}—Mn1—O10^{v}	91.90 (16)	C5—O9—Mn0	126.2 (3)
O10^{iv}—Mn1—O10^{v}	91.89 (16)	C5—O10—Mn1^{xv}	124.8 (3)
O12^{vi}—Mn2—O12^{iv}	93.92 (15)	C6—O11—Mn0	125.7 (3)
O12^{vi}—Mn2—O12^{vii}	93.92 (15)	C6—O12—Mn2^{xvi}	129.7 (3)
O12^{iv}—Mn2—O12^{vii}	93.92 (15)	O2—C1—O1	125.1 (5)
O12^{vi}—Mn2—O4^{viii}	82.24 (13)	O4—C2—O3	126.3 (5)
O12^{iv}—Mn2—O4^{viii}	173.37 (13)	O5—C3—O6	126.5 (5)
O12^{vii}—Mn2—O4^{viii}	91.74 (14)	O8—C4—O7	125.4 (5)
O12^{vi}—Mn2—O4	173.37 (13)	O9—C5—O10	127.5 (5)
O12^{iv}—Mn2—O4	91.74 (14)	O11—C6—O12	126.8 (5)
O12^{vii}—Mn2—O4	82.24 (13)	N22—C22—C21	111.4 (4)
O4^{viii}—Mn2—O4	92.44 (15)	N21—C21—C22	110.0 (5)
Dihedral (°)			
Mn1—O2—C1—O1	−159.0 (4)	Mn0—O7—C4—O8	−176.3 (4)
Mn0—O1—C1—O2	−175.4 (4)	Mn0—O9—C5—O10	177.0 (5)
Mn2—O4—C2—O3	174.3 (4)	Mn1^{xv}—O10—C5—O9	−175.3 (5)
Mn0—O3—C2—O4	−179.6 (4)	Mn0—O11—C6—O12	−172.5 (5)

Mn0—O5—C3—O6	179.1 (4)	Mn2^{xvi}—O12—C6—O11	−177.5 (4)
Mn3—O6—C3—O5	168.6 (4)	N22—C22—C21—N21	173.5 (4)
Mn3^{xiv}—O8—C4—O7	175.0 (4)		
DAECoF			
Bond (Å)			
Co0—O3	2.082 (7)	Co3—O8^{iii}	2.123 (7)
Co0—O5	2.092 (7)	O1—C1	1.252 (11)
Co0—O11	2.100 (7)	O2—C1	1.231 (11)
Co0—O9	2.102 (7)	O3—C2	1.242 (12)
Co0—O1	2.107 (7)	O4—C2	1.238 (12)
Co0—O7	2.112 (8)	O5—C3	1.243 (12)
Co1—O2	2.089 (7)	O6—C3	1.258 (13)
Co1—O2^{i}	2.089 (7)	O7—C4	1.242 (12)
Co1—O2^{ii}	2.089 (7)	O8—C4	1.239 (13)
Co1—O10^{iii}	2.090 (7)	O8—Co3^{xiv}	2.123 (7)
Co1—O10^{iv}	2.090 (7)	O9—C5	1.242 (12)
Co1—O10^{v}	2.090 (7)	O10—C5	1.245 (12)
Co2—O12^{iii}	2.093 (7)	O10—Co1^{xv}	2.090 (7)
Co2—O12^{vi}	2.093 (7)	O11—C6	1.236 (12)
Co2—O12^{vii}	2.093 (7)	O12—C6	1.236 (12)
Co2—O4	2.100 (7)	O12—Co2^{xvi}	2.093 (7)
Co2—O4^{viii}	2.100 (7)	N21A—C21A	1.37 (2)
Co2—O4^{ix}	2.100 (7)	N22A—C22A	1.46 (3)
Co3—O6^{x}	2.089 (7)	C21A—C22A	1.58 (2)
Co3—O6	2.089 (7)	N21B—C21B	1.45 (6)
Co3—O6^{xi}	2.089 (7)	N22B—C22B	1.57 (5)
Co3—O8^{xii}	2.123 (7)	C22B—C21B	1.46 (5)
Co3—O8^{xiii}	2.123 (7)		
Angle (°)			
O3—Co0—O5	91.7 (3)	O12^{vi}—Co2—O4^{ix}	84.8 (3)
O3—Co0—O11	85.2 (3)	O12^{vii}—Co2—O4^{ix}	92.6 (3)
O5—Co0—O11	176.5 (3)	O4—Co2—O4^{ix}	92.2 (4)
O3—Co0—O9	175.8 (3)	O4^{viii}—Co2—O4^{ix}	92.2 (4)
O5—Co0—O9	91.0 (3)	O6^{x}—Co3—O6	93.4 (3)
O11—Co0—O9	92.2 (3)	O6^{x}—Co3—O6^{xi}	93.4 (3)
O3—Co0—O1	92.2 (3)	O6—Co3—O6^{xi}	93.4 (3)
O5—Co0—O1	90.9 (3)	O6^{x}—Co3—O8^{xii}	88.0 (3)
O11—Co0—O1	90.7 (4)	O6—Co3—O8^{xii}	178.6 (4)
O9—Co0—O1	84.5 (3)	O6^{xi}—Co3—O8^{xii}	87.0 (3)
O3—Co0—O7	91.1 (3)	O6^{x}—Co3—O8^{xiii}	178.6 (4)
O5—Co0—O7	87.6 (3)	O6—Co3—O8^{xiii}	87.0 (3)
O11—Co0—O7	90.9 (4)	O6^{xi}—Co3—O8^{xiii}	88.0 (3)
O9—Co0—O7	92.2 (3)	O8^{xii}—Co3—O8^{xiii}	91.7 (3)
O1—Co0—O7	176.4 (3)	O6^{x}—Co3—O8^{iii}	87.0 (3)
O2—Co1—O2^{i}	91.4 (3)	O6—Co3—O8^{iii}	88.0 (3)
O2—Co1—O2^{ii}	91.4 (3)	O6^{xi}—Co3—O8^{iii}	178.6 (4)
O2^{i}—Co1—O2^{ii}	91.4 (3)	O8^{xii}—Co3—O8^{iii}	91.7 (3)
O2—Co1—O10^{iii}	91.3 (3)	O8^{xiii}—Co3—O8^{iii}	91.7 (3)
O2^{i}—Co1—O10^{iii}	174.8 (3)	C1—O1—Co0	127.8 (7)
O2^{ii}—Co1—O10^{iii}	84.1 (3)	C1—O2—Co1	127.8 (7)
O2—Co1—O10^{iv}	174.8 (3)	C2—O3—Co0	126.0 (7)
O2^{i}—Co1—O10^{iv}	84.1 (3)	C2—O4—Co2	125.3 (7)
O2^{ii}—Co1—O10^{iv}	91.3 (3)	C3—O5—Co0	128.0 (7)
O10^{iii}—Co1—O10^{iv}	93.4 (3)	C3—O6—Co3	128.6 (7)
O2—Co1—O10^{v}	84.1 (3)	C4—O7—Co0	126.3 (7)
O2^{i}—Co1—O10^{v}	91.3 (3)	C4—O8—Co3^{xiv}	125.4 (7)
O2^{ii}—Co1—O10^{v}	174.8 (3)	C5—O9—Co0	125.1 (7)

O10^{iii}—Co1—O10^{v}	93.4 (3)	C5—O10—Co1^{xv}	124.8 (6)
O10^{iv}—Co1—O10^{v}	93.4 (3)	C6—O11—Co0	127.3 (7)
O12^{iii}—Co2—O12^{vi}	90.7 (4)	C6—O12—Co2^{xvi}	128.2 (7)
O12^{iii}—Co2—O12^{vii}	90.7 (4)	O2—C1—O1	125.9 (9)
O12^{vi}—Co2—O12^{vii}	90.7 (4)	O4—C2—O3	127.1 (10)
O12^{iii}—Co2—O4	92.6 (4)	O5—C3—O6	125.7 (10)
O12^{vi}—Co2—O4	174.4 (3)	O8—C4—O7	124.6 (10)
O12^{vii}—Co2—O4	84.8 (3)	O9—C5—O10	126.1 (9)
O12^{iii}—Co2—O4^{viii}	84.8 (3)	O12—C6—O11	126.4 (9)
O12^{vi}—Co2—O4^{viii}	92.6 (3)	N21A—C21A—C22A	110.3 (16)
O12^{vii}—Co2—O4^{viii}	174.4 (3)	N22A—C22A—C21A	114.1 (15)
O4—Co2—O4^{viii}	92.2 (4)	C21B—C22B—N22B	114 (3)
O12^{iii}—Co2—O4^{ix}	174.4 (3)	N21B—C21B—C22B	110 (3)
Dihedral (°)			
Co1—O2—C1—O1	168.2 (9)	Co0—O7—C4—O8	179.6 (8)
Co0—O1—C1—O2	178.0 (9)	Co0—O9—C5—O10	179.8 (9)
Co2—O4—C2—O3	−177.2 (10)	Co1^{xv}—O10—C5—O9	178.7 (9)
Co0—O3—C2—O4	178.6 (10)	Co2^{xvi}—O12—C6—O11	176.6 (9)
Co0—O5—C3—O6	175.7 (9)	Co0—O11—C6—O12	179.6 (9)
Co3—O6—C3—O5	−174.1 (9)	N21A—C21A—C22A—N22A	−172.8 (15)
Co1—O2—C1—O1	168.2 (9)	Co0—O7—C4—O8	179.6 (8)
DAENiF			
Bond (Å)			
Ni0—O1^{xxxvi}	2.0633 (19)	C21—OW^{xliv}	1.102 (16)
Ni0—O1^{ii}	2.0633 (19)	C21—OW^{xlv}	1.102 (16)
Ni0—O1^{i}	2.0633 (19)	C21—OW^{xlvi}	1.102 (16)
Ni0—O1^{xxxvii}	2.0633 (19)	C21—N21^{xliii}	1.294 (16)
Ni0—O1^{xxxviii}	2.0633 (19)	C21—N21^{xxxvii}	1.294 (16)
Ni0—O1	2.0633 (19)	C21—N21^{xl}	1.294 (16)
O1—C1	1.235 (3)	C21—C21^{xlvii}	1.49 (3)
C1—O1^{xxxix}	1.235 (3)	C21—N21^{xlii}	1.705 (19)
N21—N21^{xl}	0.57 (3)	C21—N21^{xli}	1.705 (19)
N21—C21^{xl}	1.294 (16)	OW—C21^{xl}	1.102 (16)
N21—OW^{xli}	1.622 (17)	OW—C21^{xlviii}	1.102 (16)
N21—C21	1.705 (19)	OW—OW^{xlii}	1.40 (4)
N21—N21^{xli}	1.75 (2)	OW—OW^{xli}	1.40 (4)
N21—N21^{xlii}	1.75 (2)	OW—N21^{xxxix}	1.622 (17)
N21—N21^{xxxvii}	1.79 (4)	OW—N21^{xlii}	1.622 (18)
N21—N21^{xliii}	1.89 (4)		
Angle (°)			
O1^{xxxvi}—Ni0—O1^{ii}	85.73 (11)	OW^{xlvi}—C21—N21^{xxxvii}	84.8 (11)
O1^{xxxvi}—Ni0—O1^{i}	90.99 (12)	N21^{xliii}—C21—N21^{xxxvii}	85.3 (12)
O1^{ii}—Ni0—O1^{i}	91.70 (8)	OW^{xliv}—C21—N21^{xl}	154.8 (17)
O1^{xxxvi}—Ni0—O1^{xxxvii}	91.70 (8)	OW^{xlv}—C21—N21^{xl}	84.8 (11)
O1^{ii}—Ni0—O1^{xxxvii}	90.99 (12)	OW^{xlvi}—C21—N21^{xl}	116.8 (15)
O1^{i}—Ni0—O1^{xxxvii}	176.33 (12)	N21^{xliii}—C21—N21^{xl}	85.3 (12)
O1^{xxxvi}—Ni0—O1^{xxxviii}	91.70 (8)	N21^{xxxvii}—C21—N21^{xl}	85.3 (12)
O1^{ii}—Ni0—O1^{xxxviii}	176.33 (12)	OW^{xliv}—C21—C21^{xlvii}	47.4 (10)
O1^{i}—Ni0—O1^{xxxviii}	85.73 (11)	OW^{xlv}—C21—C21^{xlvii}	47.4 (10)
O1^{xxxvii}—Ni0—O1^{xxxviii}	91.70 (8)	OW^{xlvi}—C21—C21^{xlvii}	47.4 (10)
O1^{xxxvi}—Ni0—O1	176.33 (12)	N21^{xliii}—C21—C21^{xlvii}	128.6 (8)
O1^{ii}—Ni0—O1	91.70 (8)	N21^{xxxvii}—C21—C21^{xlvii}	128.6 (8)
O1^{i}—Ni0—O1	91.70 (8)	N21^{xl}—C21—C21^{xlvii}	128.6 (8)
O1^{xxxvii}—Ni0—O1	85.73 (11)	OW^{xliv}—C21—N21^{xlii}	121.5 (13)
O1^{xxxviii}—Ni0—O1	90.99 (12)	OW^{xlv}—C21—N21^{xlii}	159.0 (15)
C1—O1—Ni0	127.2 (2)	OW^{xlvi}—C21—N21^{xlii}	100.3 (10)
O1—C1—O1^{xxxix}	126.8 (4)	N21^{xliii}—C21—N21^{xlii}	72 (2)

N21^{xl}—N21—C21^{xl}	127 (2)	N21^{xxxvii}—C21—N21^{xlii}	15.5 (12)
N21^{xl}—N21—OW^{xli}	169 (2)	N21^{xl}—C21—N21^{xlii}	77 (2)
C21^{xl}—N21—OW^{xli}	42.6 (9)	C21^{xlvii}—C21—N21^{xlii}	143.6 (5)
N21^{xl}—N21—C21	37.1 (13)	OW^{xliv}—C21—N21	159.0 (15)
C21^{xl}—N21—C21	92.1 (11)	OW^{xlv}—C21—N21	100.3 (10)
OW^{xli}—N21—C21	131.6 (12)	OW^{xlvi}—C21—N21	121.5 (13)
N21^{xl}—N21—N21^{xli}	84 (5)	N21^{xliii}—C21—N21	77 (2)
C21^{xl}—N21—N21^{xli}	47.4 (6)	N21^{xxxvii}—C21—N21	72 (2)
OW^{xli}—N21—N21^{xli}	87.6 (9)	N21^{xl}—C21—N21	15.5 (12)
C21—N21—N21^{xli}	59.1 (4)	C21^{xlvii}—C21—N21	143.6 (5)
N21^{xl}—N21—N21^{xlii}	95 (3)	N21^{xlii}—C21—N21	61.9 (9)
C21^{xl}—N21—N21^{xlii}	47.4 (6)	OW^{xliv}—C21—N21^{xli}	100.3 (10)
OW^{xli}—N21—N21^{xlii}	74.4 (10)	OW^{xlv}—C21—N21^{xli}	121.5 (13)
C21—N21—N21^{xlii}	59.1 (4)	OW^{xlvi}—C21—N21^{xli}	159.0 (15)
N21^{xli}—N21—N21^{xlii}	60.001 (2)	N21^{xliii}—C21—N21^{xli}	15.5 (12)
N21^{xl}—N21—N21^{xxxvii}	77 (4)	N21^{xxxvii}—C21—N21^{xli}	77 (2)
C21^{xl}—N21—N21^{xxxvii}	64.8 (15)	N21^{xl}—C21—N21^{xli}	72 (2)
OW^{xli}—N21—N21^{xxxvii}	92.4 (15)	C21^{xlvii}—C21—N21^{xli}	143.6 (5)
C21—N21—N21^{xxxvii}	43.4 (9)	N21^{xlii}—C21—N21^{xli}	61.9 (9)
N21^{xli}—N21—N21^{xxxvii}	64 (2)	N21—C21—N21^{xli}	61.9 (9)
N21^{xlii}—N21—N21^{xxxvii}	18.6 (12)	C21^{xl}—OW—C21^{xlviii}	85 (2)
N21^{xl}—N21—N21^{xliii}	68 (3)	C21^{xl}—OW—OW^{xlii}	50.4 (8)
C21^{xl}—N21—N21^{xliii}	61.5 (15)	C21^{xlviii}—OW—OW^{xlii}	50.4 (8)
OW^{xli}—N21—N21^{xliii}	103.5 (16)	C21^{xl}—OW—OW^{xli}	50.4 (8)
C21—N21—N21^{xliii}	41.8 (9)	C21^{xlviii}—OW—OW^{xli}	50.4 (8)
N21^{xli}—N21—N21^{xliii}	17.7 (9)	OW^{xlii}—OW—OW^{xli}	60.0
N21^{xlii}—N21—N21^{xliii}	59 (2)	C21^{xl}—OW—N21^{xxxix}	133.6 (19)
N21^{xxxvii}—N21—N21^{xliii}	56.8 (3)	C21^{xlviii}—OW—N21^{xxxix}	52.6 (8)
OW^{xliv}—C21—OW^{xlv}	79.2 (15)	OW^{xlii}—OW—N21^{xxxix}	84.6 (14)
OW^{xliv}—C21—OW^{xlvi}	79.2 (15)	OW^{xli}—OW—N21^{xxxix}	101.0 (8)
OW^{xlv}—C21—OW^{xlvi}	79.2 (15)	C21^{xl}—OW—N21^{xlii}	52.6 (8)
OW^{xliv}—C21—N21^{xliii}	84.8 (11)	C21^{xlviii}—OW—N21^{xlii}	133.6 (19)
OW^{xlv}—C21—N21^{xliii}	116.8 (15)	OW^{xlii}—OW—N21^{xlii}	101.0 (8)
OW^{xlvi}—C21—N21^{xliii}	154.8 (17)	OW^{xli}—OW—N21^{xlii}	84.6 (14)
OW^{xliv}—C21—N21^{xxxvii}	116.8 (15)	N21^{xxxix}—OW—N21^{xlii}	174 (2)
OW^{xlv}—C21—N21^{xxxvii}	154.8 (17)		
Dihedral (°)			
Ni0—O1—C1—O1^{xxxix}	179.32 (19)	OW^{xli}—N21—C21—N21^{xxxvii}	31 (4)
N21^{xl}—N21—C21—OW^{xliv}	93 (11)	N21^{xli}—N21—C21—N21^{xxxvii}	84 (3)
C21^{xl}—N21—C21—OW^{xliv}	−70 (4)	N21^{xlii}—N21—C21—N21^{xxxvii}	13 (3)
OW^{xli}—N21—C21—OW^{xliv}	−87 (5)	N21^{xliii}—N21—C21—N21^{xxxvii}	89.3 (9)
N21^{xli}—N21—C21—OW^{xliv}	−34 (4)	C21^{xl}—N21—C21—N21^{xl}	−163 (13)
N21^{xlii}—N21—C21—OW^{xliv}	−105 (4)	OW^{xli}—N21—C21—N21^{xl}	179 (14)
N21^{xxxvii}—N21—C21—OW^{xliv}	−118 (3)	N21^{xli}—N21—C21—N21^{xl}	−127 (13)
N21^{xliii}—N21—C21—OW^{xliv}	−29 (3)	N21^{xlii}—N21—C21—N21^{xl}	162 (13)
N21^{xl}—N21—C21—OW^{xlv}	7 (11)	N21^{xxxvii}—N21—C21—N21^{xl}	149 (10)
C21^{xl}—N21—C21—OW^{xlv}	−156.0 (16)	N21^{xliii}—N21—C21—N21^{xl}	−122 (10)
OW^{xli}—N21—C21—OW^{xlv}	−174 (3)	N21^{xl}—N21—C21—C21^{xlvii}	−17 (13)
N21^{xli}—N21—C21—OW^{xlv}	−120.4 (16)	C21^{xl}—N21—C21—C21^{xlvii}	180.000 (9)
N21^{xlii}—N21—C21—OW^{xlv}	168.3 (16)	OW^{xli}—N21—C21—C21^{xlvii}	162.3 (14)
N21^{xxxvii}—N21—C21—OW^{xlv}	155.3 (16)	N21^{xli}—N21—C21—C21^{xlvii}	−144.34 (19)
N21^{xliii}—N21—C21—OW^{xlv}	−115.4 (16)	N21^{xlii}—N21—C21—C21^{xlvii}	144.34 (19)
N21^{xl}—N21—C21—OW^{xlvi}	−77 (12)	N21^{xxxvii}—N21—C21—C21^{xlvii}	131 (3)
C21^{xl}—N21—C21—OW^{xlvi}	120.4 (18)	N21^{xliii}—N21—C21—C21^{xlvii}	−139 (3)
OW^{xli}—N21—C21—OW^{xlvi}	103 (3)	N21^{xl}—N21—C21—N21^{xlii}	−162 (13)
N21^{xli}—N21—C21—OW^{xlvi}	156.1 (18)	C21^{xl}—N21—C21—N21^{xlii}	35.66 (19)
N21^{xlii}—N21—C21—OW^{xlvi}	84.8 (17)	OW^{xli}—N21—C21—N21^{xlii}	17.9 (15)

N21^{xxxvii}—N21—C21—OW^{xlvi}	71.8 (19)	N21^{xli}—N21—C21—N21^{xlii}	71.3 (4)
N21^{xliii}—N21—C21—OW^{xlvi}	161 (2)	N21^{xxxvii}—N21—C21—N21^{xlii}	−13 (3)
N21^{xl}—N21—C21—N21^{xliii}	122 (10)	N21^{xliii}—N21—C21—N21^{xlii}	76 (3)
C21^{xl}—N21—C21—N21^{xliii}	−41 (3)	N21^{xl}—N21—C21—N21^{xli}	127 (13)
OW^{xli}—N21—C21—N21^{xliii}	−58 (4)	C21^{xl}—N21—C21—N21^{xli}	−35.66 (19)
N21^{xli}—N21—C21—N21^{xliii}	−5 (3)	OW^{xli}—N21—C21—N21^{xli}	−53.4 (13)
N21^{xlii}—N21—C21—N21^{xliii}	−76 (3)	N21^{xlii}—N21—C21—N21^{xli}	−71.3 (4)
N21^{xxxvii}—N21—C21—N21^{xliii}	−89.3 (9)	N21^{xxxvii}—N21—C21—N21^{xli}	−84 (3)
N21^{xl}—N21—C21—N21^{xxxvii}	−149 (10)	N21^{xliii}—N21—C21—N21^{xli}	5 (3)
C21^{xl}—N21—C21—N21^{xxxvii}	49 (3)		
DAEZnF			
Bond (Å)			
Zn0—O7	2.087 (9)	Zn3—O8^{xiii}	2.102 (9)
Zn0—O1	2.093 (9)	O1—C1	1.238 (15)
Zn0—O11	2.100 (9)	O2—C1	1.241 (15)
Zn0—O3	2.112 (9)	O3—C2	1.217 (16)
Zn0—O5	2.115 (9)	O4—C2	1.264 (17)
Zn0—O9	2.119 (9)	O5—C3	1.230 (15)
Zn1—O2	2.093 (9)	O6—C3	1.237 (15)
Zn1—O2^{xvi}	2.093 (9)	O7—C4	1.227 (15)
Zn1—O2^{xvii}	2.093 (9)	O8—C4	1.225 (15)
Zn1—O10^{x}	2.099 (9)	O8—Zn3^{iv}	2.102 (9)
Zn1—O10^{xlix}	2.099 (9)	O9—C5	1.229 (15)
Zn1—O10^{l}	2.099 (9)	O10—C5	1.221 (14)
Zn2—O12^{xviii}	2.093 (9)	O10—Zn1^{xiv}	2.099 (9)
Zn2—O12^{xv}	2.093 (9)	O11—C6	1.223 (15)
Zn2—O12^{xlix}	2.093 (9)	O12—C6	1.276 (16)
Zn2—O4^{xlii}	2.115 (9)	O12—Zn2^{vi}	2.093 (9)
Zn2—O4	2.115 (9)	N21A—C21A	1.49 (3)
Zn2—O4^{xli}	2.115 (9)	N22A—C22A	1.46 (3)
Zn3—O6^{li}	2.090 (9)	C21A—C22A	1.56 (3)
Zn3—O6^{lii}	2.090 (9)	N21B—C21B	1.53 (5)
Zn3—O6	2.091 (9)	N22B—C22B	1.42 (5)
Zn3—O8^{xlix}	2.102 (9)	C21B—C22B	1.41 (5)
Zn3—O8^{liii}	2.102 (9)		
Angle (°)			
O7—Zn0—O1	175.3 (3)	O12^{xv}—Zn2—O4^{xli}	87.5 (3)
O7—Zn0—O11	91.2 (4)	O12^{xlix}—Zn2—O4^{xli}	179.0 (5)
O1—Zn0—O11	91.6 (4)	O4^{xlii}—Zn2—O4^{xli}	91.7 (5)
O7—Zn0—O3	91.1 (4)	O4—Zn2—O4^{xli}	91.7 (5)
O1—Zn0—O3	92.7 (4)	O6^{li}—Zn3—O6^{lii}	91.2 (4)
O11—Zn0—O3	89.6 (4)	O6^{li}—Zn3—O6	91.2 (4)
O7—Zn0—O5	85.0 (3)	O6^{lii}—Zn3—O6	91.2 (4)
O1—Zn0—O5	92.2 (4)	O6^{li}—Zn3—O8^{xlix}	174.4 (3)
O11—Zn0—O5	176.2 (4)	O6^{lii}—Zn3—O8^{xlix}	84.3 (4)
O3—Zn0—O5	90.3 (5)	O6—Zn3—O8^{xlix}	92.2 (4)
O7—Zn0—O9	91.9 (4)	O6^{li}—Zn3—O8^{liii}	92.2 (4)
O1—Zn0—O9	84.3 (4)	O6^{lii}—Zn3—O8^{liii}	174.4 (3)
O11—Zn0—O9	89.9 (4)	O6—Zn3—O8^{liii}	84.3 (4)
O3—Zn0—O9	177.0 (4)	O8^{xlix}—Zn3—O8^{liii}	92.6 (4)
O5—Zn0—O9	90.4 (4)	O6^{li}—Zn3—O8^{xiii}	84.3 (4)
O2—Zn1—O2^{xvi}	93.4 (4)	O6^{lii}—Zn3—O8^{xiii}	92.2 (4)
O2—Zn1—O2^{xvii}	93.4 (4)	O6—Zn3—O8^{xiii}	174.4 (3)
O2^{xvi}—Zn1—O2^{xvii}	93.4 (4)	O8^{xlix}—Zn3—O8^{xiii}	92.6 (4)
O2—Zn1—O10^{x}	174.2 (3)	O8^{liii}—Zn3—O8^{xiii}	92.6 (4)
O2^{xvi}—Zn1—O10^{x}	84.7 (4)	C1—O1—Zn0	124.5 (8)
O2^{xvii}—Zn1—O10^{x}	92.2 (4)	C1—O2—Zn1	125.6 (8)

O2—Zn1—O10^{xlix}	92.2 (4)	C2—O3—Zn0	127.0 (9)
O2^{xvi}—Zn1—O10^{xlix}	174.2 (3)	C2—O4—Zn2	126.4 (8)
O2^{xvii}—Zn1—O10^{xlix}	84.7 (4)	C3—O5—Zn0	127.7 (8)
O10^{x}—Zn1—O10^{xlix}	89.9 (4)	C3—O6—Zn3	129.1 (8)
O2—Zn1—O10^{l}	84.7 (4)	C4—O7—Zn0	125.3 (8)
O2^{xvi}—Zn1—O10^{l}	92.2 (4)	C4—O8—Zn3^{iv}	125.7 (8)
O2^{xvii}—Zn1—O10^{l}	174.2 (3)	C5—O9—Zn0	128.6 (8)
O10^{x}—Zn1—O10^{l}	89.9 (4)	C5—O10—Zn1^{xiv}	128.5 (8)
O10^{xlix}—Zn1—O10^{l}	89.9 (4)	C6—O11—Zn0	128.5 (9)
O12^{xviii}—Zn2—O12^{xv}	93.1 (4)	C6—O12—Zn2^{vi}	128.8 (8)
O12^{xviii}—Zn2—O12^{xlix}	93.1 (4)	O1—C1—O2	126.9 (12)
O12^{xv}—Zn2—O12^{xlix}	93.1 (4)	O3—C2—O4	125.2 (12)
O12^{xviii}—Zn2—O4^{xlii}	179.0 (5)	O5—C3—O6	126.6 (11)
O12^{xv}—Zn2—O4^{xlii}	87.7 (4)	O8—C4—O7	128.5 (12)
O12^{xlix}—Zn2—O4^{xlii}	87.5 (3)	O10—C5—O9	126.6 (11)
O12^{xviii}—Zn2—O4	87.5 (3)	O11—C6—O12	126.1 (12)
O12^{xv}—Zn2—O4	179.0 (5)	N21A—C21A—C22A	109.7 (19)
O12^{xlix}—Zn2—O4	87.7 (4)	N22A—C22A—C21A	109.4 (17)
O4^{xlii}—Zn2—O4	91.7 (5)	C22B—C21B—N21B	118 (3)
O12^{xviii}—Zn2—O4^{xli}	87.7 (4)	C21B—C22B—N22B	112 (3)
Dihedral (°)			
Zn0—O1—C1—O2	−179.9 (11)	Zn0—O7—C4—O8	179.8 (11)
Zn1—O2—C1—O1	−178.4 (11)	Zn1^{xiv}—O10—C5—O9	−167.0 (11)
Zn0—O3—C2—O4	−178.4 (11)	Zn0—O9—C5—O10	−177.8 (10)
Zn2—O4—C2—O3	171.3 (11)	Zn0—O11—C6—O12	−178.5 (11)
Zn0—O5—C3—O6	−177.4 (11)	Zn2^{vi}—O12—C6—O11	168.6 (11)
Zn3—O6—C3—O5	−172.8 (11)	N21A—C21A—C22A—N22A	172.0 (17)
Zn3^{iv}—O8—C4—O7	177.6 (11)	N21B—C21B—C22B—N22B	174 (3)

Symmetry code(s): (i) −x+y+1, −x+2, z; (ii) −y+2, x−y+1, z; (iii) −y+1, x−y, z; (iv) −y+2/3, x−y+1/3, z+1/3; (v) −x+y, −x+1, z; (vi) x−2/3, y−1/3, z−1/3; (vii) −y+4/3, x−y+2/3, z−1/3; (viii) −x+y+1/3, −x+2/3, z−1/3; (ix) x−1/3, y−2/3, z+1/3; (x) −x+y+2/3, −x+4/3, z+1/3; (xi) z−1, x+1, y; (xii) y−1, z, x+1; (xiii) y, z, x; (xiv) z, x, y−1; (xv) x, y, z−1; (xvi) z, x+1, y−1; (xvii) −x+y+1, −x+1, z; (xviii) −x+1, −x+y+1, −z+1; (xix) −y+1, x−y+1, z; (xx) −y, x−y, z; (xxi) −x+y, −x, z; (xxii) x, x−y, −z+1/2; (xxiii) −x+y, y, −z+1/2; (xxiv) y, −x+y, z+1/2; (xxv) −x, −x+y, −z+1; (xxvi) −y, x−y+1, z; (xxvii) −x+y−2/3, −x+2/3, z−1/3; (xxviii) x+1/3, y+2/3, z−1/3; (xxix) −y+2/3, x−y+4/3, z+1/3

Vibrational Spectroscopy

Table S3. The correlation diagram of theoretical modes for *R*3 and $P6_322$ (in parentheses).

Ion	Free-ion symmetry	Site symmetry	Factor-group symmetry
$HCOO^-$	C_{2v}	C_3 (C_2)	C_3 (D_6)
	A_1, A_2, B_1, B_2	A, E (A, B)	A, E (A_1, A_2, B_1, B_2, E_1, E_2)
H_2O	C_{2v}	C_3 (D_3)	C_3 (D_6)
	A_1, A_2, B_1, B_2	A, E (A_1, A_2, E)	A, E (A_1, A_2, B_1, B_2, E_1, E_2)
DAE^{2+}	C_{2h}	C_3 (D_3)	C_3 (D_6)
	A_g, A_u, B_g, B_u	A, E (A_1, A_2, E)	A, E (A_1, A_2, B_1, B_2, E_1, E_2)
M^{2+}		C_3 (D_3)	C_3 (D_6)
		A, E (A_1, A_2, E)	A, E (A_1, A_2, B_1, B_2, E_1, E_2)

Table S4. The assignment of the bands at room temperature. The abbreviations are explained at the foot of the table.

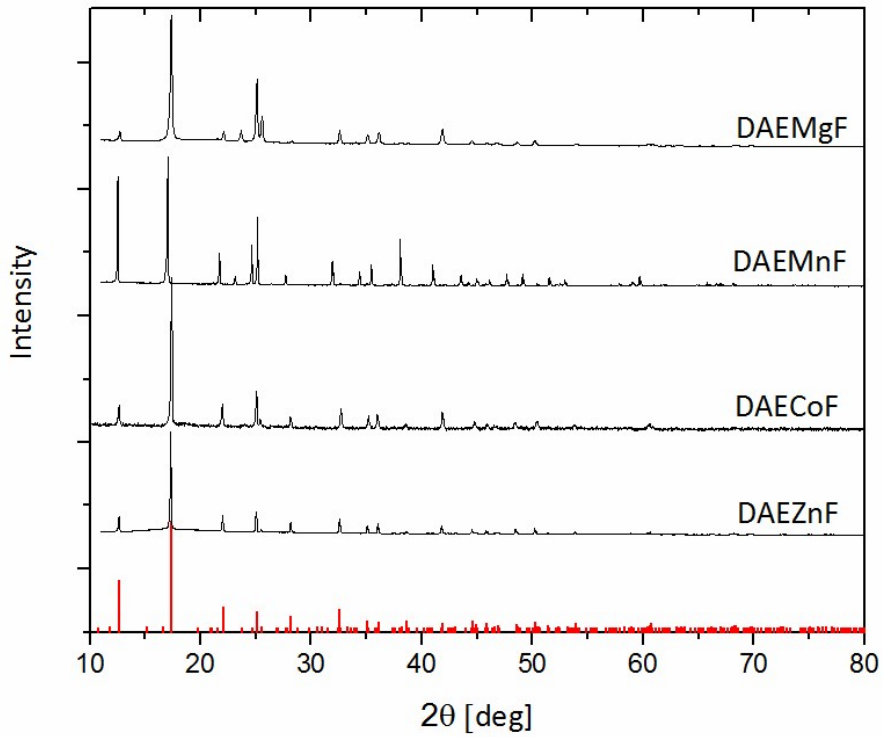
DAEMgF		DAEMnF		DAECoF		DAENiF		DAEZnF		Assignment
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	
3392sh		3380sh		3396sh		3412sh		3345sh		νH_2O
		3235sh						3207m		$\nu_{as}NH_3^+$
3194m		3156m		3197m		3173m	3199vw			$\nu_{as}NH_3^+$
3034m	3016w	3028m	3011w	3033m	3016w	3030m	3015w	3032m	3016w	$\nu_{as}CH_2$
2993m	2984w	2947m	2984w		2988w		2988w		2989w	$\nu_{as}CH_2$
2955m	2976sh	2913m	2975w	2948m	2976sh	2938m	2975sh	2938m	2976w	ν_sCH_2
2875m	2875m	2857m	2858m	2877m	2877m	2876m	2878m	2878m	2878m	νCH $\nu_sNH_3^+$
2859m	2858m	2838m	2840m	2856m	2856m	2862m	2856m	2854m	2855m	νCH $\nu_sNH_3^+$
2728w	2755vw	2727w	2751vw	2716w	2722w	2717w	2727vw	2717w	2716w	2x1370
	2728vw		2723vw							2x1360
2585vw		2593vw		2578vw		2585w		2567vw		combination
2058w	2135vw	2060w	2123vw	2036vw	2123vw	2044vw	2125vw	2047vw	2126vw	combination
1659sh		1652sh		1647sh		1645sh		1648sh		δH_2O
1636sh	1632vw	1632sh	1636vw	1631s	1628vw	1623sh	1626vw	1632s	1633w	$\delta_{as}NH_3^+$
1609vs	1592vw	1602sh	1571vw	1597sh	1570vw	1579vs	1570vw	1599vs	1571w	$\delta_{as}NH_3^+$ $\nu_{as}COO^-$
	1570vw	1585vs	1559vw	1579vs	1552vw		1552vw	1582vs	1549w	$\delta_sNH_3^+$ $\nu_{as}COO^-$
1502w	1478vw		1509vw	1499vw	1494vw		1496vw	1499vw		$\delta_sNH_3^+$
1475w		1483w	1486vw	1468w		1465w		1471w	1473w	δCH_2
1458vw		1457vw		1455sh				1457sh		δCH_2
1444vw	1444m	1444vw	1444m	1443vw	1442w	1443w	1441w	1443vw	1443w	δCH_2
1390sh	1381sh	1388m	1378vs	1377sh	1373sh	1375s	1373sh	1378sh	1376vs	δCH
1378s	1375vs	1375s	1371vs	1374s	1366vs		1366vs	1374s	1369vs	δCH
1367s	1369vs	1362s	1361vs	1360s	1355sh	1353s	1355sh	1359s	1362vs	ν_sCOO^-
1358s	1357vs	1352s	1353vs	1349s	1347s		1347s	1349s	1349s	ν_sCOO^-
	1339w		1340sh		1340w		1339w	1339sh	1339w	ν_sCOO^- ωCH_2
1248w	1228vw	1248w	1230vw	1247w	1230vw	1246w	1230vw	1248w	1223w	tCH_2

1100m		1105m		1095m		1093m		1097w		νCC
1069vw	1070m	1065w	1065m	1070w	1069w	1070w	1068w	1070vw	1070m	νCC
1045w	1048sh	1049w	1052sh	1046w	1056sh		1055vw	1047w		γCH τCH_2
1021w	1020vw	1016w	1016vw	1023w	1035vw	1023w	1034vw	1022w	1022vw	νCN
933w	927w	935w	927w	930w	926w	929w	925vw	931w	926w	νCN ρNH_3^+
819sh	807m	809m	810sh	821sh	807sh	818m	806w	818sh	805w	ρNH_3^+
809m		797m	796m	809m	805m			805m		ρNH_3^+
769w	769w	768m	769w	769m	768vw	769w		769w		δCOO^-
721w		723w		719w		713w		718w		δCOO^- γH_2O
685w		664w		687w				687w		γH_2O
	473w		470w				471vw		474w	δNCCN
	221m								218m	T'(M)
			203sh		205m		205m		201m	T'(M) T'$HCOO^-$
			180s		185m		185m		179sh	L $HCOO^-$
	151s		145sh		151s 141s		161sh		158s 150s	T'(M) L $HCOO^-$
	131sh		137vs		131s		152s 141s		130s	T'(M)
			123sh							L(DAE)
	108sh		111sh		110s		112s		114sh	L(DAE)
							93s			T'(DAE)

Key: s-very strong, s-strong, m-medium, w-weak, vw-very weak; ν_s–symmetric stretching, ν_{as}-asymmetric stretching, ν_s–symmetric stretching, ν_{as}–asymmetric stretching, δ_{as}-asymmetric bending, δ_s, δ-symmetric bending (scissoring), ρ-rocking, ω-wagging, τ-twisting (torsion), T–translation, L–libration.

Powder X-ray diffraction

a)



b)

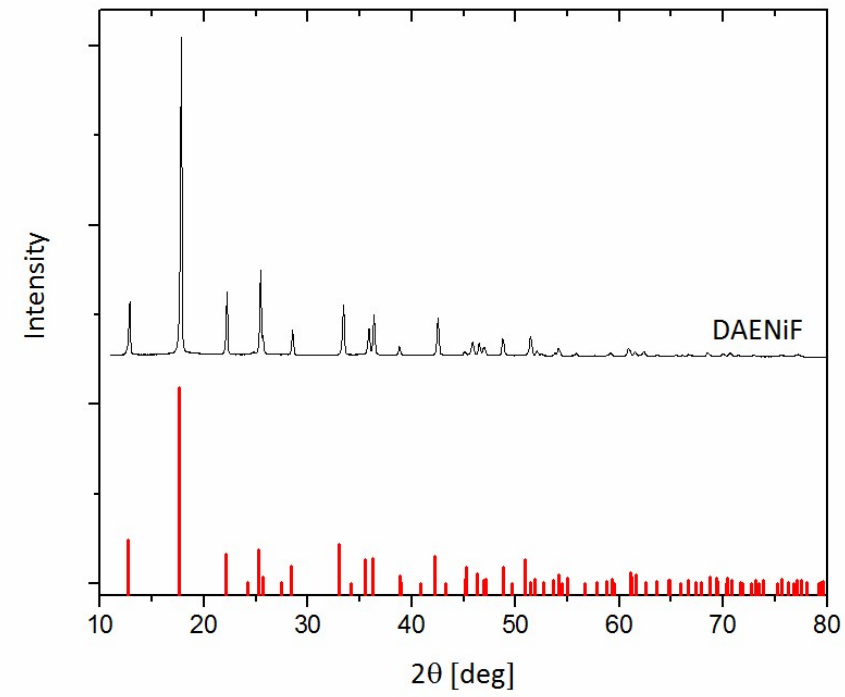


Fig. S1. Powder X-ray diffractogram of the samples referenced against the single-crystal pattern (red) for a) Mg-, Mn-, Co- and Zn-, b) Ni-analogues.

Differential Scanning Calorimetry

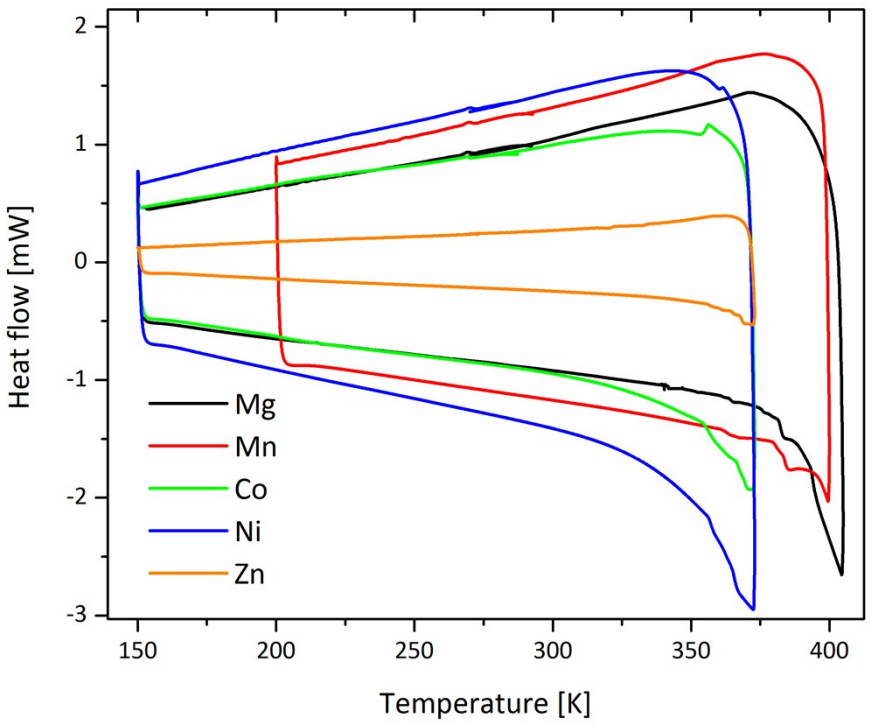
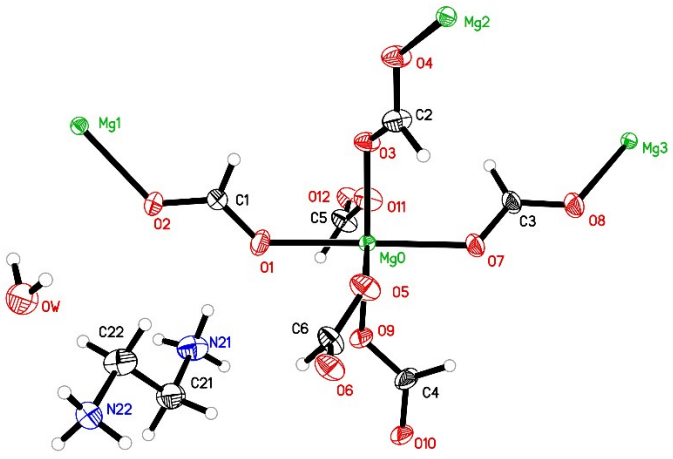


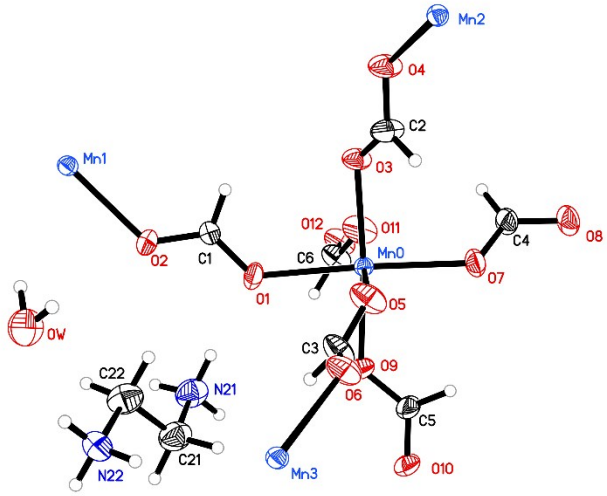
Fig. S2. The differential scanning calorimetric curves for DAEMF, where M=Mg, Mn, Co, Ni and Zn.

Single-crystal X-ray diffraction

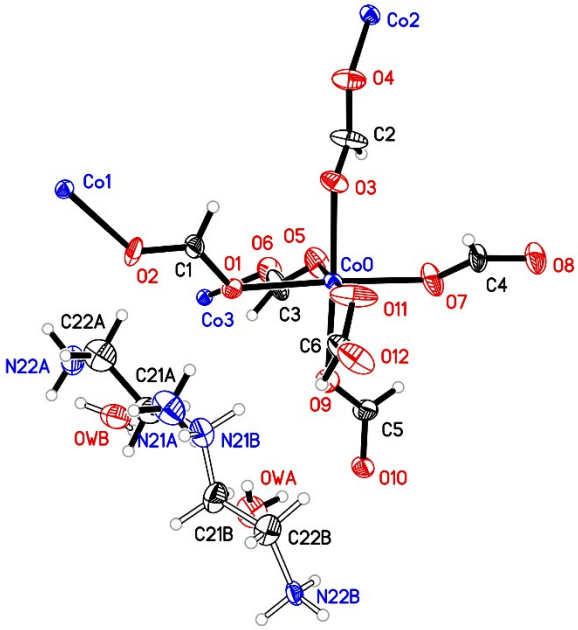
a)



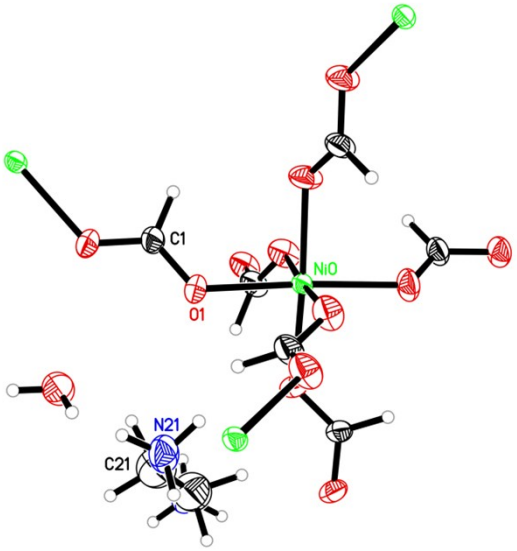
b)



c)



d)



e)

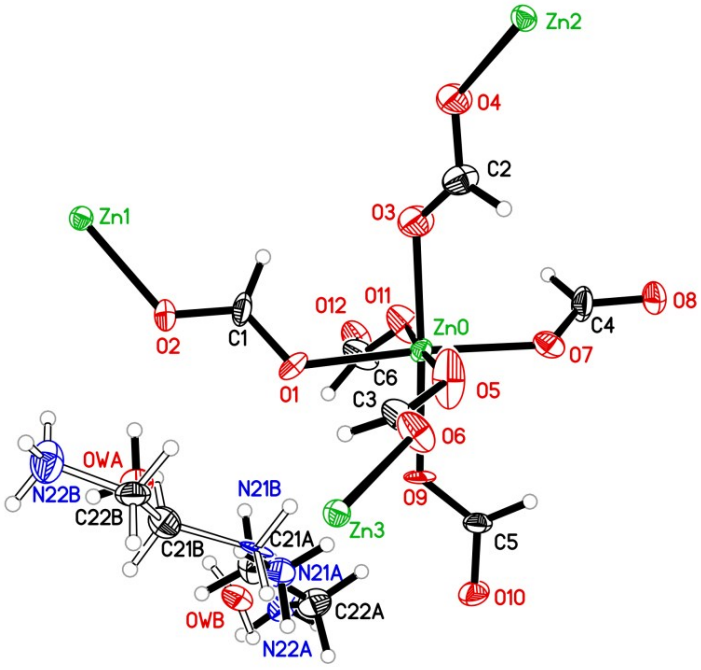


Fig. S3. The ORTEP presentation and the number scheme of asymmetric part of the unit cells for a) DAEMgF, b) DAEMnF, c) DAECoF, d) DAENiF, e) DAEZnF. The thermal ellipsoids are shown with 50% probability for non-hydrogen atoms.

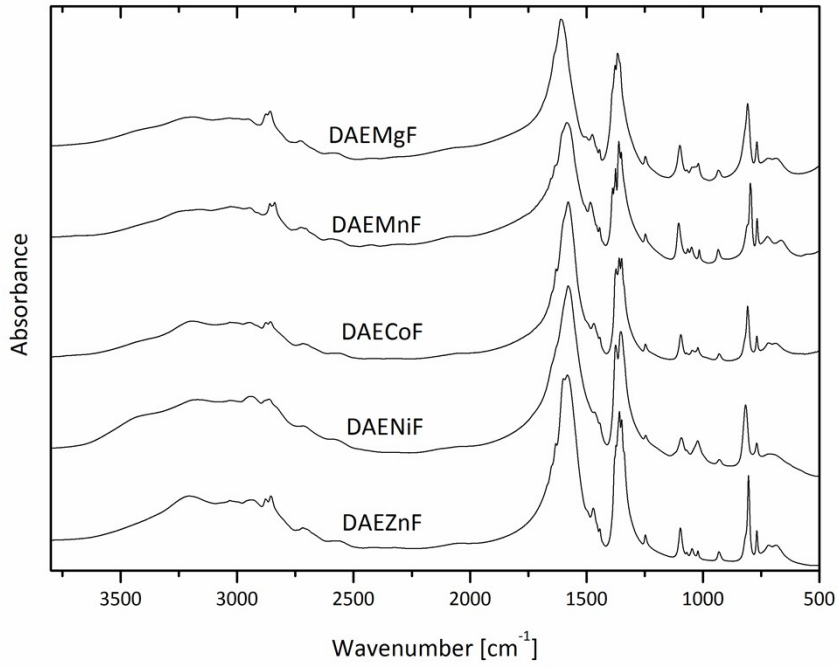


Fig. S4. The IR spectra of the DAEMF compounds at room temperature.

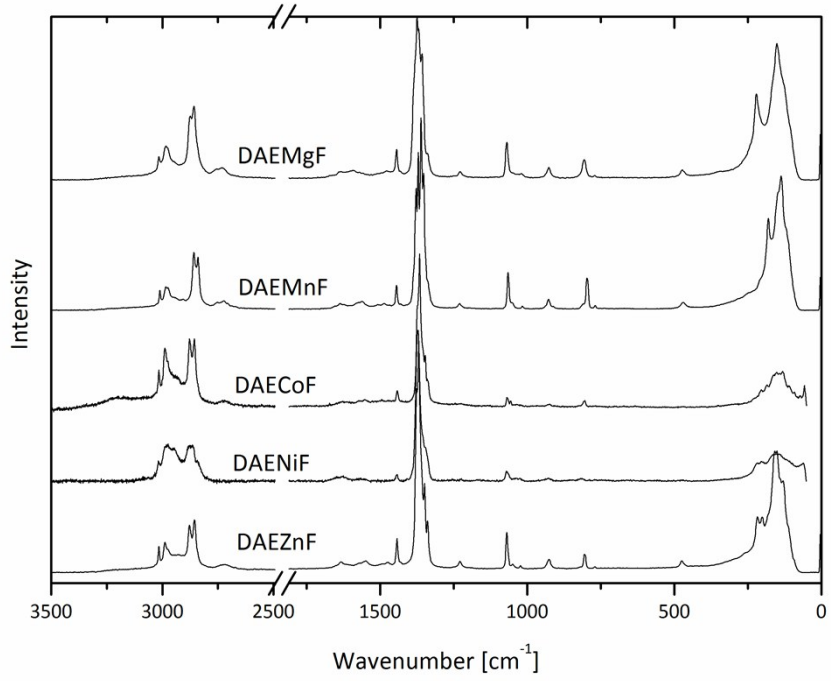


Fig. S5. The Raman spectra of the DAEMF compounds at room temperature.

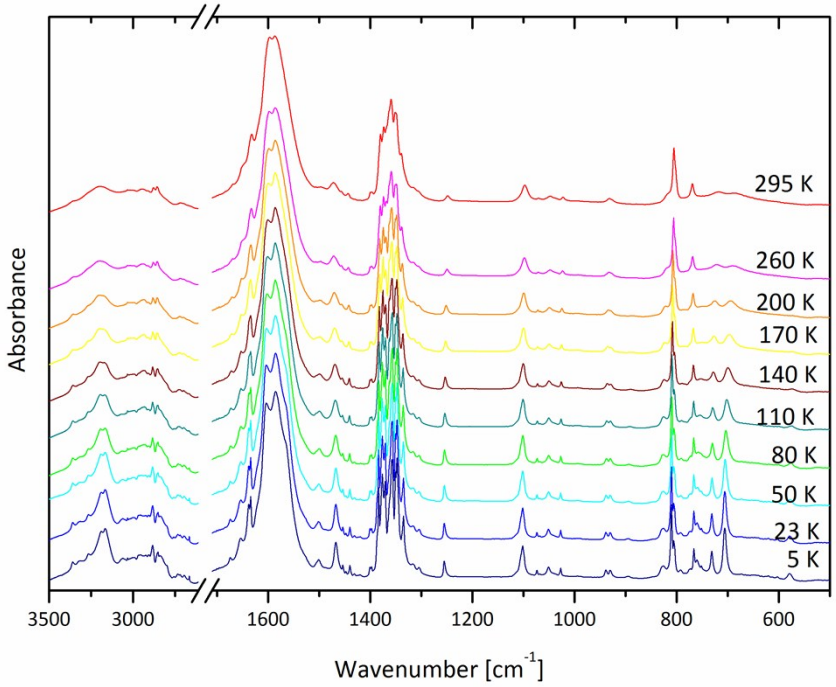


Fig. S6. The temperature-dependent IR spectra of DAEZnF.

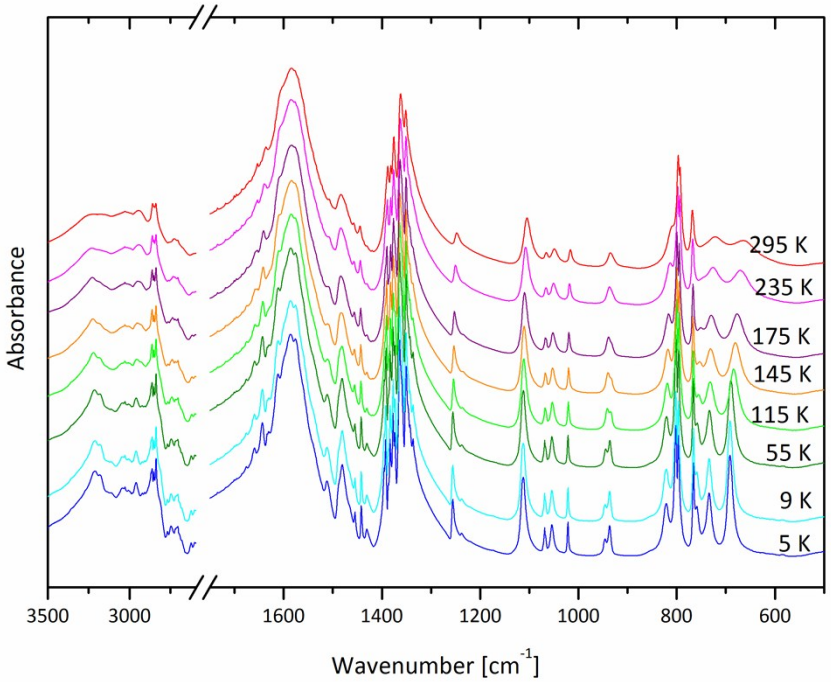


Fig. S7. The temperature-dependent IR spectra of DAEMnF.

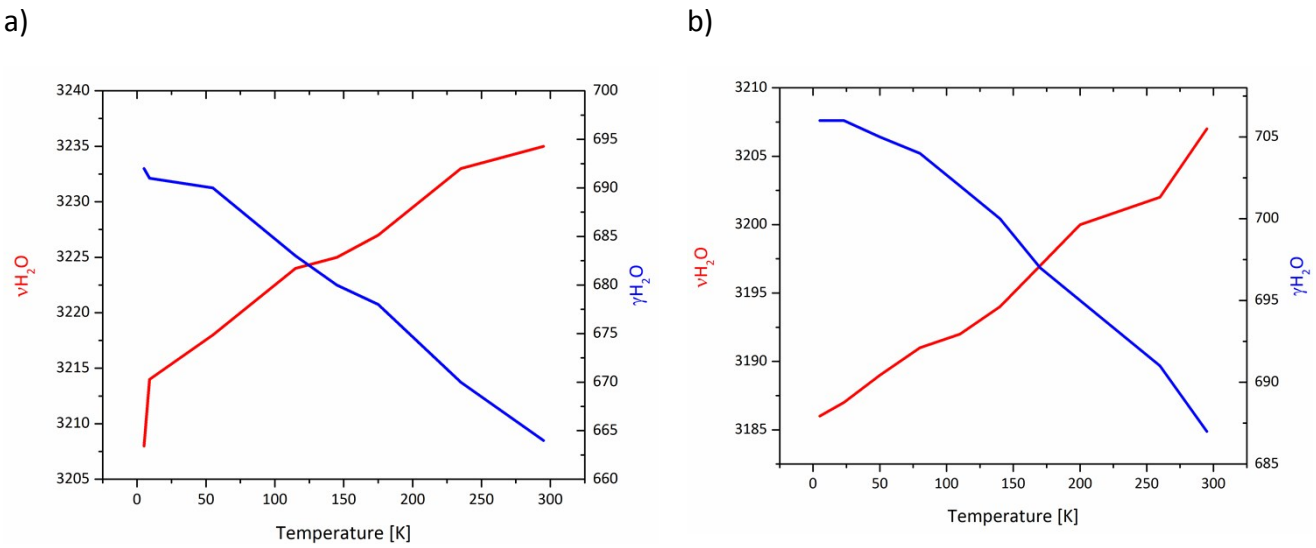


Fig. S8. The wavenumber shift of the water stretching (red) and out-of-plane (blue) vibration in a) DAEMnF and b) DAEZnF.

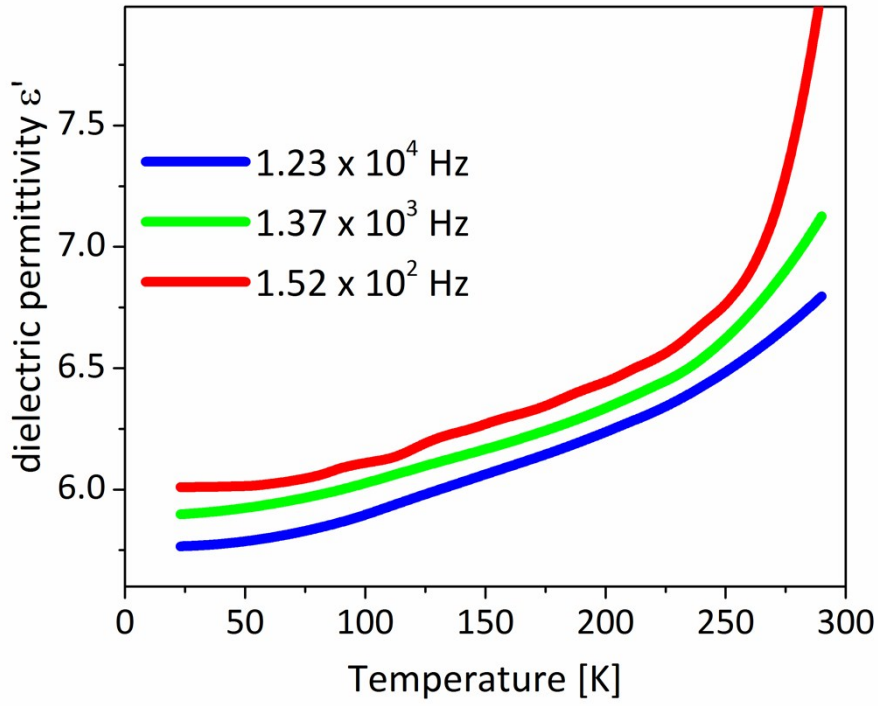


Fig. S9. The temperature dependence of dielectric permittivity of DAENiF sample.

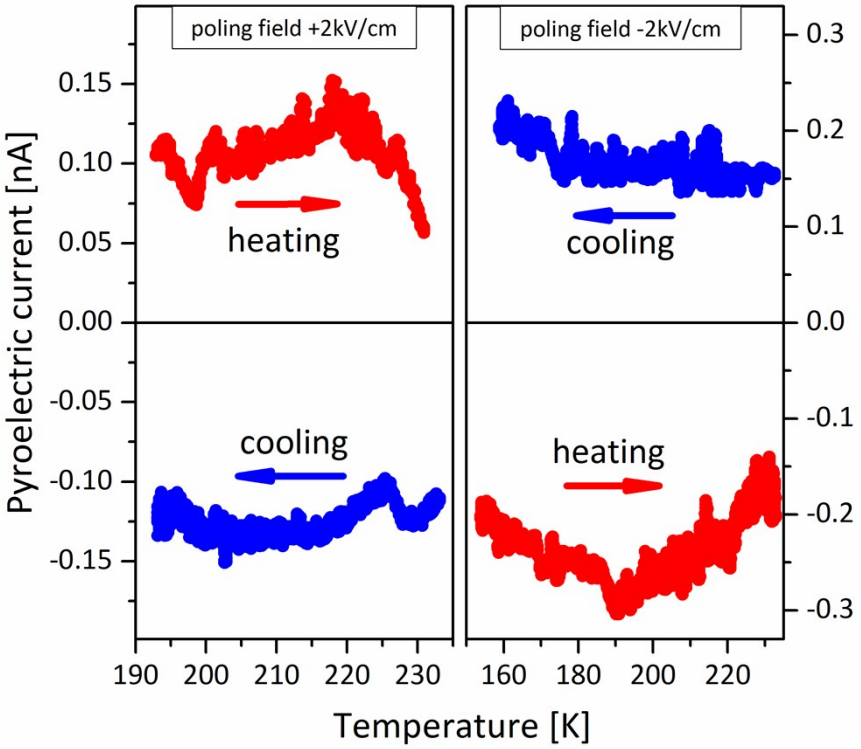


Fig. S10. The pyroelectric current as a function of temperature of DAEMgF for two reversed poling fields (± 2kV/cm) both for cooling and heating.